

***Ab initio* study of Mn doped BN nanosheets**

Tudor Luca Mitran

MDEO Research Center – University of Bucharest, Faculty of Physics,
Bucharest-Magurele, Romania

Oldenburg – 20.04.2012

Table of contents

1. Density Functional Theory

2. SIESTA method

3. Diluted magnetic semiconductors

4. Magnetism in Mn doped boron nitride (BN) nanosheets

Density Functional Theory

Traditional approach: find approximate solutions for the Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 - \sum_{j,i} \frac{e_0^2 Z_i}{|r_j - R_i|} + \frac{1}{2} \sum_{j \neq i} \frac{e_0^2}{|r_j - r_i|} - E \right\} \psi(r_1, \dots, r_N) = 0$$

Not trivial even for N=2 !

Usual quantum chemistry methods: semi-empirical \longrightarrow require experimental data (not rigorous)
post-Hartree-Fock \longrightarrow practical only for low N ($\ll 100$)

Problems of interest in solid state physics: $N \in (\sim 100, \infty)$

One possible solution \longrightarrow **DFT**

Hohenberg \longrightarrow P. Hohenberg and W. Kohn. **Phys. Rev.**, **136 B864 (1964)**
Kohn \longrightarrow
Sham \longrightarrow W. Kohn and L. J. Sham. **Phys. Rev.**, **140 A1133 (1965)**

Main idea: replace the N electron wavefunction with an electron density !

Density Functional Theory

Hohenberg-Kohn theorems:

1. The potential $V(r)$ is determined uniquely by the ground state electron density $n(r)$
2. A universal functional for the energy $E(n(r))$ can be defined valid for any external potential $V(r)$. For a particular external potential, the ground state energy (even degenerate) is given by the density that minimizes the functional.

Kohn-Sham equations:
$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(\vec{r}) \right) \psi_i(\vec{r}) = E_i \psi_i(\vec{r})$$

Schrödinger-like equation for system of non-interacting particles that generates the **same electron density $n(r)$ as the real system of interacting particles**

$$E[\psi_i(\vec{r})] = T_e + U_{nn} + U_{ne} + U_{ee} + E_{xc}$$

$$U_{nn} = \frac{1}{2} e_0^2 \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \quad U_{ne} = \int V_n(\vec{r}) n(\vec{r}) d^3 r \quad U_{ee} = \frac{1}{2} \int V^H(\vec{r}) n(\vec{r}) d^3 r$$

$$V_n(\vec{r}) = -e_0^2 \sum \frac{Z_\alpha}{|\vec{r} - \vec{R}_\alpha|} \quad V^H(\vec{r}) = e_0^2 \int \frac{n(\vec{r}') d^3 r'}{|\vec{r} - \vec{r}'|}$$

$$\nabla^2 V^H(\vec{r}) = -4\pi e_0^2 n(\vec{r})$$

Density Functional Theory

$$n(\vec{r}) = \sum g_i |\psi_i(\vec{r})|^2 \longleftarrow \text{K.S. orbitals} \longrightarrow \int \psi_i^*(\vec{r}) \psi_j(\vec{r}) d^3r = \delta_{ij}$$

$$T_e = \sum_i g_i \int \psi_i^*(\vec{r}) \left(\frac{\hbar^2}{2m} \nabla^2 \psi_i(\vec{r}) \right) d^3r$$

Much lower weight than previous terms but plays important role, especially in strongly correlated materials because it “hides” **multiparticle effects**. It is the “**glue**” that bonds atoms together.

$$E_{xc} = \int f_{xc}(n(\vec{r})) d^3r$$

Only problem ...

The exchange correlation energy is not known exactly !

Must use an approximation for E_{xc}

Type	Parametrization “flavor”
→	LDA (Ceperley-Alder, Perdew-Wang)
→	GGA (Perdew-Burke-Ernzenhof, Wu-Cohen, ...)

$E_{xc} = E_x + E_c$

Effect of Pauli exclusion principle → E_x

In U_{ee} electrons only interact with the **average** position of other electrons. **Direct** Coulomb interaction is ignored ! → E_c

E_{xc} effectively reduces the local charge density

Density Functional Theory

Derivation of the Kohn-Sham equations

We must minimize: $E[\psi_i(\vec{r})] = T_e + U_{nn} + U_{ne} + U_{ee} + E_{xc}$

With the orthogonality constraint: $\int \psi_i^*(\vec{r})\psi_i(\vec{r})d^3r = 0$

Use Lagrange multipliers:

$$\frac{\delta}{\delta\psi_i^*(\vec{r})} \left(T_e + U_{nn} + U_{ne} + U_{ee} + E_{xc} - \sum_i \lambda_i \int \psi_i^*(\vec{r})\psi_i(\vec{r})d^3r \right) = 0$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\vec{r}) + V_{KS}(\vec{r})\psi_i(\vec{r}) = \frac{\lambda_i}{g_i}\psi_i(\vec{r})$$

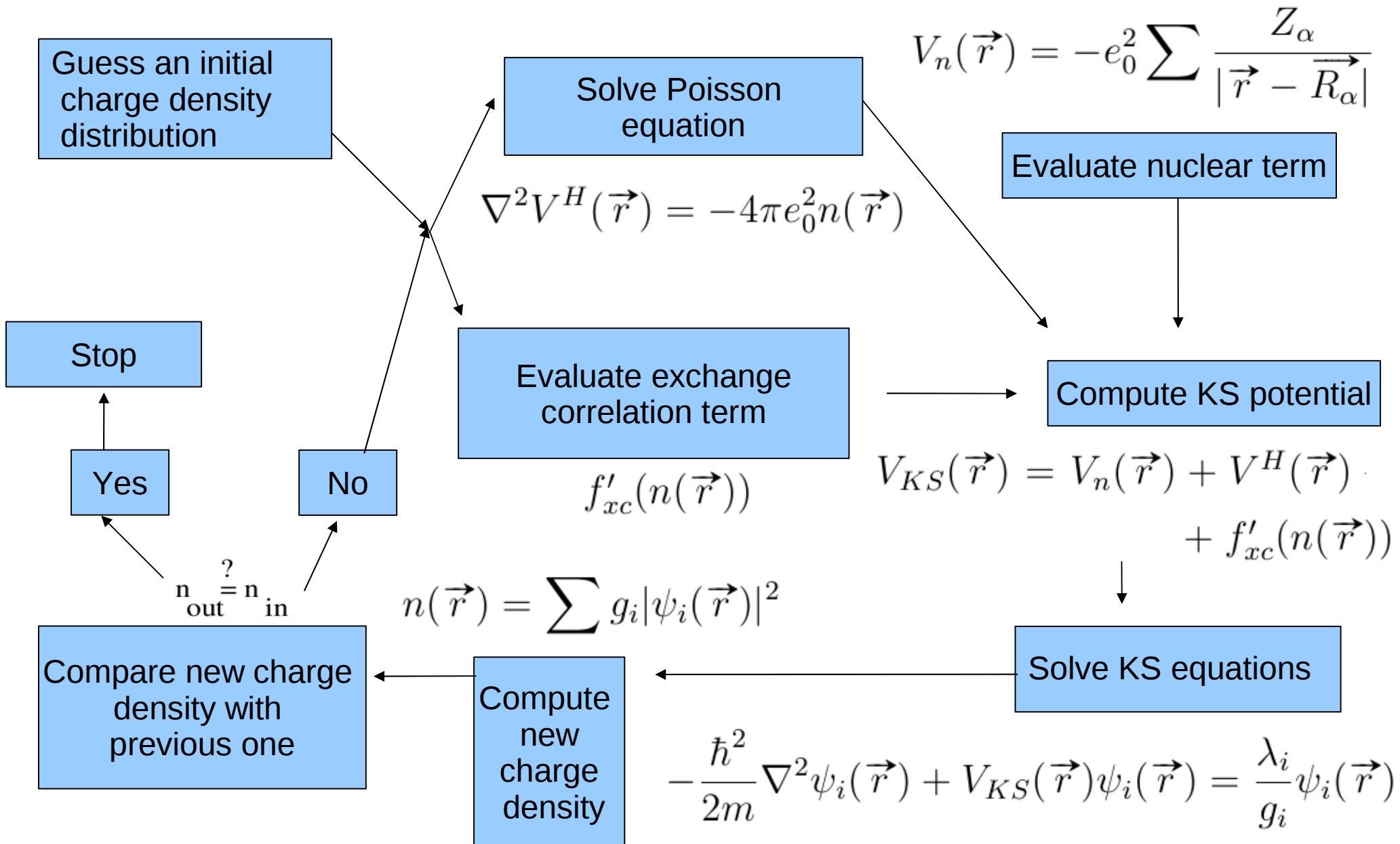
$$V_{KS}(\vec{r}) = V_n(\vec{r}) + V^H(\vec{r}) + f'_{xc}(n(\vec{r}))$$

$$\frac{\lambda_i}{g_i} = E_i$$

Kohn-Sham equations: $\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\vec{r}) \right) \psi_i(\vec{r}) = E_i\psi_i(\vec{r})$

