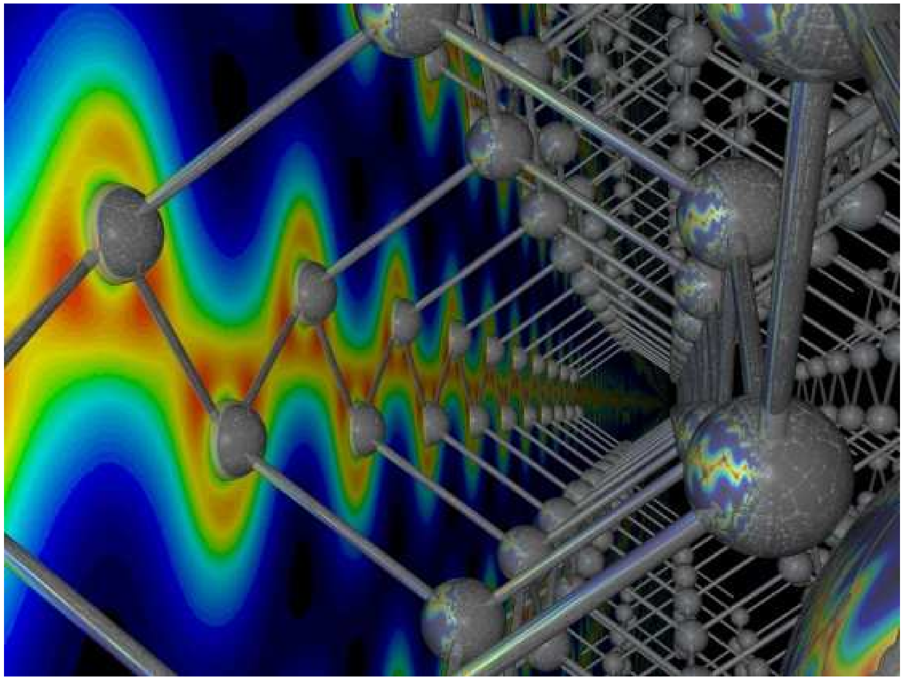
Metal-insulator transitions

What can we learn from electronic structure calculations?



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Thought required.. [What about Kohn theory (1964) and modern reinterpretations?]

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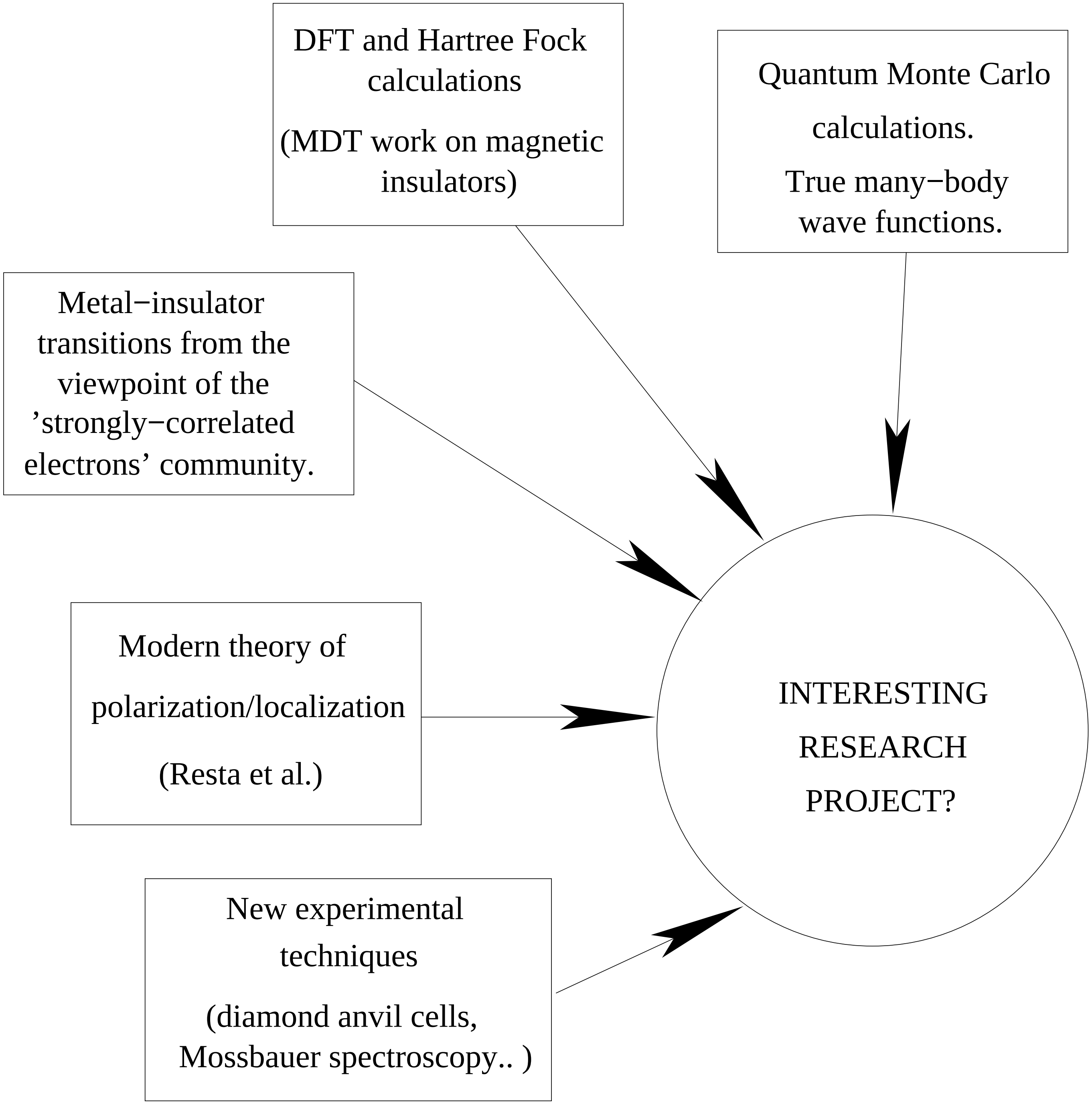
Associated questions

- What is meant by *localized/delocalized electrons*?
- What are *strongly correlated electrons*?

Connections



DFT and Hartree Fock calculations

(MDT work on magnetic insulators)

Quantum Monte Carlo calculations.

True many−body wave functions.

Metal−insulator transitions from the viewpoint of the ’strongly−correlated electrons’ community.

Modern theory of polarization/localization

(Resta et al.)

New experimental techniques

(diamond anvil cells, Mossbauer spectroscopy..)

INTERESTING

RESEARCH

PROJECT?

Books

- *Metal-insulator Transitions* 2nd edition, N. Mott (Taylor-Francis 1990)
- *The Mott Metal-insulator Transition : Models and Methods*, F.Gebhard (Springer, 1997)

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GEBHARD IS GOSPEL

i.e. for the purposes of this talk, Gebhard is taken to represent the 'strongly-correlated electron' viewpoint, which we will attempt to understand and interpret in terms more familiar to practitioners of computational electronic structure theory.

Two fundamental requirements for electron transport

Two fundamental requirements for electron transport

- Quantum-mechanical states for electron-hole excitations must be available at energies immediately above the energy of the ground state since the external field provides vanishingly small energy ($\omega \longrightarrow 0$)

- These excitations must describe delocalized charges that can contribute to transport over the macroscopical sample size.

Scenarios for gap formation

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- Quantum phase transition

Gap opens as a consequence of the competition between the carriers' kinetic and interaction energy.

$\Longrightarrow$ "robust gap" (doesn't disappear at high T)

- Thermodynamic phase transitions

Gap opens as a consequence of the formation of long-range order (symmetry breaking) at some finite temperature.

$\Longrightarrow$ "soft gap" (disappears at high T)

Gebhard classification of insulators

Specify four basic classes of insulator, based on dominant interaction that causes the insulating behaviour.

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Electron-electron interaction

- Mott insulators due to the electrons' interaction with each other.

Gebhard on band theory

"*For a band insulator the interaction between electrons and the periodic ion potential gives rise to an energy gap between the lowest conduction band and the highest valence band. Consequently there are no free carriers for the transport of charge. A band insulator is possible only for an even number of valence electrons per lattice unit cell*".

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Assumptions

- "electron-electron interaction neglected or treated within effective single-electron approximation"

- "For simplicity we neglect spin-orbit coupling. As a good approximation each band is then two-fold spin degenerate i.e. each band may be occupied with two electrons per $\mathbf{k}$ point."

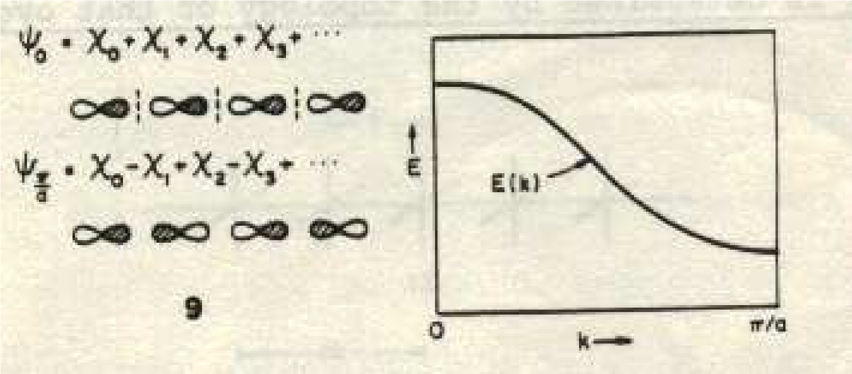
$\Longrightarrow$ completely filled bands cannot contribute to transport (since for each state with crystal momentum $\mathbf{k}$ the state with momentum $-\mathbf{k}$ is also occupied so that both contributions to transport cancel).

Band insulators

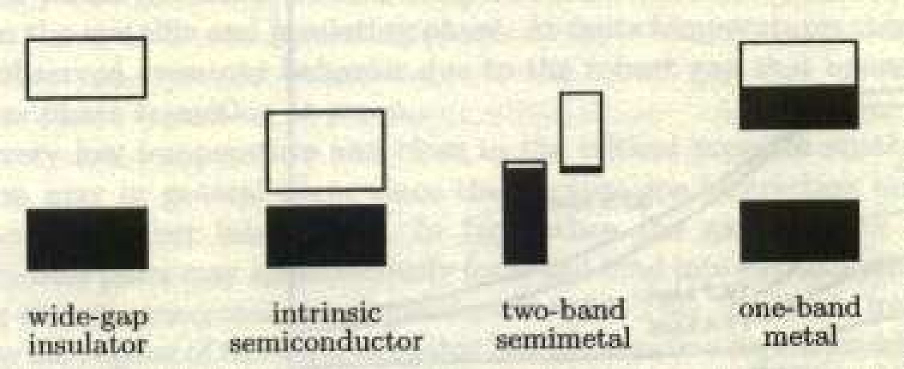
Impose periodic boundary conditions : the one-electron wave functions are then Bloch functions.

Bloch functions obey BLOCH'S THEOREM:

$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$ or $\Psi(\mathbf{r}+\mathbf{t}) = \Psi(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{t}}$



Count states in each energy range, and classify:



Increasing pressure (for example) will change shape of bands and may lead to metal-insulator transitions of various sorts.

What is a Mott insulator?

Gebhard

- *"For a Mott insulator the electron-electron interaction leads to the occurence of local moments. The gap in the excitation spectrum for charge excitations may arise from the long-range order of the pre-formed moments (Mott-Heisenberg insulator) or by a quantum phase transition induced by charge and/or spin correlations (Mott-Hubbard insulator)"*

- *"Mott insulating behaviour is understood as a cooperative many-electron phenomenon.. [It] cannot be understood within the framework of a single-electron theory - many-body effects must be included."*

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Pasternak (an experimentalist)

- *"In this* [$W > U$] *regime, the* d*-electron correlation collapses, giving rise to an insulator-metal transition concurrent with a magnetic moment breakdown. This phenomenon is called the Mott transition"*.