Density Functional Theory

Self consistency loop:



SIESTA method

(Spanish Initiative for Electronic Simulations with Thousands of Atoms)

“The SIESTA method for ab initio order-N materials simulation”

José M Soler, Emilio Artacho, Julian D Gale, Alberto García, Javier Junquera, Pablo Ordejón and Daniel Sánchez-Portal -
J. Phys.: Condens. Matter 14 2745 (2002)

<http://www.icmab.es/dmmis/leem/siesta/>

Most important feature of SIESTA: **linear scaling**, while usual DFT methods scale as N^3 !

What can you compute with it ?

- Band structure
- Electron density
- Total and partial density of states
- Electric dipole moment
- Mulliken population
- Spin polarized calculations
- Atomic forces
- Structural relaxation
- Stress tensor
- Molecular dynamics
- Phonon spectra

What else can it do ?

Ballistic electronic transport with TRANSIESTA

“Density-functional method for nonequilibrium electron transport”
Mads Brandbyge, Jose-Luis Mozos, Pablo Ordejón, Jeremy Taylor, and Kurt Stokbro
Phys. Rev. B 65 165401 (2002)

Additional visualization software:

XcrySDen A. Kokalj, **Comp. Mater. Sci. 28 155-68**

V_Sim http://www-drfmc.cea.fr/L_Sim/V_Sim/index.en.html

SIESTA method

Pseudopotentials (not absolutely necessary but they speed things up)

Main idea: replace core electrons and nuclear potential with an effective pseudopotential.

“A New Approximation Method in the Problem of Many Electrons”

H. Hellmann

J. Chem. Phys. 3, 61 (1935)

Benefits:

- “Get rid” of core electrons (not chemically active)
- “Iron out” strongly varying wavefunction (near core)

reduce the number of electrons and the basis set that will be required

Use **norm-preserving** pseudopotentials: $\int_0^{r_c} \psi^{ae*}(\vec{r})\psi^{ae}(\vec{r})dr = \int_0^{r_c} \psi^{ps*}(\vec{r})\psi^{ps}(\vec{r})dr$

How they are obtained:

- Solve all-electron radial equation
- Generate pseudo-wavefunctions
- Invert radial equation and obtain pseudopotential

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} + V(r) \right) \psi_l^{ae}(r) = E_l^{ae} \psi_l^{ae}(r)$$

Use **soft pseudopotentials** (instead of ultrasoft) for **transferability** !

SIESTA uses the fully non-local **Kleinman-Bylander** form

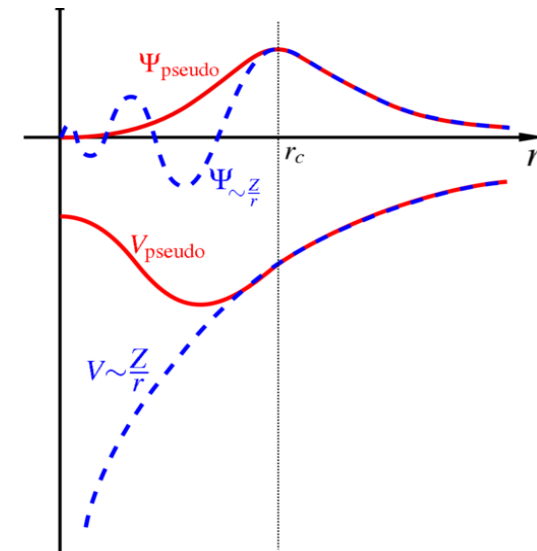
“Efficacious Form for Model Pseudopotentials”

Leonard Kleinman and D. M. Bylander

Phys. Rev. Lett. 48 20 (1982)

Non-local = separate radial and angular momentum dependent parts

Computationally efficient



SIESTA method

The basis set – Numerical atomic orbitals

SIESTA uses a **localized basis set** \longrightarrow **sparse Hamiltonian and overlap matrices**

$$\psi_i(\vec{r}) = \sum_{\mu} \phi_{\mu}(\vec{r}) c_{\mu i}$$

$$H_{\mu\nu} = \langle \phi_{\mu} | H | \phi_{\nu} \rangle = \int d\vec{r} \phi_{\mu}^*(\vec{r}) H \phi_{\nu}(\vec{r})$$

$$S_{\mu\nu} = \langle \phi_{\mu} | \phi_{\nu} \rangle = \int d\vec{r} \phi_{\mu}^*(\vec{r}) \phi_{\nu}(\vec{r})$$

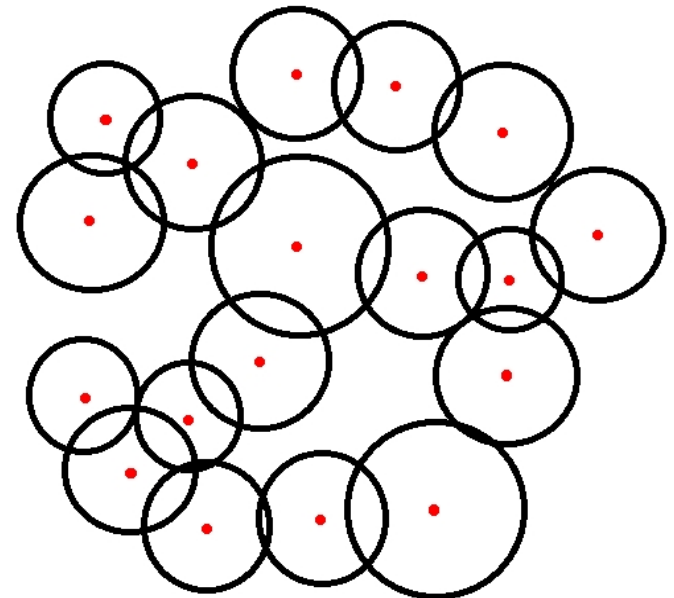
$$\begin{pmatrix} H \end{pmatrix} \begin{pmatrix} c \end{pmatrix} = E_{n\vec{k}} \begin{pmatrix} S \end{pmatrix} \begin{pmatrix} c \end{pmatrix}$$

Strict localization of the basis functions is important because the Hamiltonian and overlap matrices are evaluated on **real space grids!**

Soft confining potential \longrightarrow

$$V(r) = V_0 \frac{e^{-\frac{R_c - R_i}{r - R_i}}}{R_c - r}$$

Basis type: single zeta
double zeta
double zeta polarized



SIESTA method

Other details

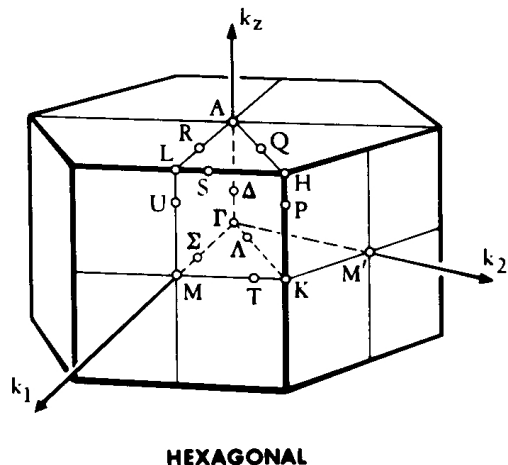
- Periodic **Born - von Karman** boundary conditions

Can also treat **non-periodic systems** if the supercell is large enough

Empty space has almost no additional computational cost (as opposed to PW approach) because of the strictly localized basis set functions.

- **Monkhorst-Pack** Brillouin zone integration

H.J. Monkhorst and J.D. Pack,
Phys. Rev. B 13 5188 (1976)

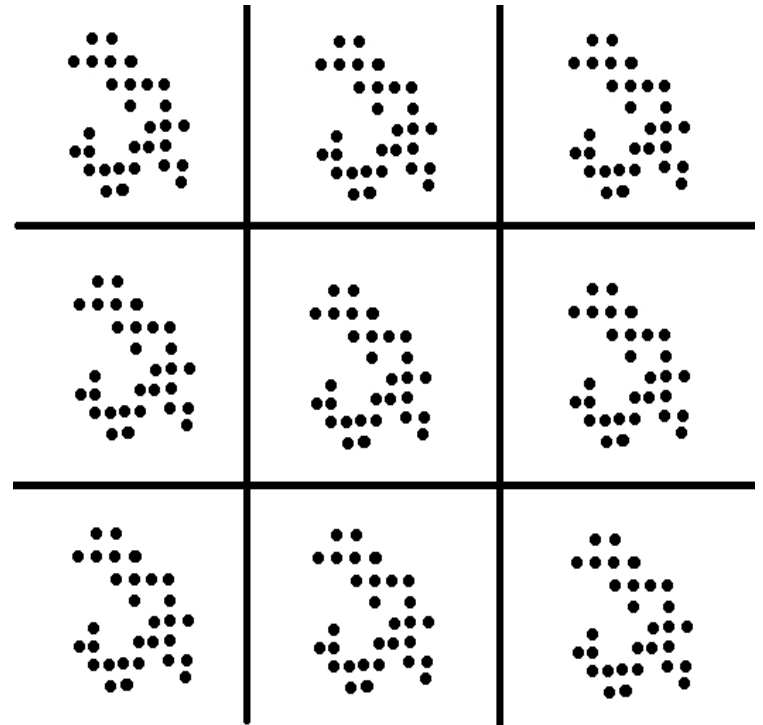


Bloch wave

$$\psi_i(k, r) = \sum_j e^{ikr} \phi_j(r) c_{ji}(k)$$

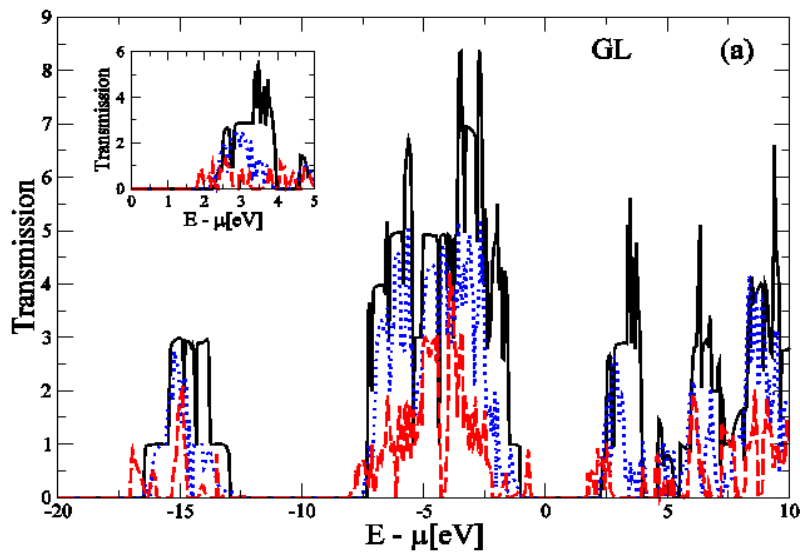
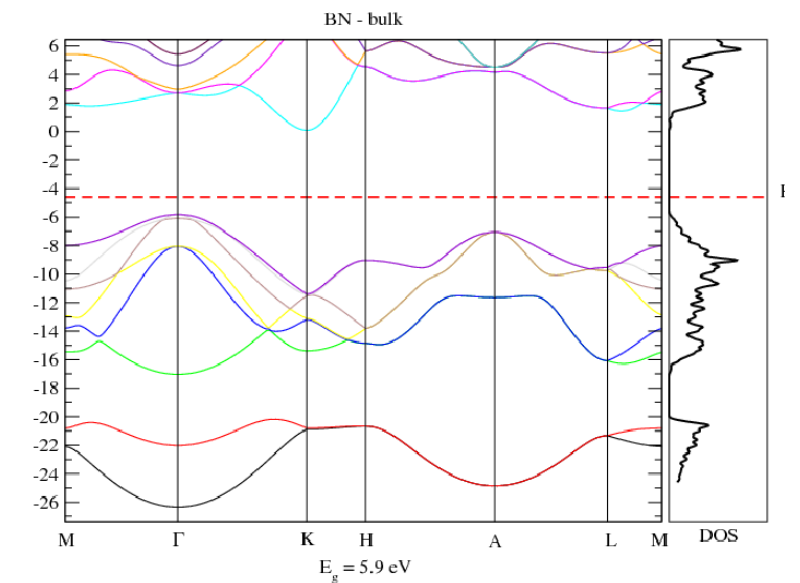
- Atomic forces: **Hellmann-Feynman** theorem
R.P. Feynman. **Phys. Rev. 56 340 (1939)**

$$F_{r_{ij}} = \frac{\partial E^{KS}}{\partial r_{ij}}$$



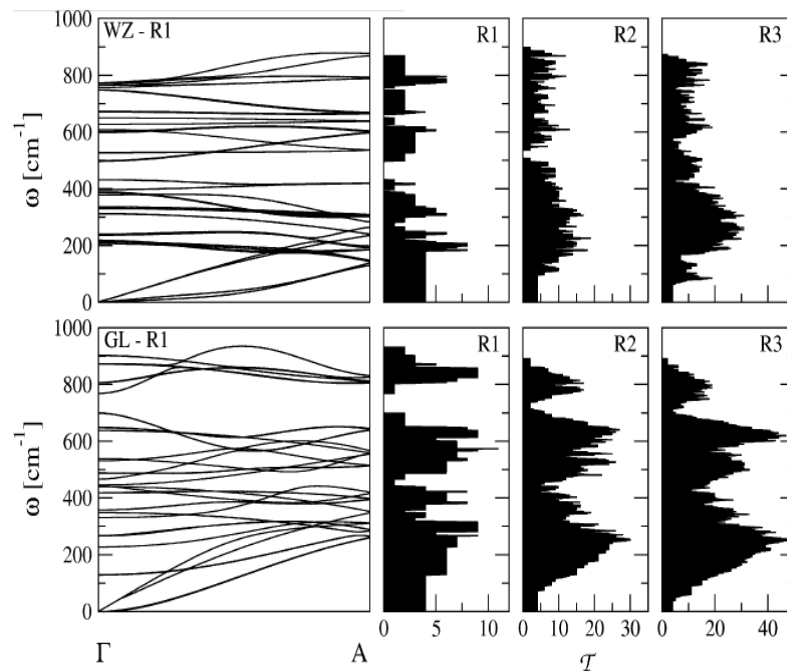
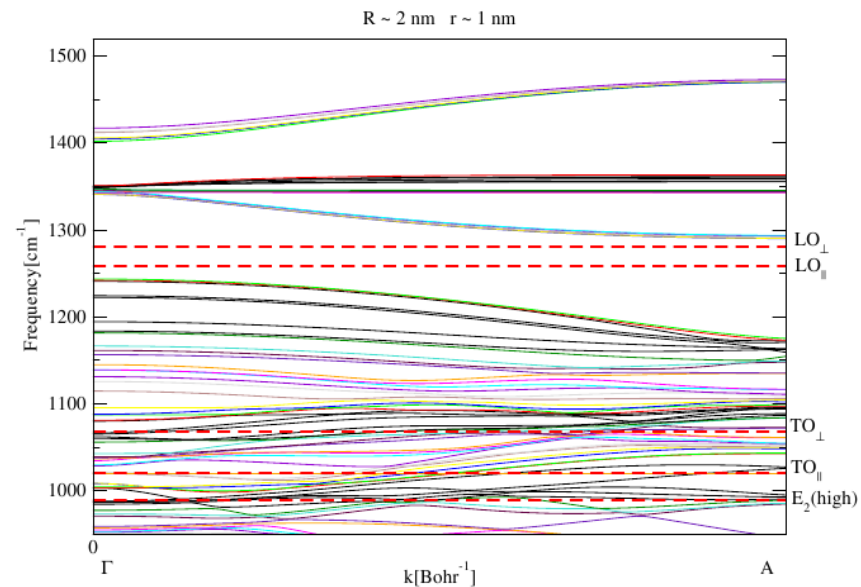
SIESTA method