Anderson insulators

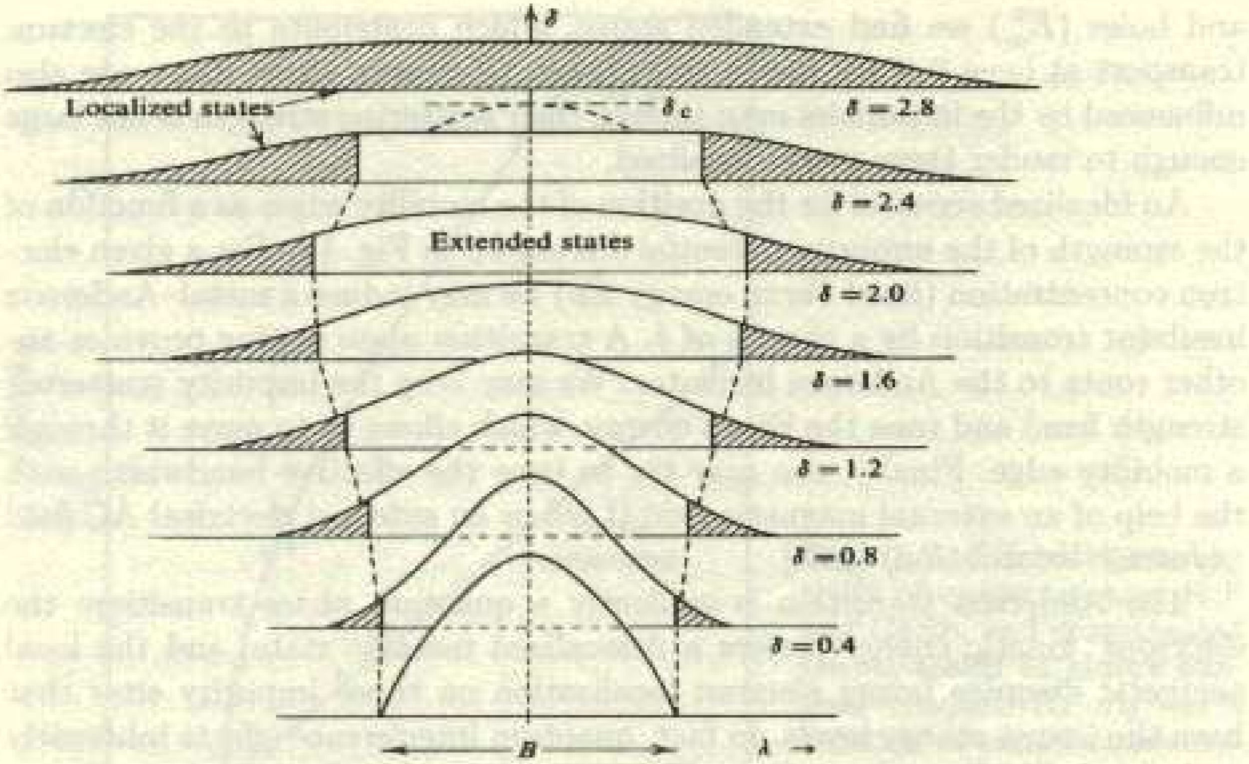
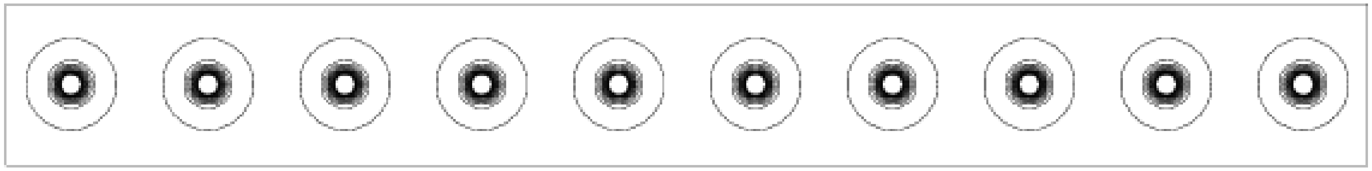


Fig. 1.6. Increasing the strength δ of the disorder potential in the Anderson model of disorder leads to a broadening of the density of states. The number of localized states increases until the mobility edges for electrons and holes coincide for δ_c. In the figure B denotes the bandwidth at zero disorder, and λ is the energy variable (from [1.52, Chap. 9.9]).

Linear chain of hydrogen atoms



"Consider a linear chain of hydrogen atoms with a lattice constant of 1 Å. This has one electron per atom in the conduction band and is therefore metallic. Imagine we now dilate the lattice parameter of the crystal to 1 metre. We would agree that at some point in this dilation process the crystal must become an insulator because certainly when the atoms are 1 metre apart they are not interacting. But band theory says that the crystal remains a metal because at all dilations the energy difference between occupied and unoccupied states remains vanishingly small. Now look at this thought experiment from the other way. Why is the crystal with a lattice parameter of 1 metre an insulator? Because to transfer an electron from one atom to another we have to supply an ionization energy, I *to remove the electron and then we recover the electron affinity,* A*, when we add the electron to the neutral H atom. The energy cost in this process is* $U = I - A$*. Band theory ignores terms such as these." [Sutton's book]*

Hubbard model

$$H = \sum_{i,j} t_{ij} a_{i\sigma} a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

DFT treatment of linear hydrogen chain

Examine linear chain of H atoms in band theory

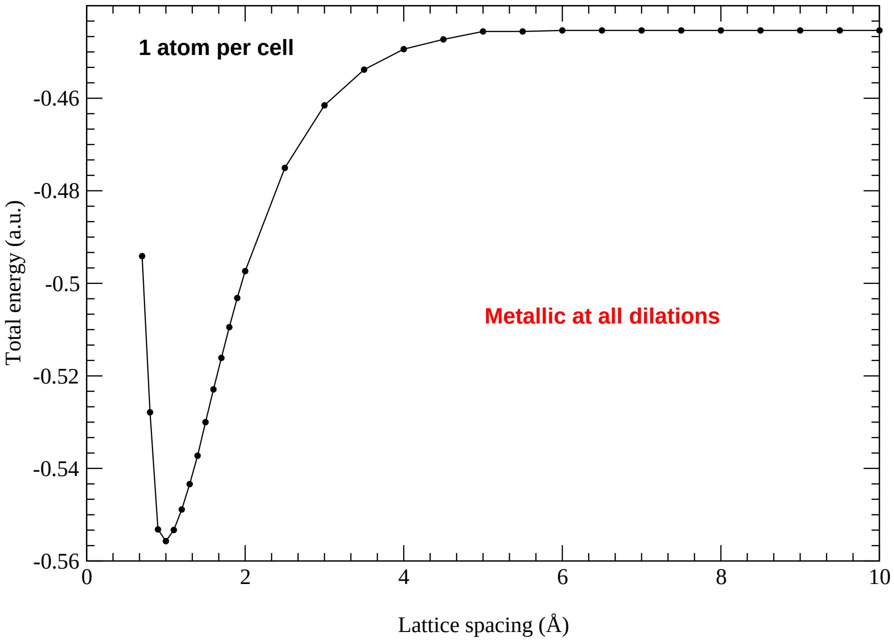
- Genuine 1-dimensional periodic boundary conditions
- High quality local (Gaussian) basis set centred on the H atoms.

Properties of isolated H atom computed with this basis

	Calculated	Exact
Total energy (HF)	-0.499993 Ha	-0.5 Ha
Virial coefficient	1.00007	1
Hyperfine coupling constant	1419.3 MHz	1420 MHz

Band theory of linear hydrogen chain

(DFT band calculations with LDA exchange-correlation functional)



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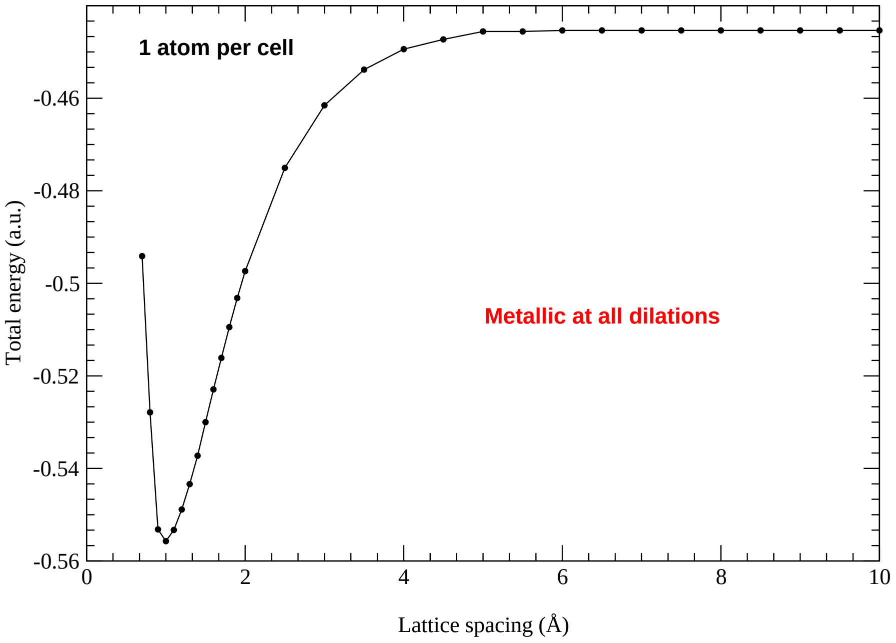
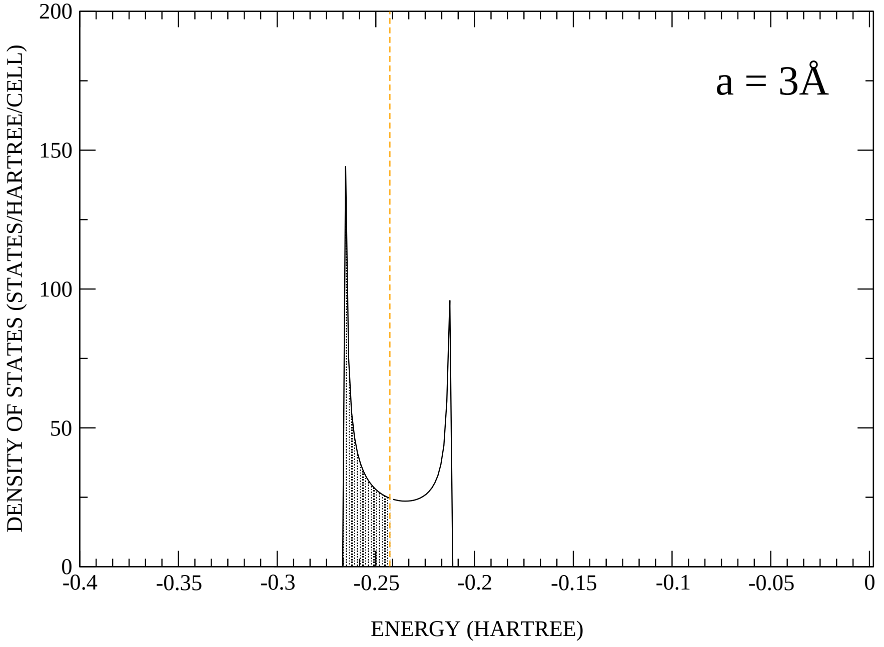
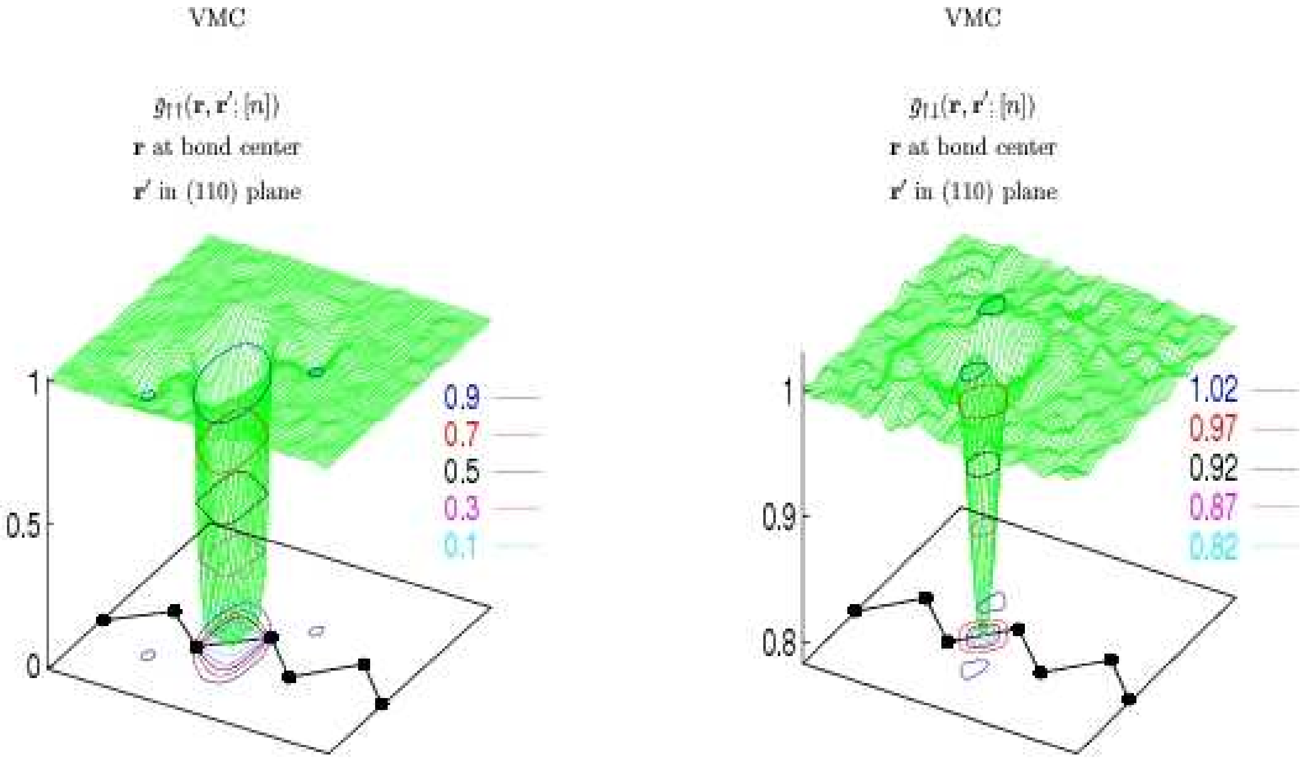


Metallic at all dilations



Correlated electron systems

"Strong Coulomb interactions" : actually statement about pair correlation funct



↑

'TRUE MANY-BODY EFFECTS' HERE

correlated electron system - "*non-vanishing pair correlation function between ↑- and ↓-electrons*"

strongly-correlated system - "*pair correlation functions for electrons of same spin and electrons of opposite spin are comparable in size*

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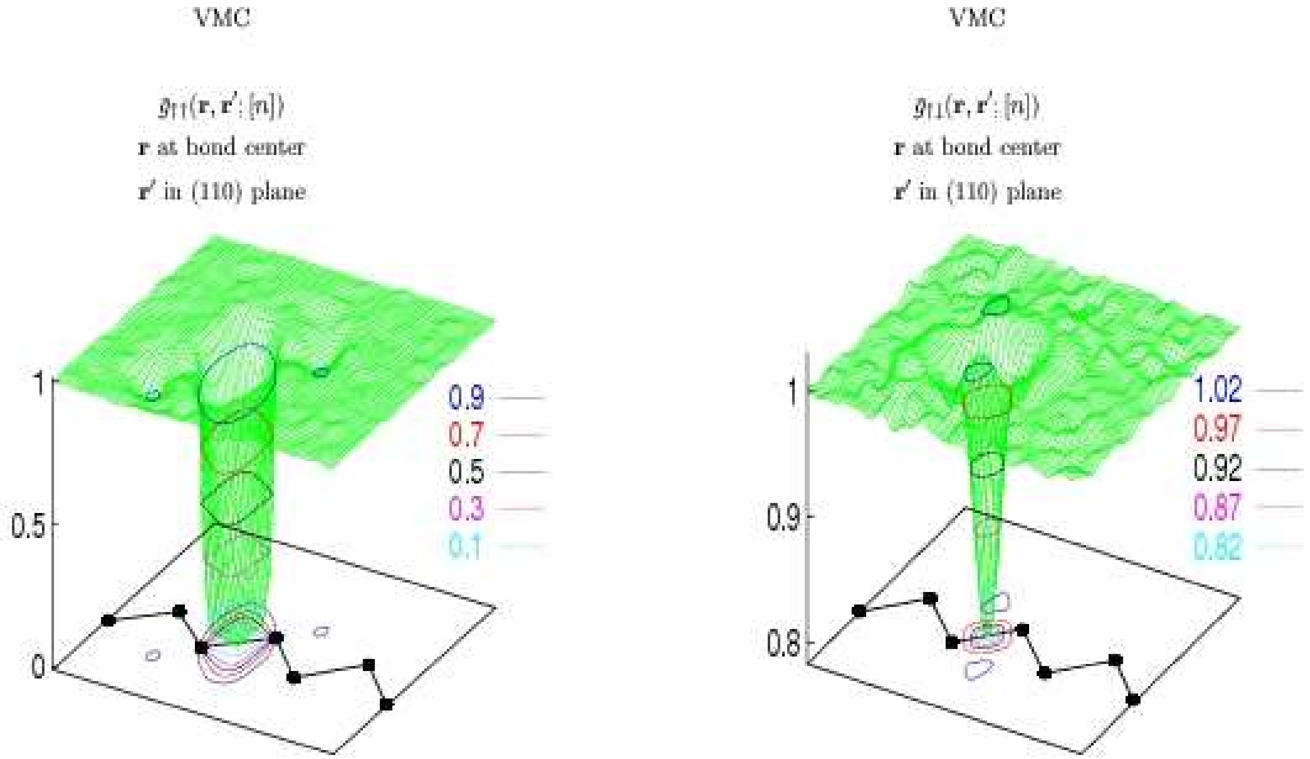

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correlated electron system - "*non-vanishing pair correlation function between ↑- and ↓-electrons*"
strongly-correlated system - "*pair correlation functions for electrons of same spin and electrons of opposite spin are comparable in size*"

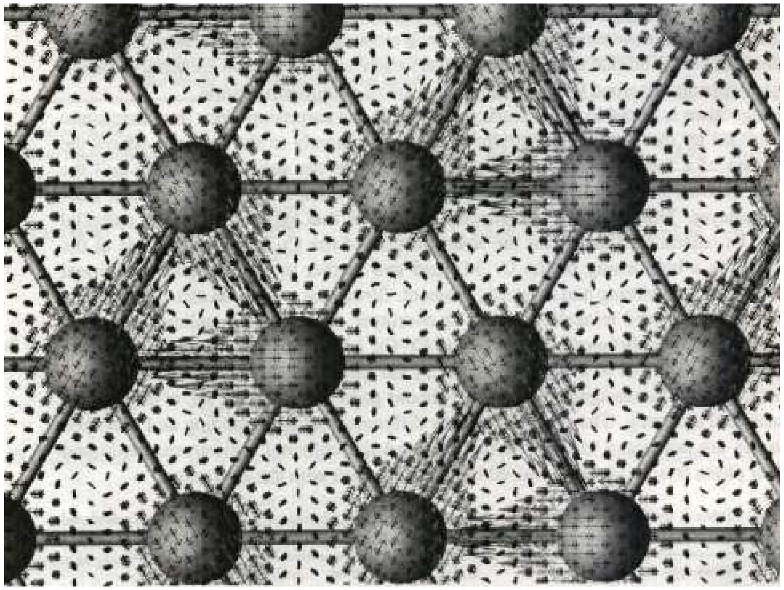
So to describe strong-correlations just need to make the wave function flexible enough for ↑- and ↓-electrons to avoid each other?

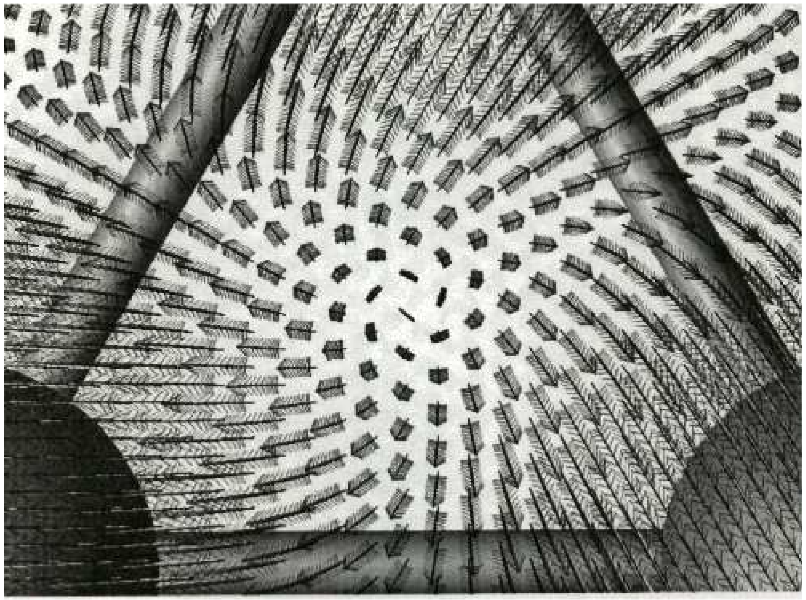
Spin polarization

Need single determinants of one-electron spin orbitals!

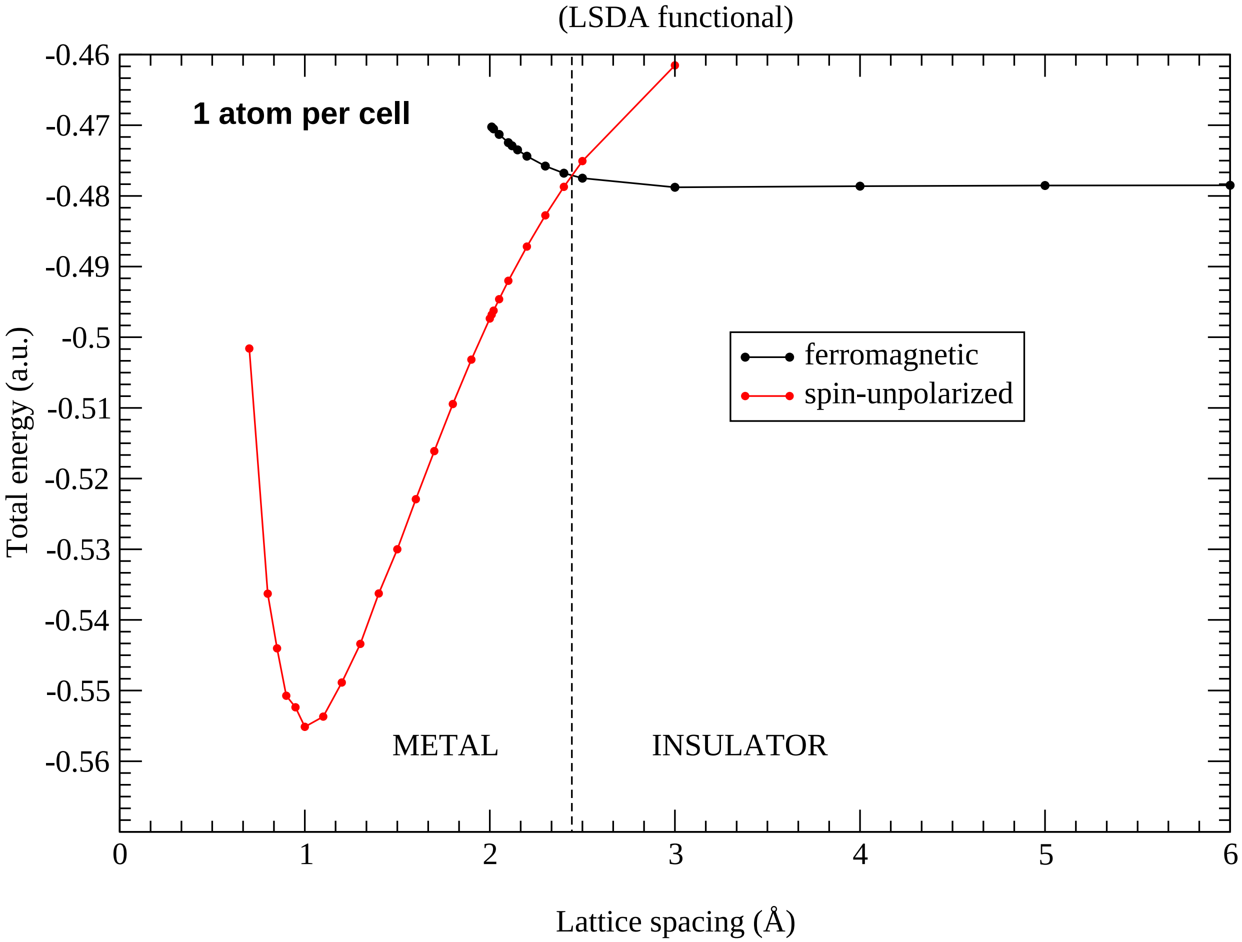
- Restricted form All spin orbitals are pure space-spin products of the form $\phi_n\alpha$ or $\phi_n\beta$ and are occupied singly or in pairs with a common orbital factor ϕ_n.
- Unrestricted form Spin orbitals no longer occupied in pairs but still pure space-spin products $\phi_n\alpha$ or $\bar{\phi}_n\beta$. However, now have different spatial factors ϕ_n and $\bar{\phi}_n$ for different spins.
- General unrestricted form No longer restrict to simple product form. Each spin orbital now a 2-component complex spinor orbital: $\Psi_1 = \phi_1^\alpha\alpha + \phi_1^\beta\beta$ and $\Psi_2 = \phi_2^\alpha\alpha + \phi_2^\beta\beta$. Non-collinear spins.