Some pretty pictures



Electronic transmission through AlN nanowires

Dig. J. Nanomat. Biostruct 6 1173 (2011)



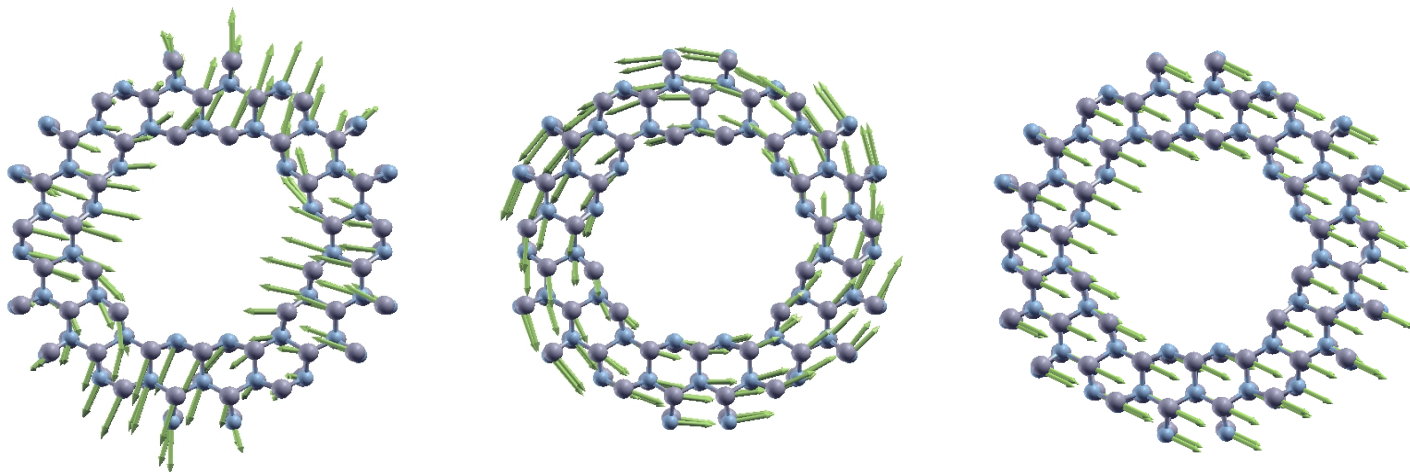
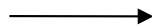
Phonon bands and transmission AlN nanowires

Comp. Mat. Sci. 50 2955 (2011)

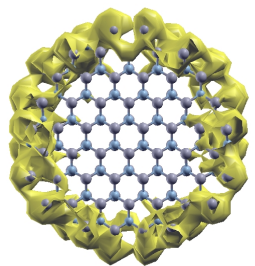
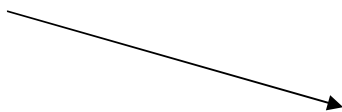
SIESTA method

Some pretty pictures

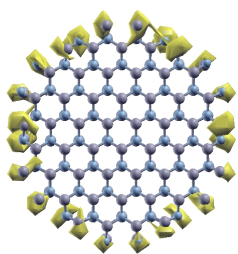
Visualizing phonon modes in BN nanotubes



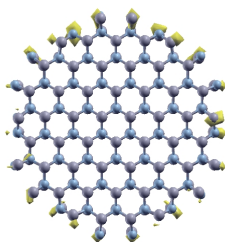
Wave functions in BN nanowires and nanotubes



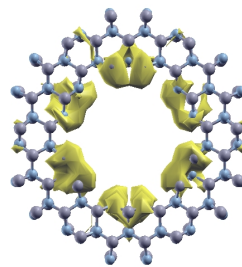
A-11



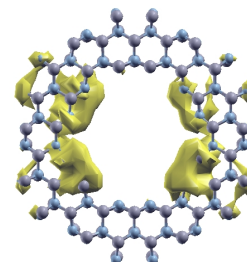
A-12



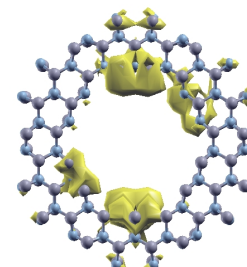
A-13



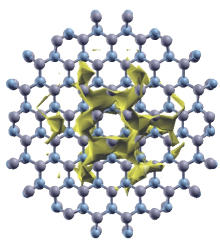
E-1



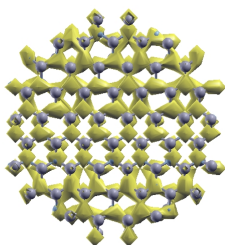
E-2



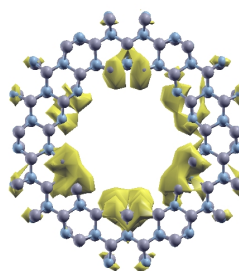
E-3



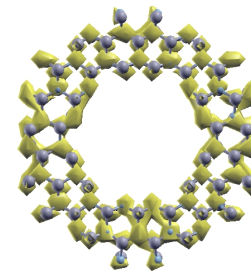
A-2



A-3



E-4



E-5

Diluted magnetic semiconductors

Goals:

- Combine the **transport properties of semiconductors** with the **magnetic properties of metals and semi-metals**
- Don't use just the charge transport but also that of **spin** → **spintronics**
- Bridge classical semiconductor circuits with spin based electronics

Advantages over traditional semiconductor based electronics:

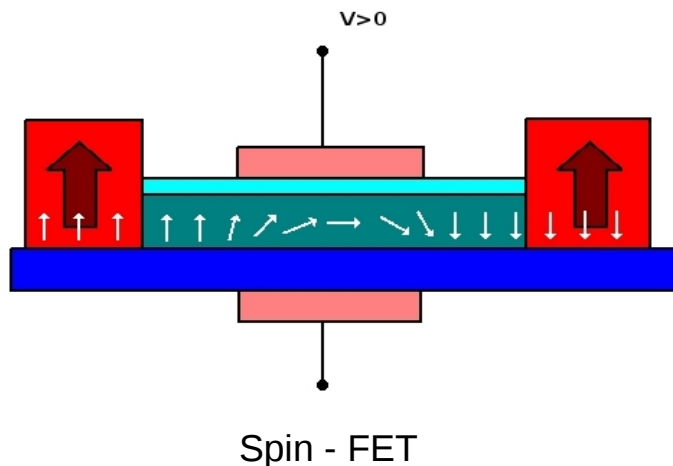
- Increased data processing speed
- Decreased power consumption
- Increased integration densities
- Non-volatile memory
- Universal memory (RAM + storage)
- “Instant” power-on computers
- Rugged (radiation hard) circuits

Practical uses:

- Magnetic memory storage
- Spin based field effect transistors
- GMR magnetic sensors
- Spin valves
- Spin-LEDs
- Magnetic logic circuits
- Spin based THz optical sensors

... and more exotic ones:

- Quantum computing
- Magnetic cellular automata
- Magnetic domain-wall based circuits



Supriyo Datta and Biswajit Das
Appl. Phys. Lett. 56 665 (1990)
T. Dietl et al.
Science 287 1019-1022 (2000)
S.A.Wolf et al.
Science 294 1488-1495 (2001)

Magnetism in Mn doped boron nitride (BN) sheets

Why BN ?