Pretty pictures of non-collinear spin states

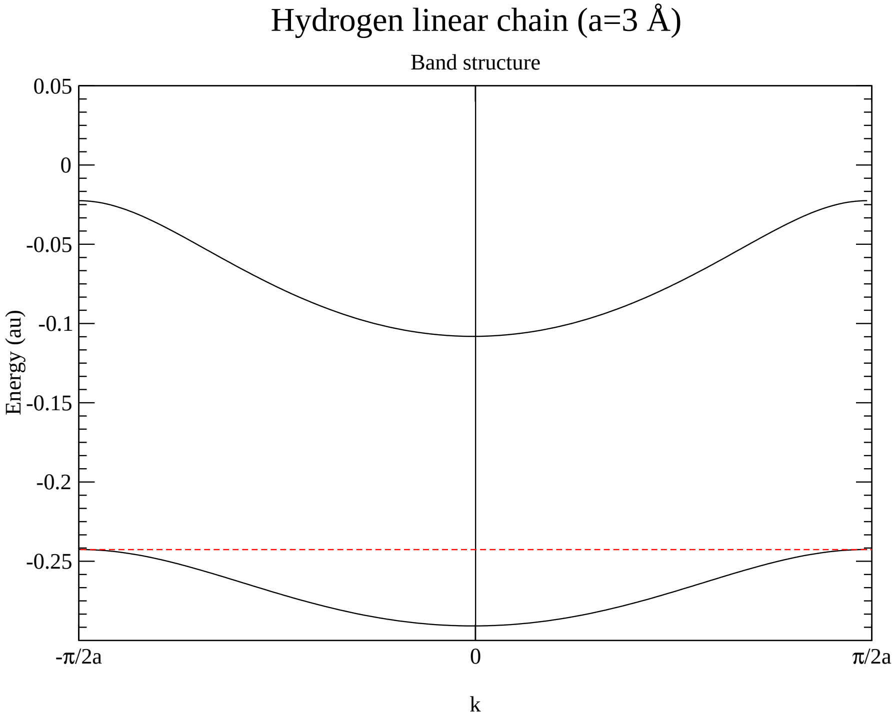




Spin-unrestricted band treatment of linear hydrogen chain



Band structure of linear hydrogen chain



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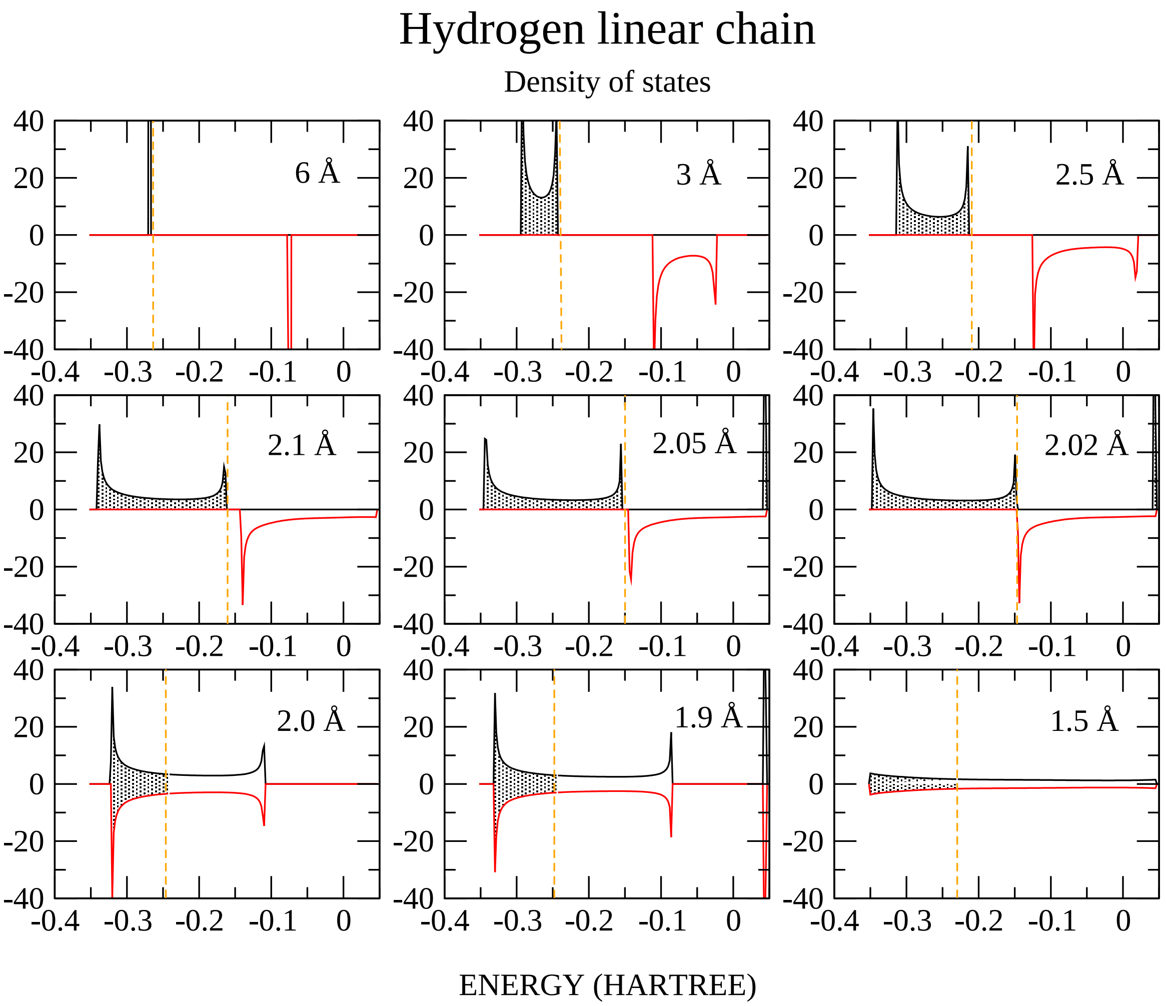

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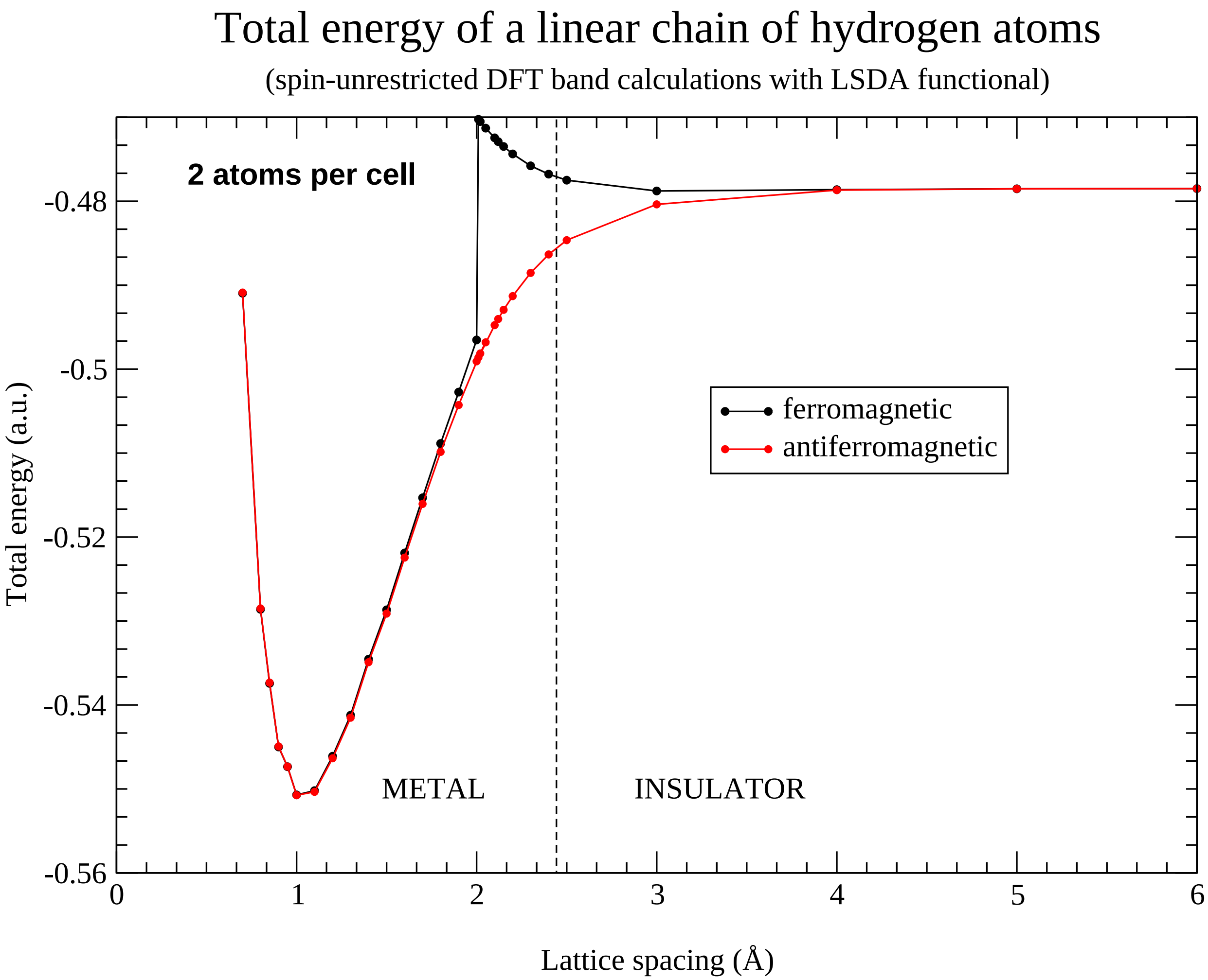
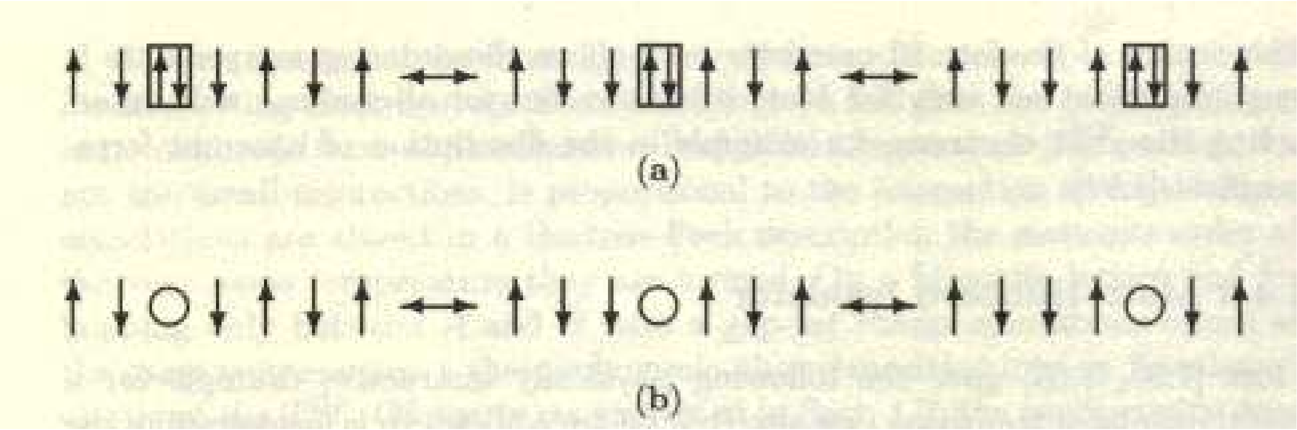


Hubbard bands

[Mott book]

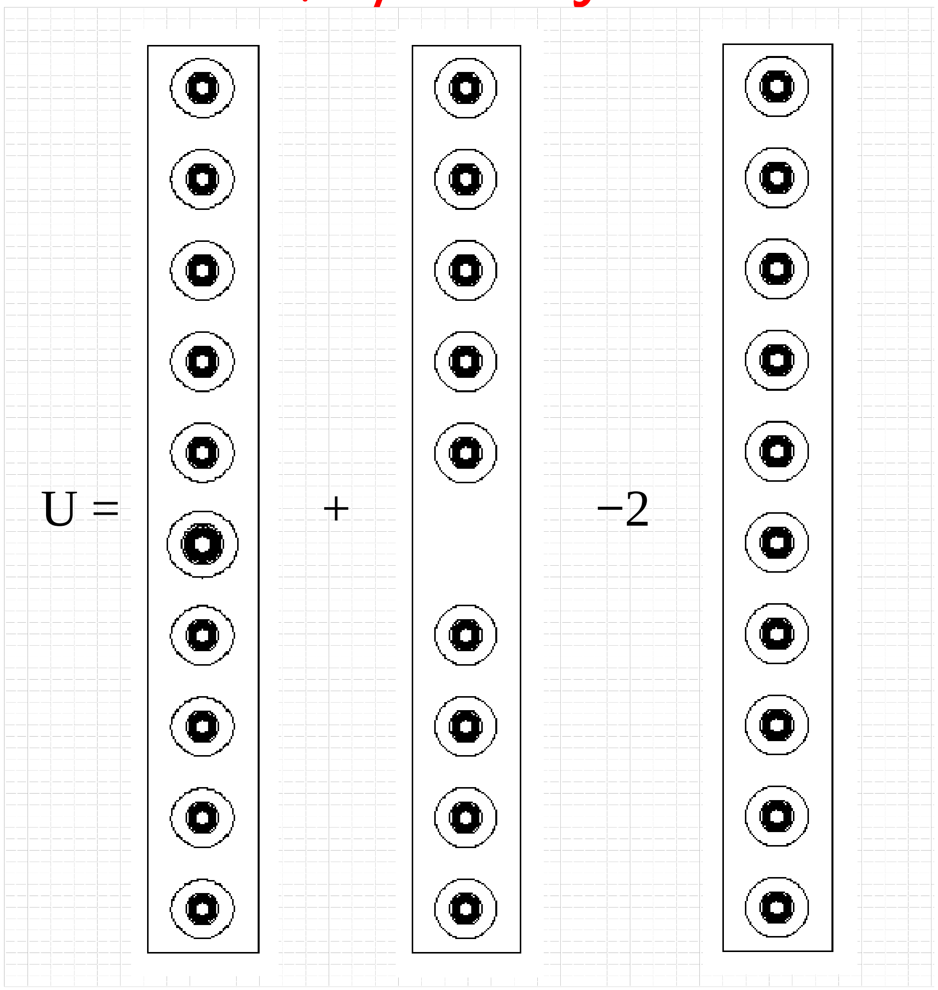


Let ψ_i be the many electron wave function with an extra electron on atom i. A state in which the electron moves with wave number k can be described by the many-electron wave function:

$$\sum_i e^{ika_i}\psi_i$$

These states form a band of energies - this is called the upper Hubbard band - (a). Similarly, the lower Hubbard band - (b) - represents a band of states in which a 'hole' can move. Metal-insulator transition occurs when these bands overlap.

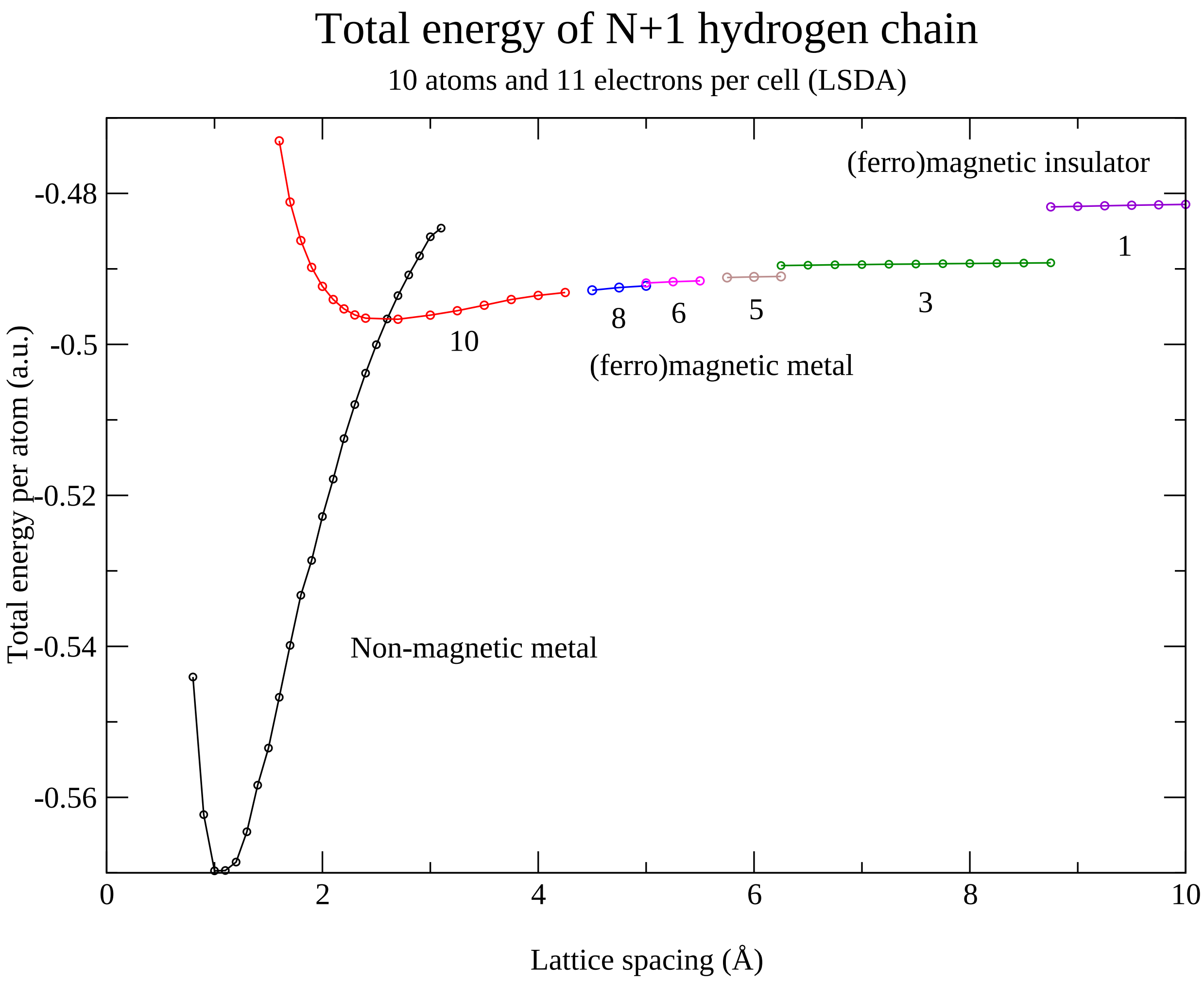
N+1/N-1 system



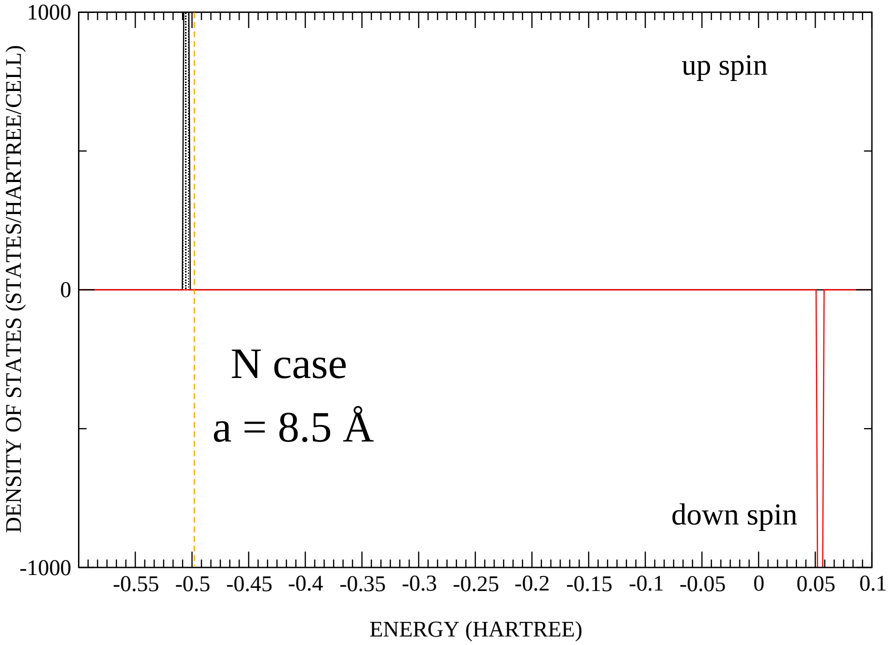
	LSDA (eV)	UHF (eV)	B3LYP (eV)
U (as above)	11.44	13.03	12.01
U (Band gap)	5.30	11.99	8.56

Should be around 13 eV.

N+1 system


Total energy of N+1 hydrogen chain
10 atoms and 11 electrons per cell (LSDA)
(ferro)magnetic insulator
1
3
5
6
8
10
(ferro)magnetic metal
Non-magnetic metal
-0.48
-0.5
-0.52
-0.54
-0.56
Total energy per atom (a.u.)
0
2
4
6
8
10
Lattice spacing (Å)

Effect of extra electron on the density of states



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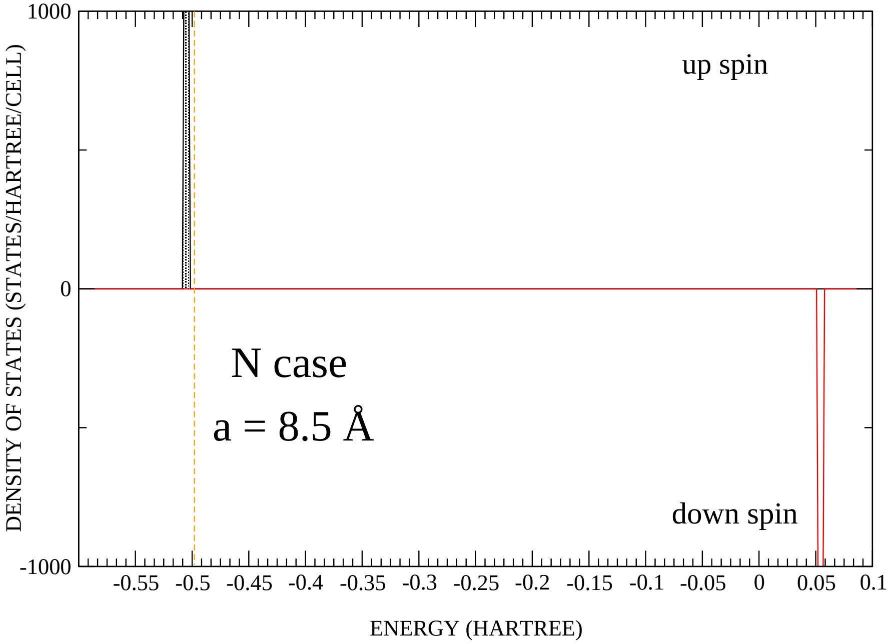

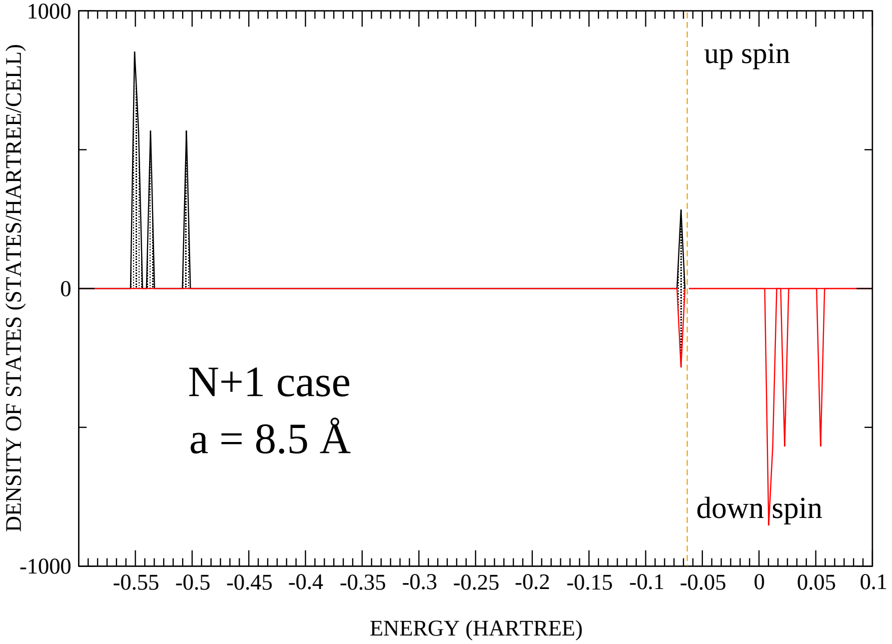

Localization

Insulating state of matter is characterized by gap to low-lying excitations, but also by qualitative features of the ground state - which sustains macroscopic polarization and is localized.

Kohn 1964

Localization is a property of the many-electron wave function: insulating behaviour arises whenever the ground state wave function of an extended system breaks up into a sum of functions Ψ_M which are localized in essentially disconnected regions R_M of configuration space i.e.

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \sum_{M=-\infty}^{+\infty} \Psi_M(\mathbf{x}_1, \ldots, \mathbf{x}_N)$$

where for a large supercell Ψ_M and $\Psi_{M'}$ have an exponentially small overlap for $M' \neq M$. Under such a hypothesis, Kohn proved that the dc conductivity vanishes.

Hence, electronic localization in insulators does not occur in real space (charge density) but in configuration space (wave function).

Many-body phase operators

- Both macroscopic polarization and electron localization are expectation values of 'many-body phase operators' $z_N^{(\alpha)}$, where

$$z_N^{(x)} = \langle \Psi | e^{i \frac{2\pi}{L} \sum_{i=1}^{N} x_i} | \Psi \rangle$$

These quantities are zero for metals!

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- Phase of $z_N^{(\alpha)}$ used to define the macroscopic polarization of an insulator.

- Modulus of $z_N^{(\alpha)}$ used to define the localization tensor $\langle r_\alpha r_\beta \rangle$ (finite in insulators, diverges in metals).

Interesting connections

One-particle density matrix

$$\langle r_\alpha r_\beta \rangle = \frac{1}{2n_b} \int\limits_{cell} d\mathbf{r} \int\limits_{allspace} d\mathbf{r}' (\mathbf{r}-\mathbf{r}')_\alpha (\mathbf{r}-\mathbf{r}')_\beta |P(\mathbf{r},\mathbf{r}')|^2$$

which is the second moment of the (squared) density matrix in the coordinate $\mathbf{r}-\mathbf{r}'$.

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Conductivity

$$\langle r_\alpha r_\beta \rangle = \frac{\hbar V_c}{2\pi e^2 n_b} \int_0^\infty \frac{d\omega}{\omega} \, \mathrm{Re}\, \sigma_{\alpha\beta}(\omega)$$

where $\sigma_{\alpha\beta}$ is the conductivity tensor. LHS property of *ground state*, RHS measurable property related to *electronic excitations* $\Longrightarrow$ localization tensor is a measurable property.