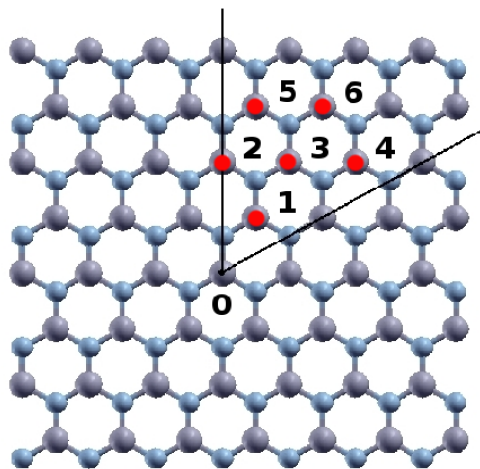
- Wide band gap semiconductor (~ 5.5 eV)
- Successfully produced as bulk-3D (cubic, hexagonal, wurtzite), **2D (sheets)**, 1D (nanotubes, nanowires)
- Possible counterpart for graphene

What we looked for :

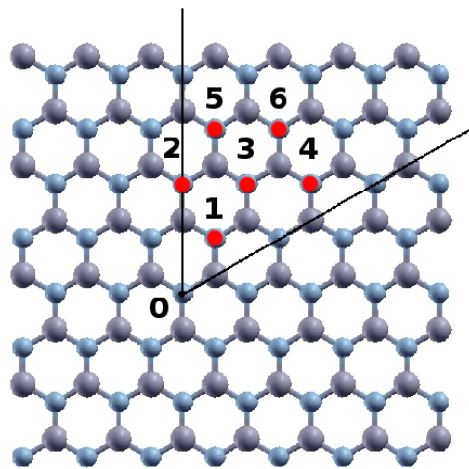
- Defect formation energies
- Clustering tendency of Mn impurities
- Distance dependent exchange couplings
- Optimal doping concentration

The systems that we investigated:

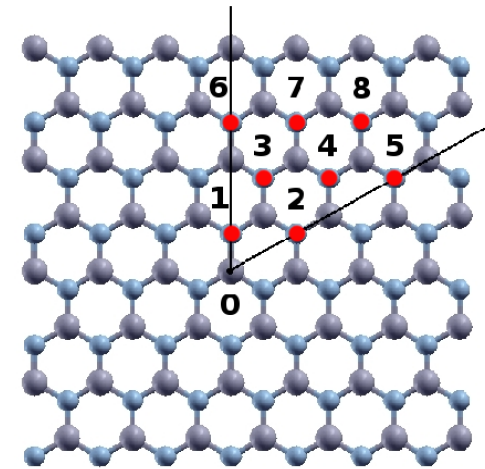
2D single layer BN nanosheets doped (substitutionally) with Mn ions



B-B



N-N

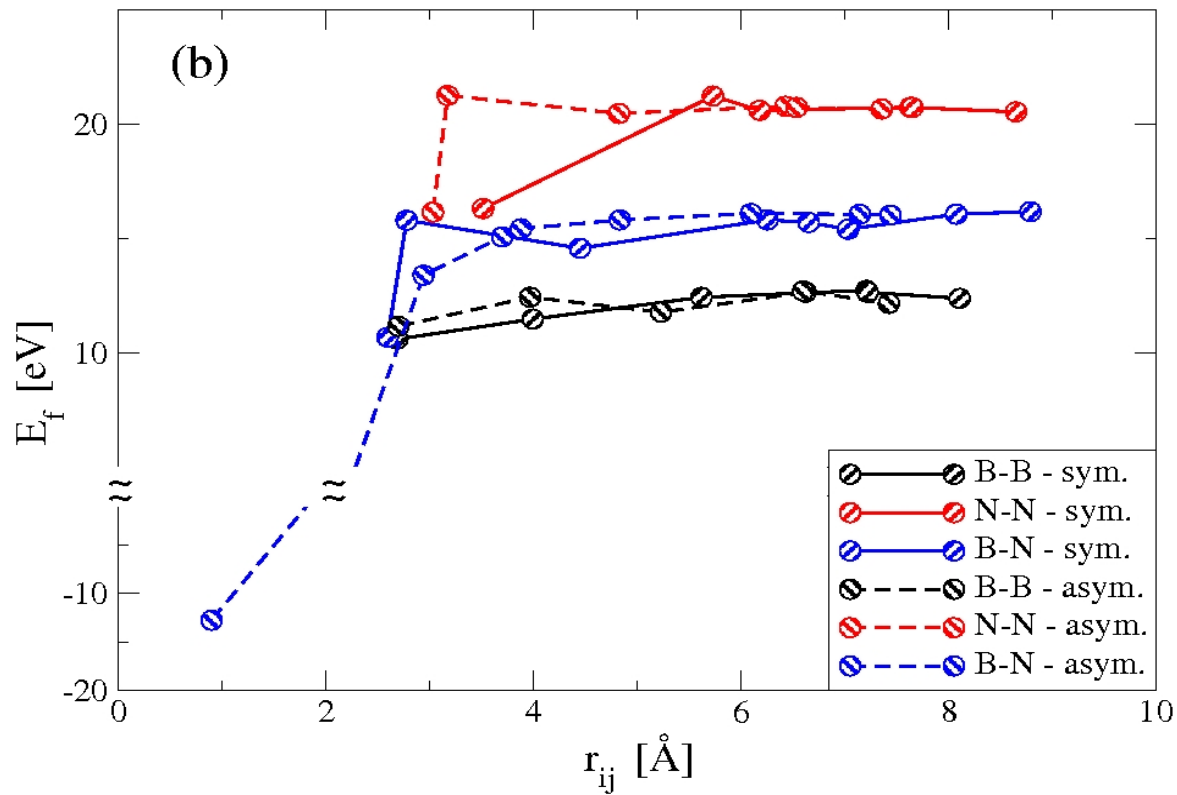


B-N

Magnetism in Mn doped boron nitride (BN) sheets

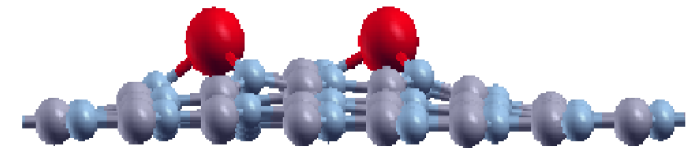
Structural relaxation and formation energy

$$E_f(X, q) = E_{def}^{(tot)} - E_{perf}^{(tot)} - n_B \mu_{bulk}^B - n_N \mu_{bulk}^N - n_X \mu^X$$

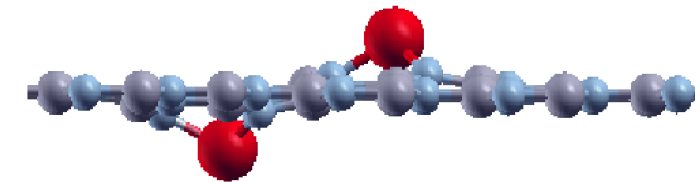


$$E_f^{BB} < E_f^{BN} < E_f^{NN}$$

Relaxation precision:
< 0.04 eV/Å



asymmetrical



symmetrical

Magnetism in Mn doped boron nitride (BN) sheets

Exchange couplings

Model Hamiltonian used – Ising-like:

$$E_{tot}(\{s_i\}) = -J^{(0)} - \sum_i J_i^{(1)} s_i - \sum_{(i,j)} J_{ij}^{(2)} s_i s_j - \sum_{(i,j,k)} J_{ijk}^{(3)} s_i s_j s_k - \sum_{(i,j,k,l)} J_{ijkl}^{(4)} s_i s_j s_k s_l - \dots$$