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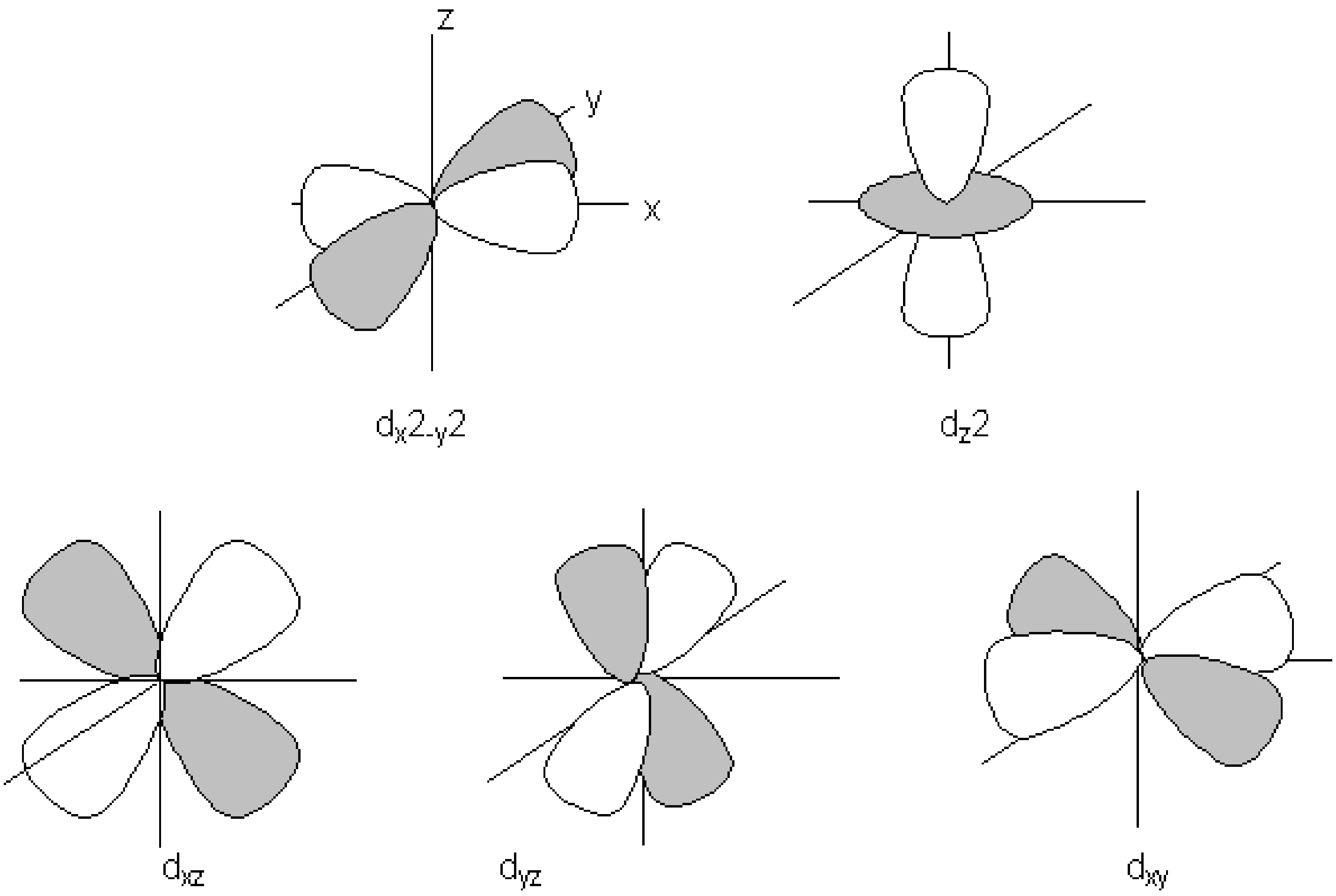
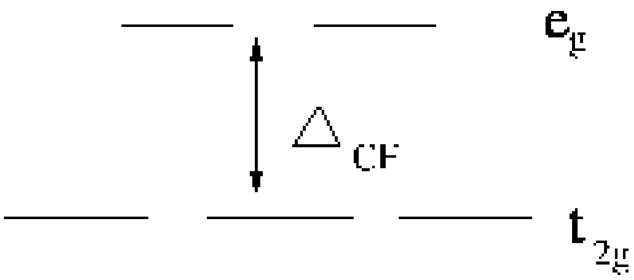
"Nearsightedness"

is the fact that the density matrix $P(\mathbf{r}-\mathbf{r}')$ is short range in the variable $\mathbf{r}-\mathbf{r}'$. The localization tensor is a measure of this.

'Crystal field' splitting of d orbitals (octahedral coordination)





Electronic states in NiO

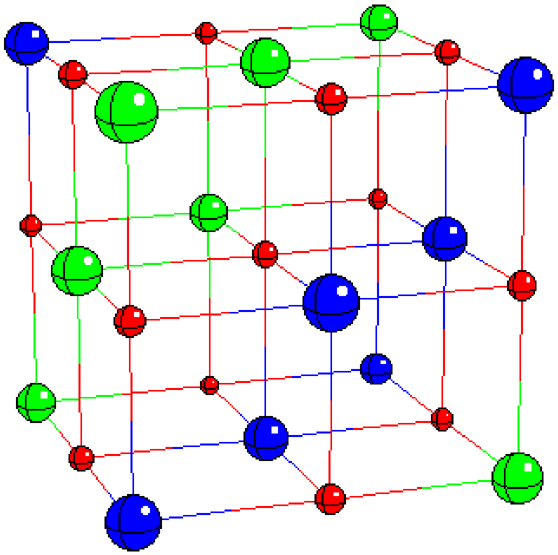
Interactions:

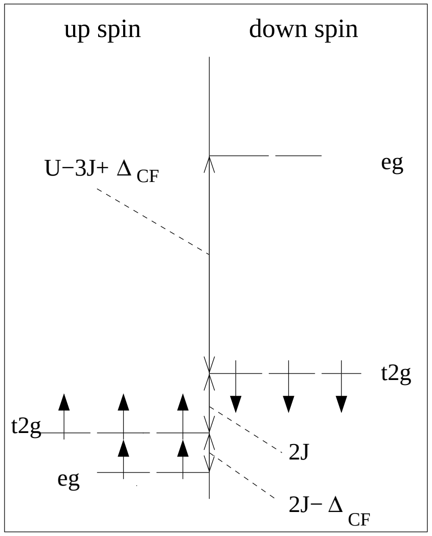
Parameterize on-site interactions in terms of U and U' (Coulomb interactions between electrons in same (U) or different (U') d orbitals) and J (exchange interaction between same spin electrons). Augment with Δ_{CF} i.e. crystal-field splitting energy due to neighbours.

On a Ni site in NiO:

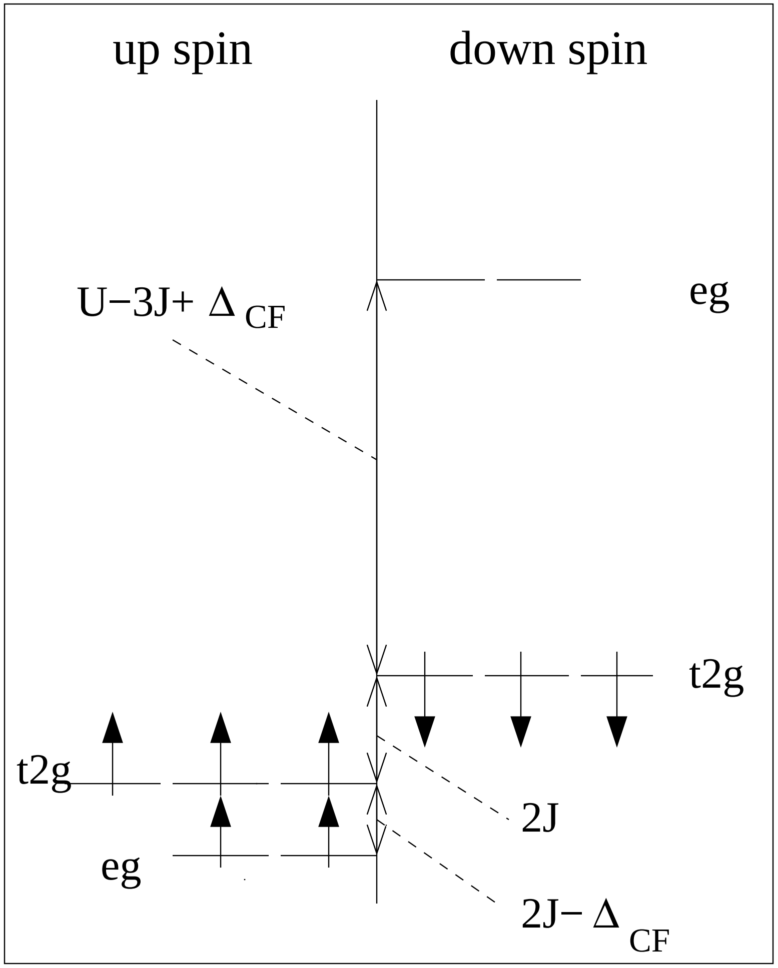
$\uparrow$-spin e_g electron feels: $7U' - 4J + \Delta_{CF}$
$\uparrow$-spin t_{2g} electron feels: $U + 6U' - 4J$
$\downarrow$-spin e_g electron feels: $U + 7U' - 3J + \Delta_{CF}$
$\downarrow$-spin t_{2g} electron feels: $U + 6U' - 2J$

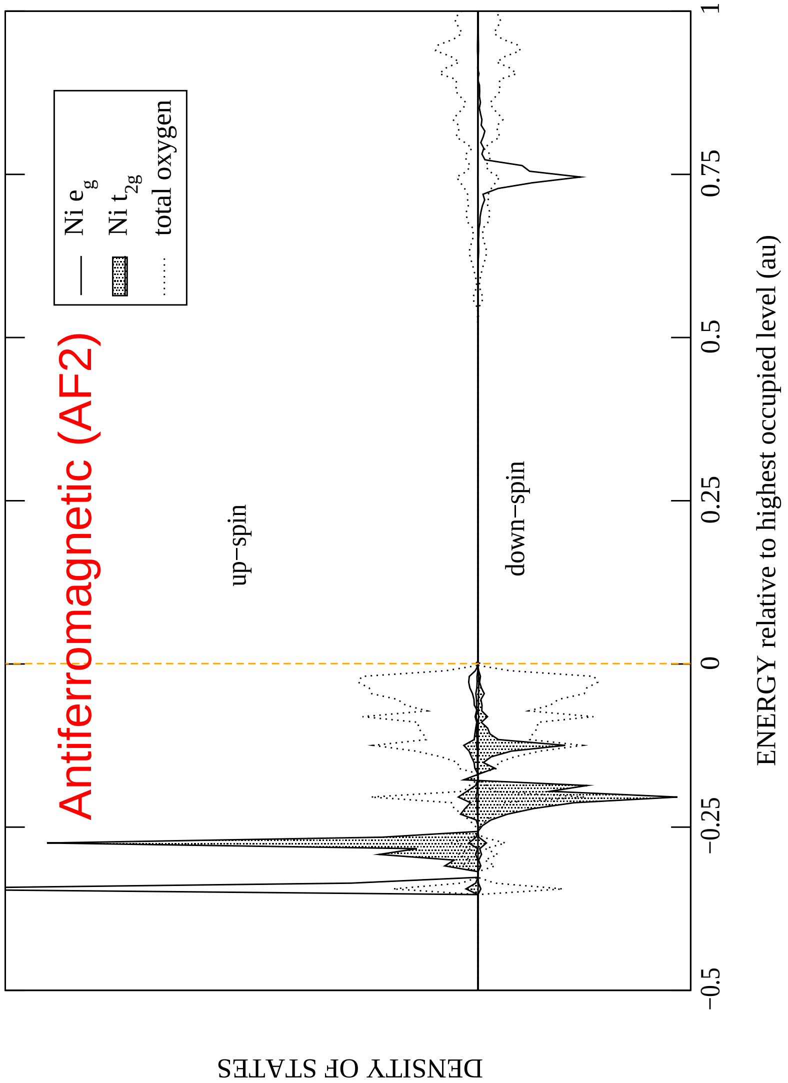
Expt: U=5.8eV, J=0.67eV, U'=4.5eV, Δ_{CF}=1.1eV



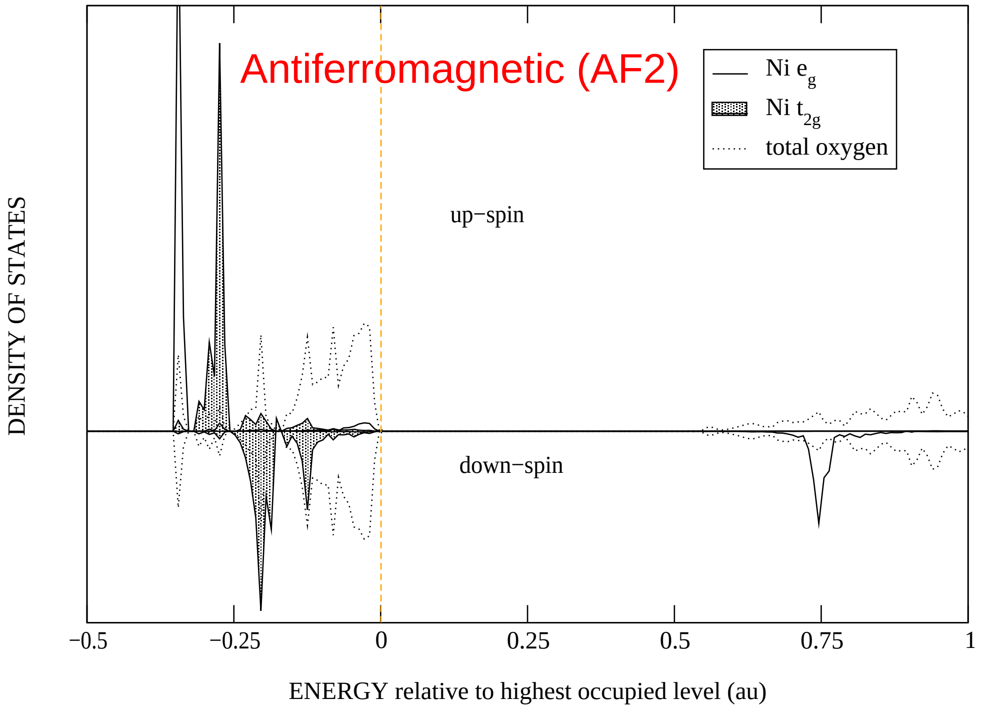


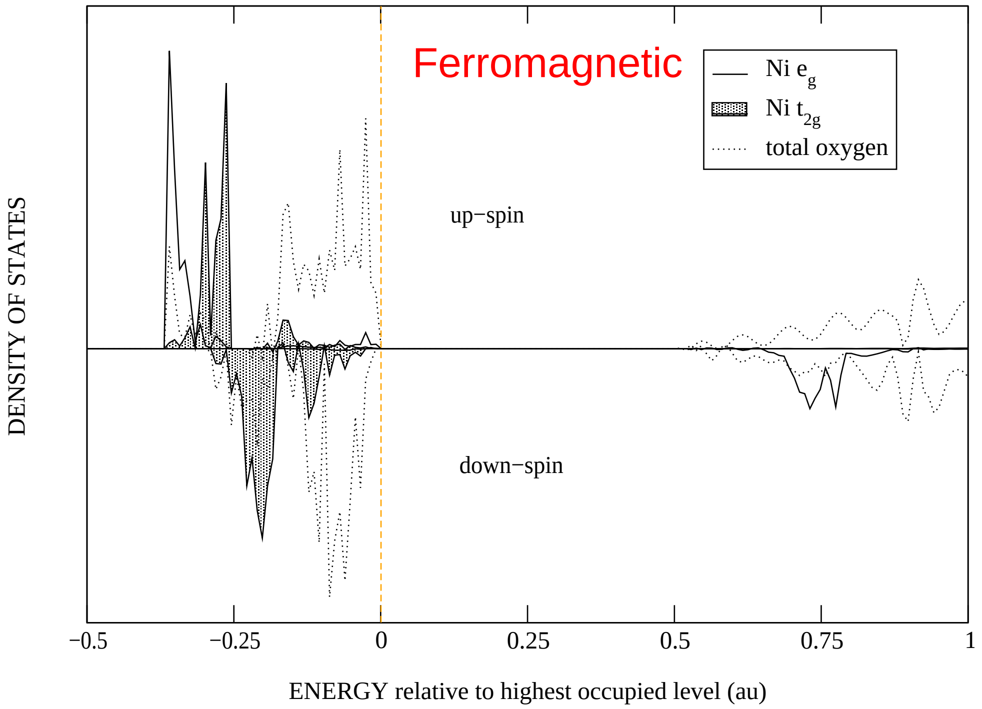
Compare model with NiO UHF DOS



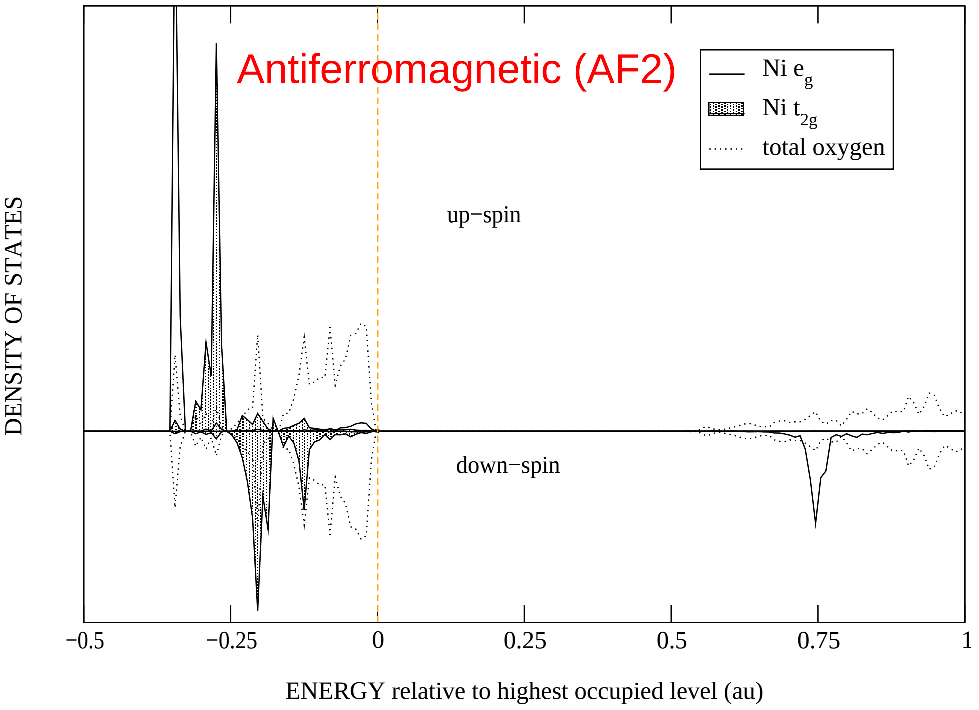


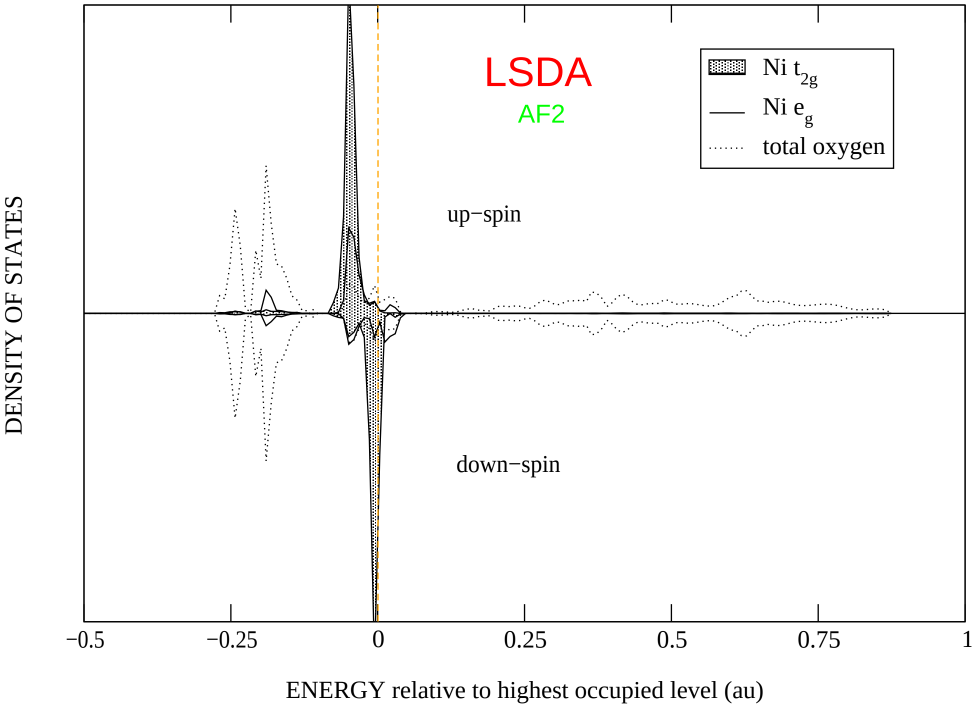
UHF : effect of magnetic ordering



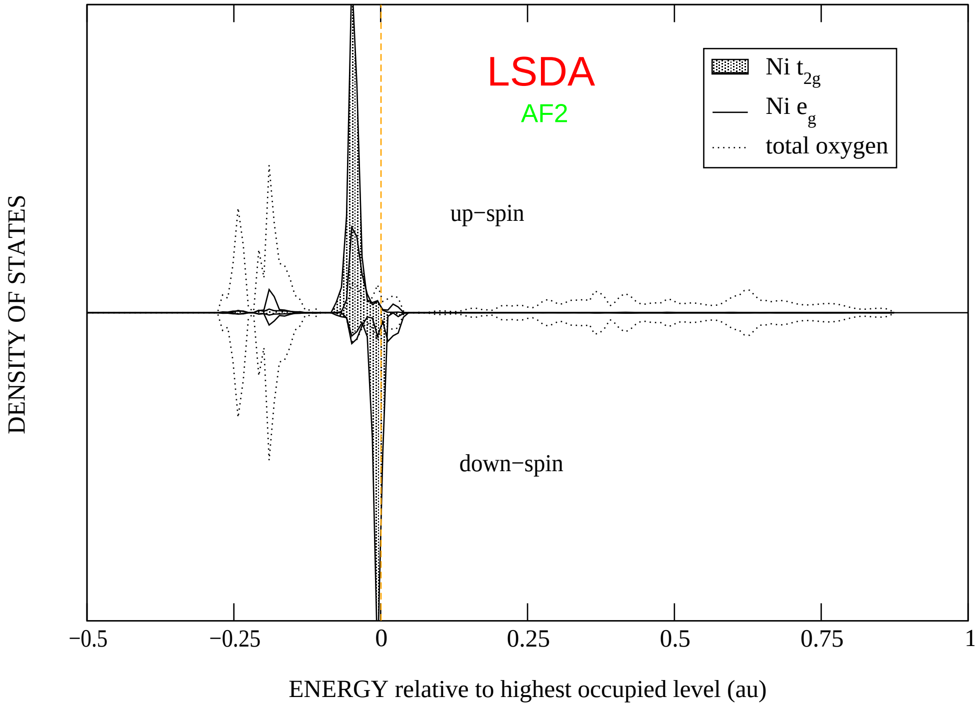


UHF vs. LDA


Antiferromagnetic (AF2)
Ni e_g
Ni t_2g
total oxygen
up−spin
down−spin
DENSITY OF STATES
−0.5
−0.25
0
0.25
0.5
0.75
1
ENERGY relative to highest occupied level (au)


LSDA
AF2
Ni t_2g
Ni e_g
total oxygen
up−spin
down−spin
DENSITY OF STATES
−0.5
−0.25
0
0.25
0.5
0.75
1
ENERGY relative to highest occupied level (au)

UHF vs. GGA


LSDA
AF2
Ni t_{2g}
Ni e_g
total oxygen
up−spin
down−spin
DENSITY OF STATES
−0.5
−0.25
0
0.25
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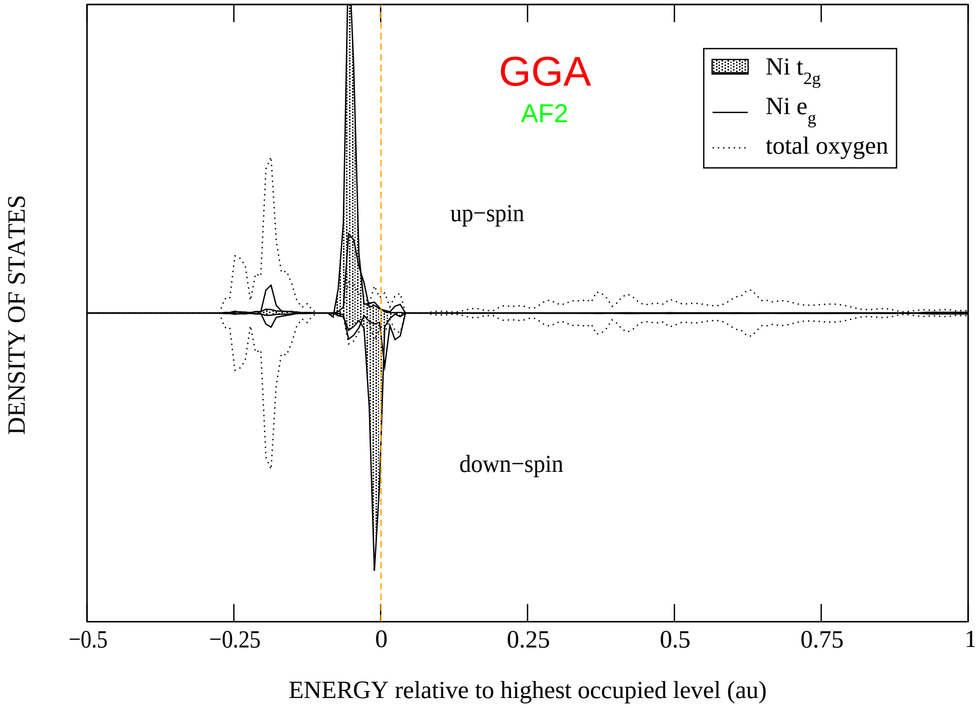
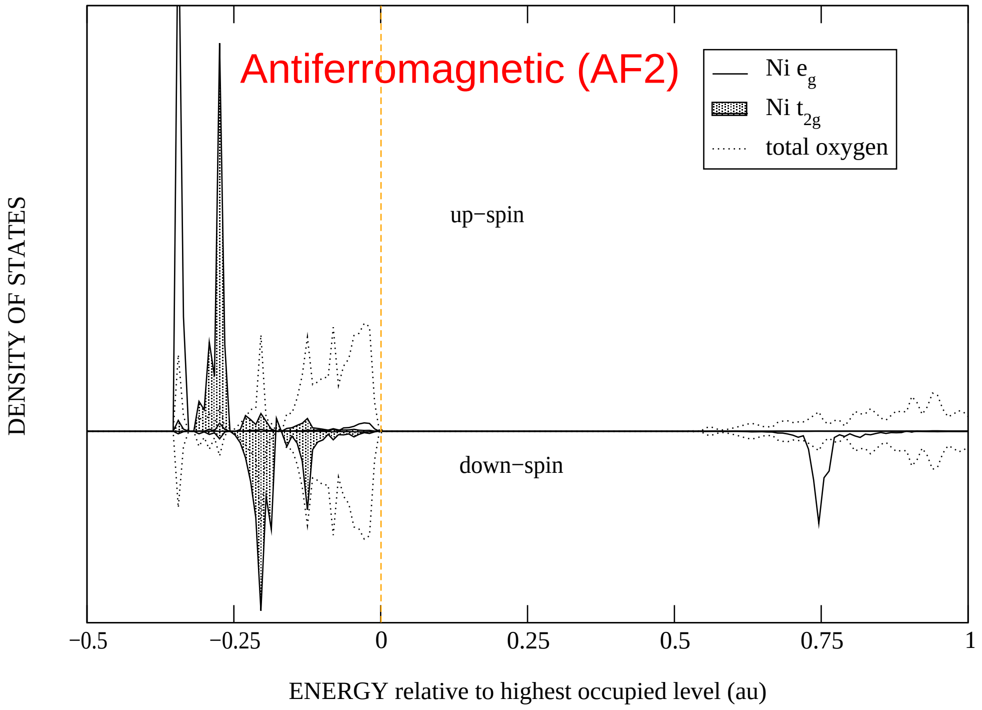