energy without magnetic interactions

external field

2-spin exchange interactions

higher order exchange couplings

2^N possible spin configurations
 C_N^k couplings

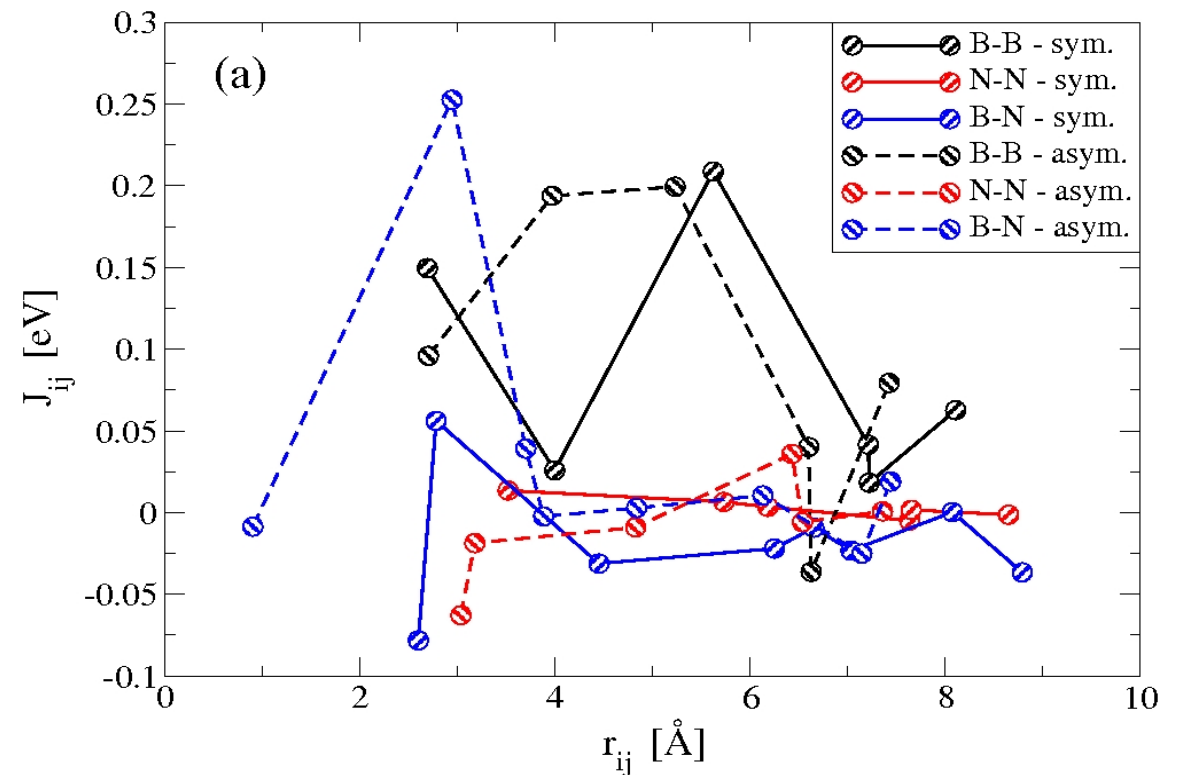
Solve a linear system of equations with a unique solution

$$\{J^{(k)}\}_k$$

No external fields, no spin-orbit interaction

if k is odd

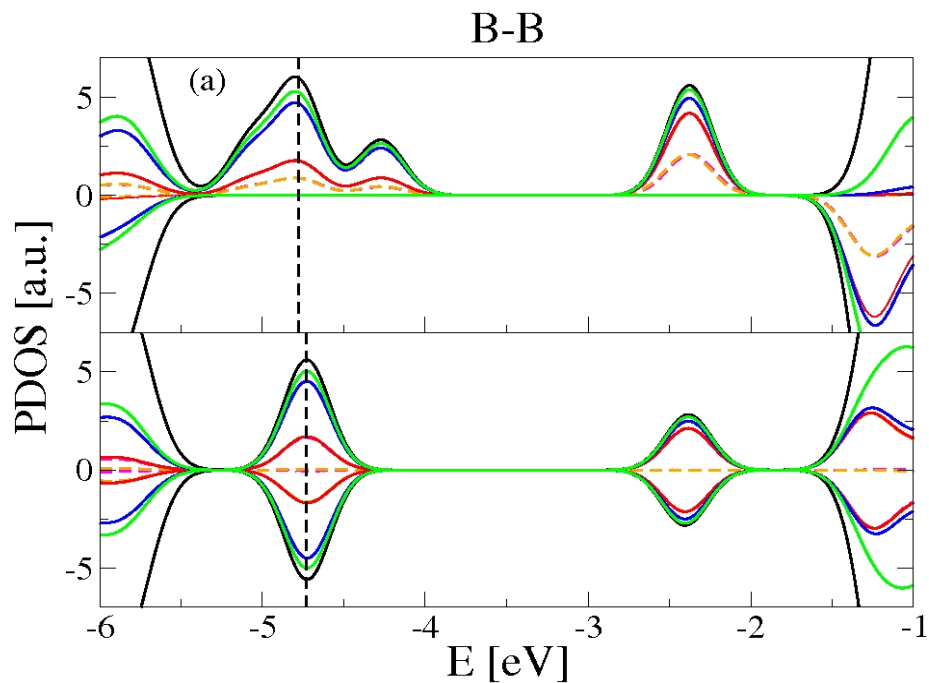
$$J^{(k)} = 0$$



Exchange couplings for two Mn impurities (relaxed lattice)

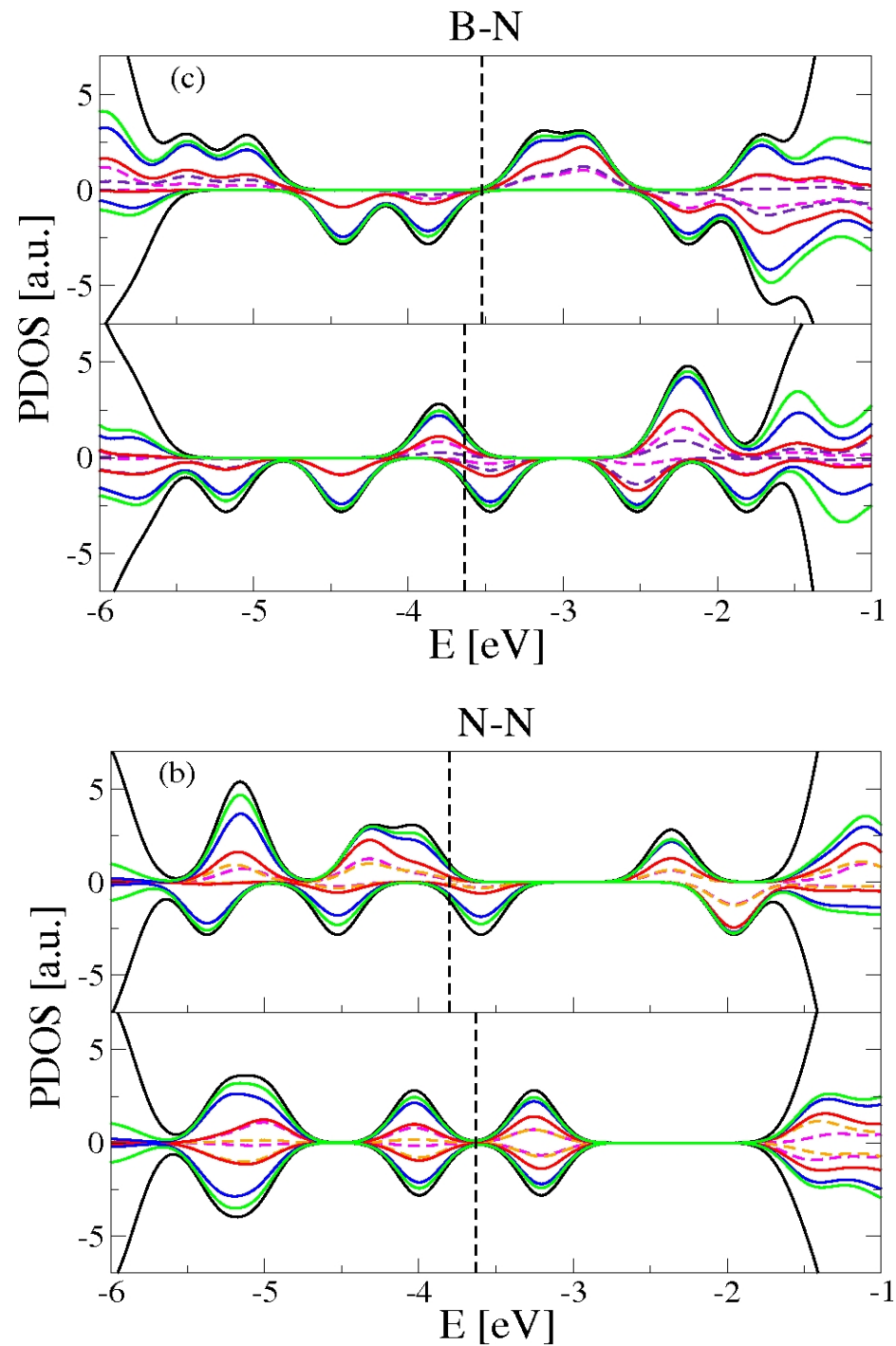
Magnetism in Mn doped boron nitride (BN) sheets