GGA
AF2
Ni t_{2g}
Ni e_g
total oxygen
up−spin
down−spin
DENSITY OF STATES
−0.5
−0.25
0
0.25
0.5
0.75
1
ENERGY relative to highest occupied level (au)

UHF vs. B3LYP


Antiferromagnetic (AF2)
Ni e_g
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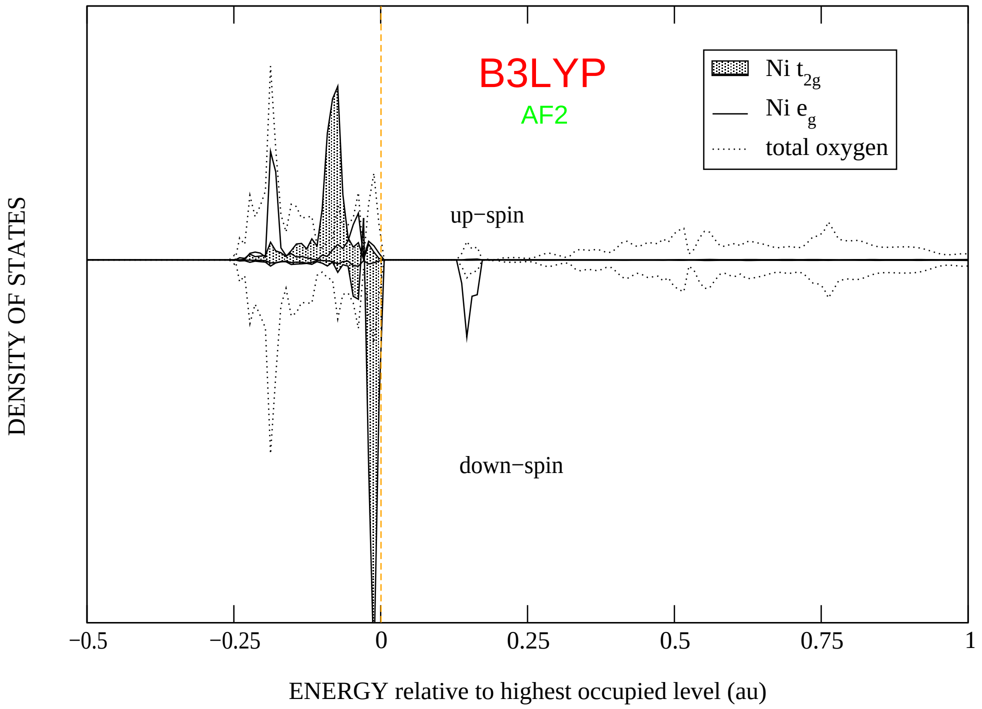
B3LYP
AF2
Ni t_{2g}
Ni e_g
total oxygen
up−spin
down−spin
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0
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0.75
1
ENERGY relative to highest occupied level (au)

Band gaps with the B3LYP functional

Material	Expt. (eV)	B3LYP (eV)
Si	3.5	3.8
Diamond	5.5	5.8
GaAs	1.4	1.5
ZnO	3.4	3.2
Al_2O_3	9.0	8.5
Cr_2O_3	3.3	3.4
MgO	7.8	7.3
MnO	3.6	3.8
NiO	4.3	3.9
TiO_2	3.0	3.4
FeS_2	1.0	2.0
ZnS	3.7	3.5

Orbital interactions

How do orbitals interact in the Hartree-Fock approximation?

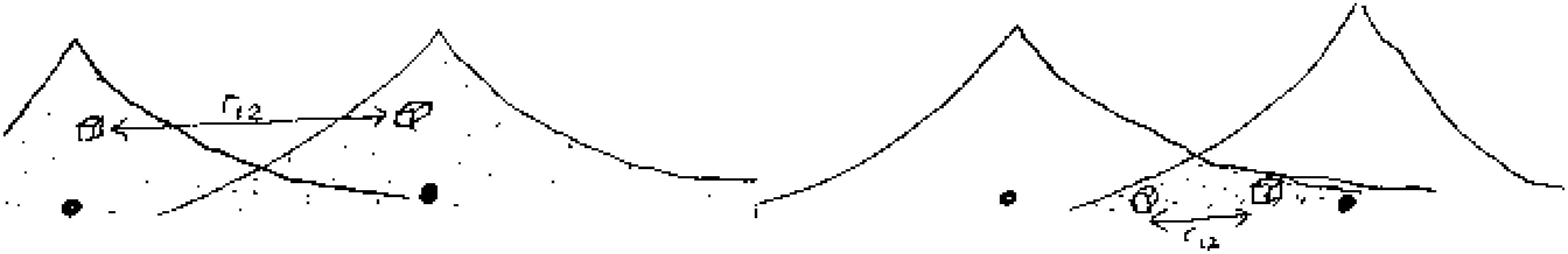
$$E_0 = \sum_a \langle a|\hat{h}|a\rangle + \sum_{ab} \langle aa \,\|\, bb\rangle - \langle ab \,\|\, ba\rangle$$

Coulomb interaction

$$\boxed{\langle aa \,\|\, bb\rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \;\; |\phi_a(\mathbf{r}_1)|^2 \, \frac{1}{r_{12}} \, |\phi_b(\mathbf{r}_2)|^2}$$

exchange interaction

$$\boxed{\langle ab \,\|\, ba\rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \; \phi_a^*(\mathbf{r}_1)\phi_b^*(\mathbf{r}_1)\frac{1}{r_{12}}\phi_b(\mathbf{r}_2)\phi_a(\mathbf{r}_2)}$$



Self-interaction - Hartree-Fock case

- Label orbitals occupied $(a, b, \ldots)$ or virtual $(i, j, \ldots)$. What is the expression for the orbital energy?

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Occupied

$$\epsilon_a = \langle \phi_a | \hat{h} | \phi_a \rangle + \sum_{b=1}^{N} \left(\langle \phi_a \phi_a \, || \, \phi_b \phi_b \rangle - \langle \phi_a \phi_b \, || \, \phi_b \phi_a \rangle \right)$$

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Virtual

$$\epsilon_i = \langle \phi_i | \hat{h} | \phi_i \rangle + \sum_{b=1}^{N} (\langle \phi_i \phi_i \,\|\, \phi_b \phi_b \rangle - \langle \phi_i \phi_b \,\|\, \phi_b \phi_i \rangle)$$

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- Sum over b is over occupied orbitals only. Therefore for the first expression only, one of the terms will cancel when b=a:

$$\langle\phi_a\phi_a \,\|\, \phi_a\phi_a\rangle - \langle\phi_a\phi_a \,\|\, \phi_a\phi_a\rangle = 0$$

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- Therefore in the Hartree-Fock approximation an electron does not feel its own field, since the self-interaction is cancelled by an equivalent term in the exchange energy.

Self-interaction in local density approximation to DFT

LSDA exchange energy

$$E_x = \int d\mathbf{r} \;\; \epsilon_x \left[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})\right]$$

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LSDA exchange energy

$$E_x = \int d\mathbf{r} \;\; \epsilon_x \left[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})\right]$$

Mean-field contains all the electrons

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Implications:

Self-interaction in local density approximation to DFT

LSDA exchange energy

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Mean-field contains all the electrons

Implications:

- U (interpreted as the ‘self-exchange’ term) equals J (the ‘different orbital’ exchange term).

- But U and J differ by an order of magnitude in NiO. LSDA effectively *averages* these quantities.

- Therefore additional potential U felt by unoccupied orbitals disappears, and instead all the states are shoved up in energy by something like the average of U and J.

- Local density theory lumps all these exchange interactions together and thus dilutes the effect of self-exchange and underestimates the driving force for the formation of a correlated state. This is the root of the difficulty of contemporary calculations in describing strongly-correlated systems.

What to do about it

Problem:

The effect of self-interaction and the use of simple local exchange functionals (inherent in LSDA and all GGA treatments) will often lead to the wrong ground state in magnetic insulators and other strongly correlated materials.

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Possible ways to improve this:

What to do about it

Problem:

The effect of self-interaction and the use of simple local exchange functionals (inherent in LSDA and all GGA treatments) will often lead to the wrong ground state in magnetic insulators and other strongly correlated materials.

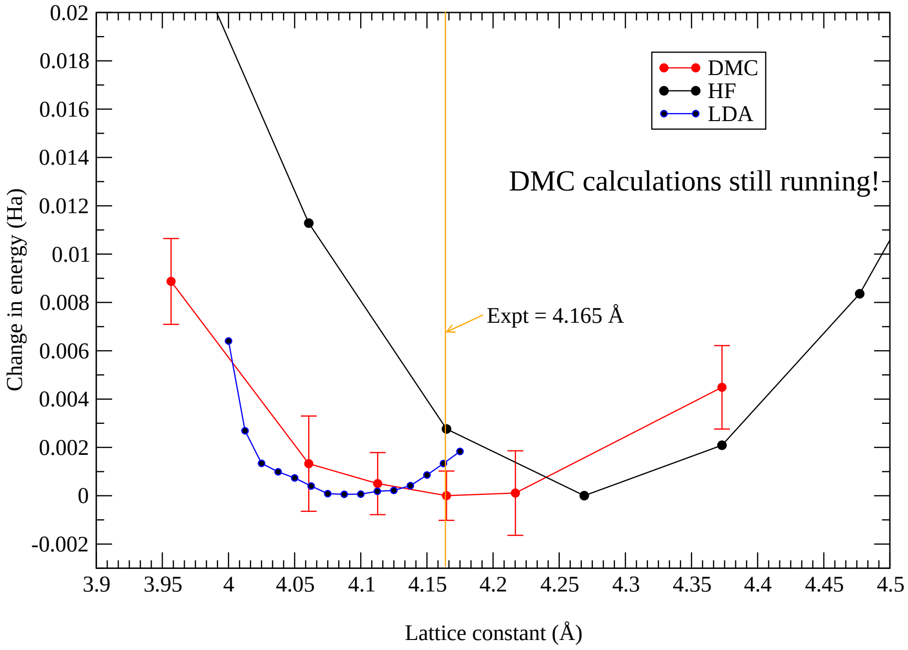
Possible ways to improve this:

- Use 'corrections' to LDA treatment (LDA+U, SIC-LDA).
- Use unrestricted Hartree-Fock calculations.
- Use 'hybrid functionals' in DFT containing some fraction of the non-local HF exchange (e.g. B3LYP)
- Use 'exact-exchange' DFT treatments currently being developed.
- Use the result of any of the above as a trial wave function for quantum Monte Carlo (which is self-interaction free).

Results for some simple properties of NiO

	a (Å)	E_C (eV)	E_g (eV)
UHF	4.26	6.2	14.2
LSDA	4.09	10.96	0
GGA	4.22	8.35	0
B3LYP	4.22	7.8	3.9
DMC(UHF)	(4.16ish?)	9.44(13)	
DMC(B3LYP)		9.19(14)	4.3(2)
Exp.	4.165	9.45(±?)	4.0–4.3

Lattice constant, a, cohesive energy, E_C, and band gap, E_g, of NiO.



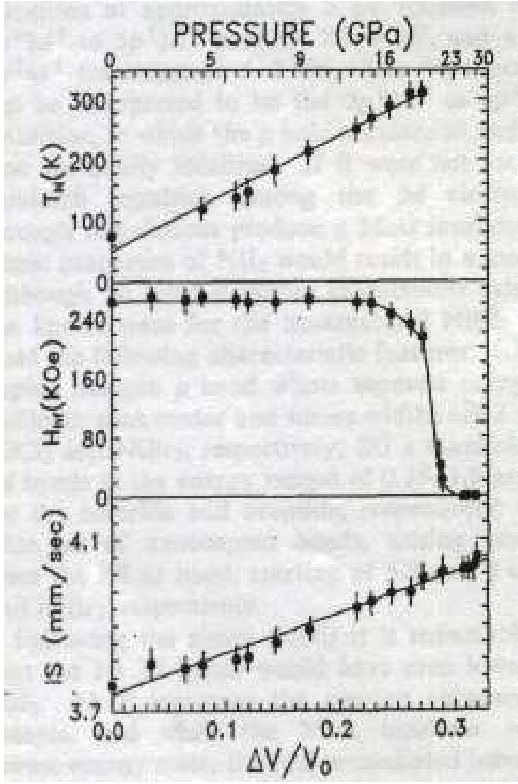
DMC calculations still running!

Real Mott transitions

Experimental techniques

- very high pressure diamond anvil cells ($\longrightarrow$ Mbar range)
- Mössbauer spectroscopy - probes spins through hyperfine fields - only high pressure method for probing sensitive magnetic phenomena like HS →LS transitions etc..
- synchrotron X-ray diffraction
- resistance measurements

Examples NiI_2, CoI_2, Fe_2O_3, FeO



Things to do (maybe)

Research

- Implement calculation of many-body phase operators in CASINO QMC code (easy!).

- Check if results of above make sense in very simple systems (like hydrogen chain!) then repeat in simple materials like aluminium and carbon.

- Check out the Mott transitions in e.g. $\mathrm{NiI_2}$, $\mathrm{CoI_2}$, $\mathrm{Fe_2O_3}$, etc. HS →LS transition in FeO with both DFT and QMC calculations.

Things to think about

- The mathematics of Berry phases and many-body phase operators in periodic boundary conditions..

- Clarify the connections between localization tensors, maximally localized Wannier functions, conductivity, nearsightedness, density matrices, Boys localization, Kohn theory, polarization etc..

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Hurray!