Partial density of states (P-DOS)



Individual Mn atoms - magenta & orange
Both Mn atoms - red
Both Mn atoms + I order neighbors - blue
Both Mn atoms + I + II order neighbors - green
Total DOS - black

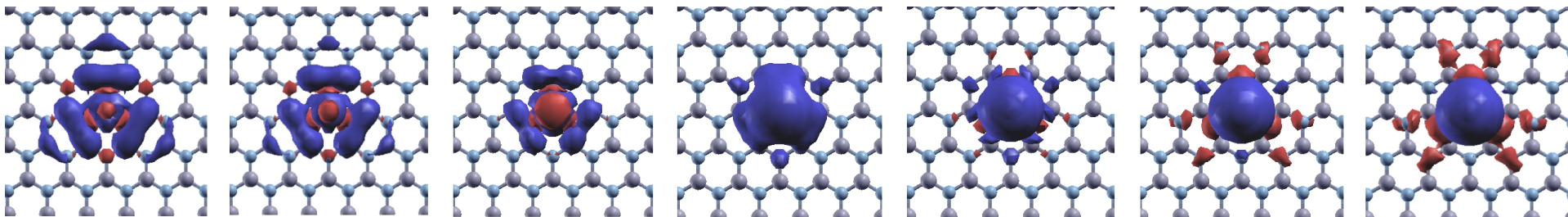
Large contribution from the polarized non-magnetic neighbors !



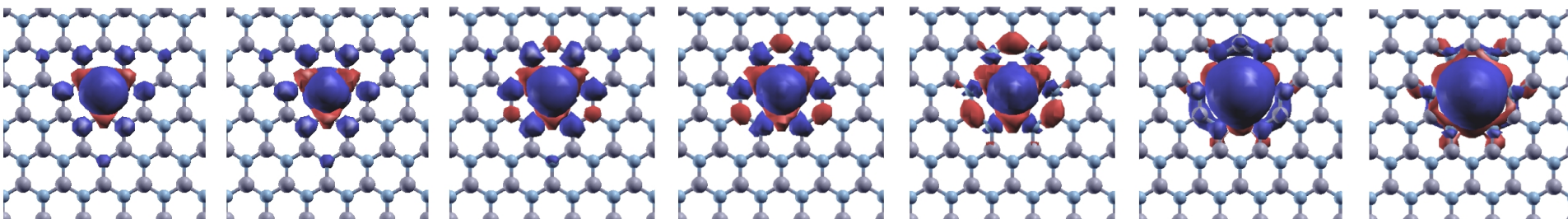
Magnetism in Mn doped boron nitride (BN) sheets

Out-of-plane displacement dependent polarization of neighbors

Spin density: B substituted with Mn



Spin density: N substituted with Mn



0.00

0.25

0.5

0.75

1.00

1.25

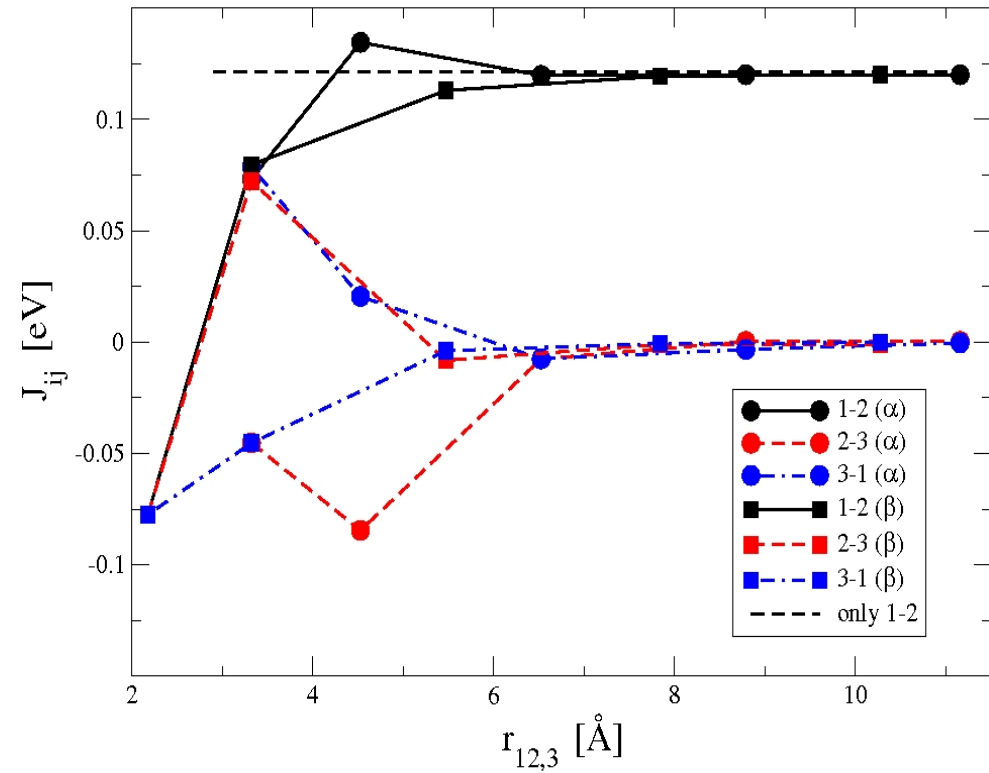
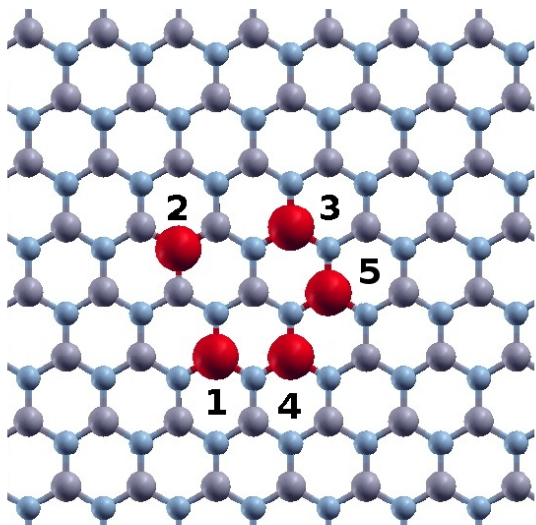
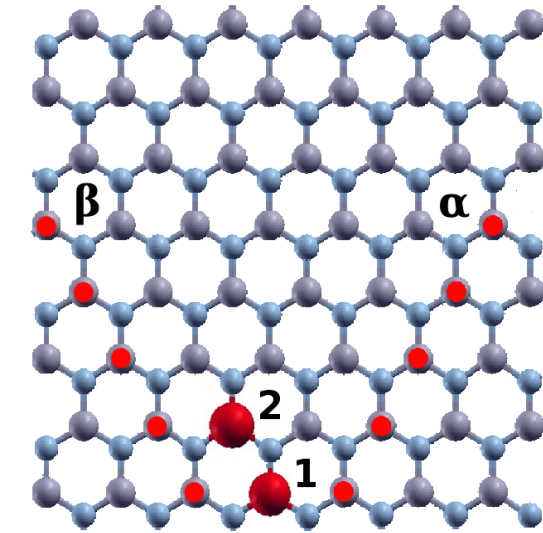
1.5

Out of plane displacements (Å)

In the case of B substitution the polarization effects are stronger which explains the larger exchange couplings for B-B substitutions.

Magnetism in Mn doped boron nitride (BN) sheets

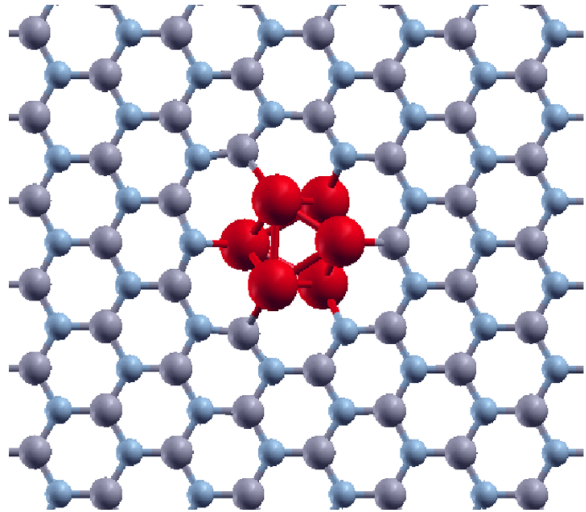
Multiple Mn impurities



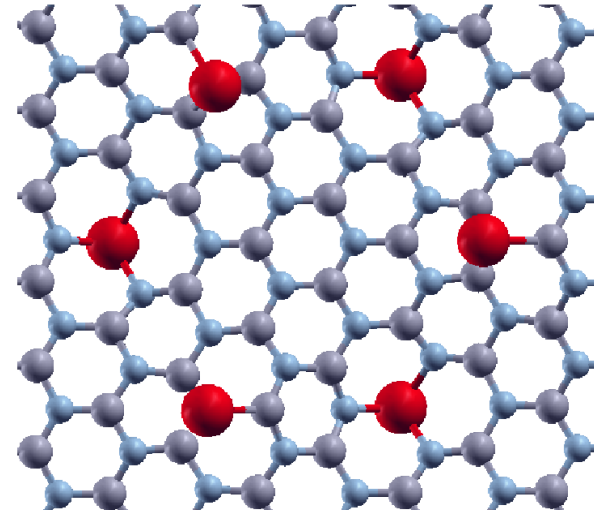
	1-2	1-3	1-4	1-5	2-3	2-4	2-5	3-4	3-5	4-5
3	-0.015	-0.123			-0.015					
4	-0.013	-0.104	0.110		0.002	$< 10^{-3}$		0.028		
5	-0.005	-0.055	0.045	0.033	-0.005	0.011	0.011	0.033	0.045	0.036

Magnetism in Mn doped boron nitride (BN) sheets

Clustering effects

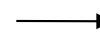


Clustered configuration
Formation energy per Mn atom
3.91 eV



Scattered configuration
Formation energy per Mn atom
7.58 eV

Formation energy of cluster is almost 50 % lower than that of the scattered configuration



**Natural clustering tendency !
Bad if not controlled !**

Magnetism in Mn doped boron nitride (BN) sheets

Ferromagnetism

Boron substitution

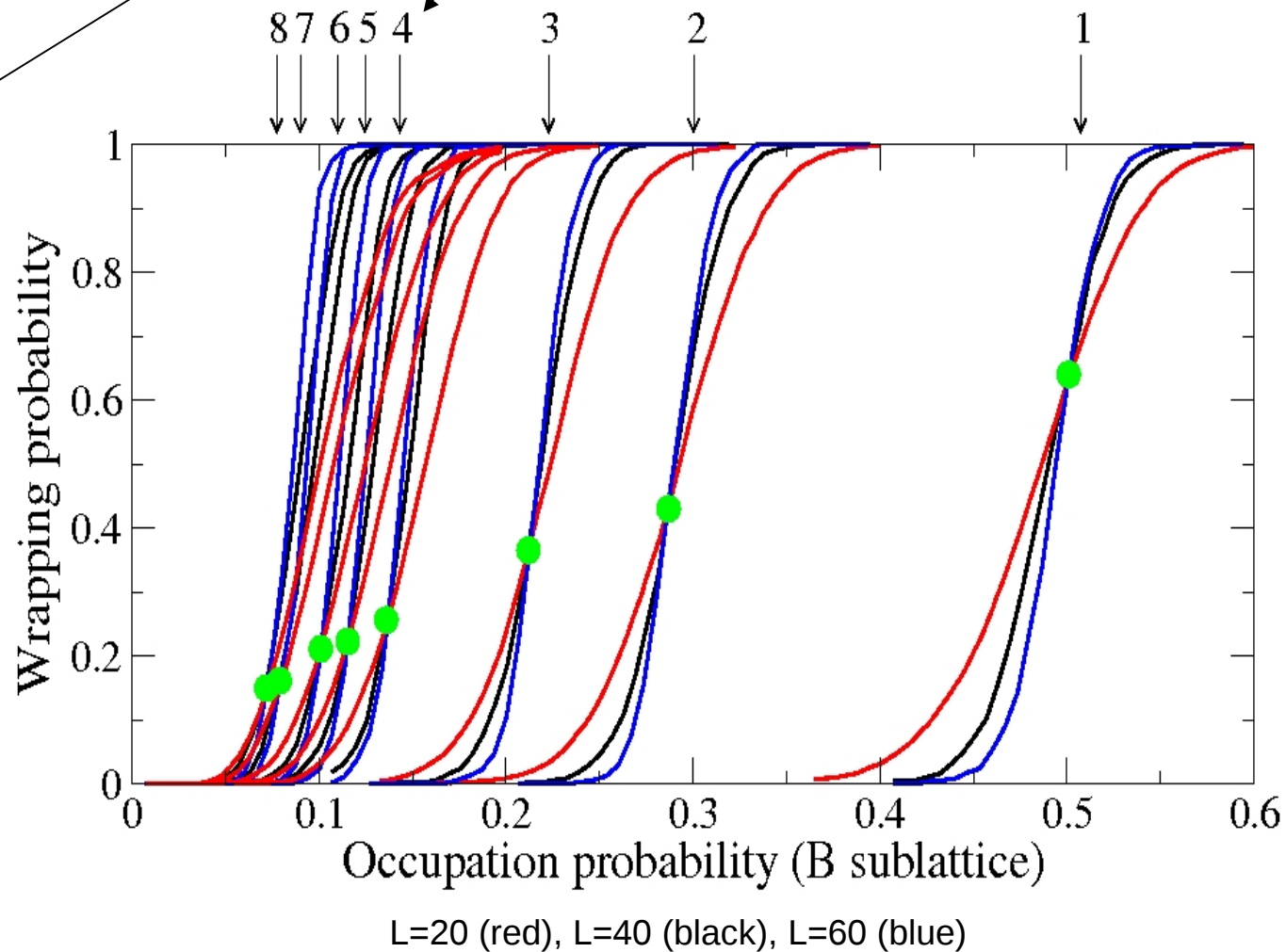


13.6 % concentration
in B sublattice

↓
**13-14 % optimal
doping concentration**
for a ferromagnetic DMS
based on Mn doped BN
nanosheets

Optimal separation of 4-6 Å and cut-off at ~7 Å

~ fourth order neighbors (6.54 Å)



Magnetism in Mn doped boron nitride (BN) sheets

Conclusions:

- Ferromagnetic, anti-ferromagnetic and spin-glass behaviors occur, depending on the substitution type
- Not only Mn atoms contribute to the magnetic behavior but also the polarized B and N neighbors
- In the case of more than two interacting impurities, the amplitude and type of the exchange interaction doesn't only depend on the substitution type but also on the configuration of the neighboring Mn atoms
- A transition from a super-paramagnetic phase to a ferromagnetic alignment takes place when the concentration is increased to 13-14 %

Thank you for your attention !