Modèle de liaisons fortes au 4ème moment pour traiter l'ordre-désordre dans les alliages

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Outline

Context

Tight Binding, moment method, SMA, FMA
- Fourth Moment Appoximation (FMA) ? What is that ?

Bulk mixing properties
- trends in the mixing excess energy from calculations for a perfect lattice
- role of diagonal and off-diagonal disorder

Surface segregation properties
- some results from a lattice approach within a slab geometry

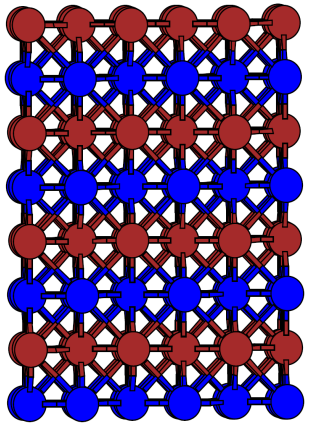
Parametrisation of the TBFMA potential
- limitations of a pure d-band description for the late TMs

Simulations based on a pure d-band TBFMA model
- illustration of the impact of the d-band filling on the segregation behaviour

Conclusions, perspectives

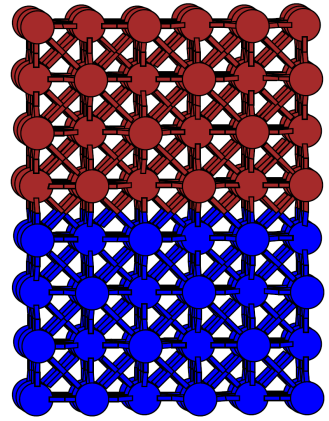
Context

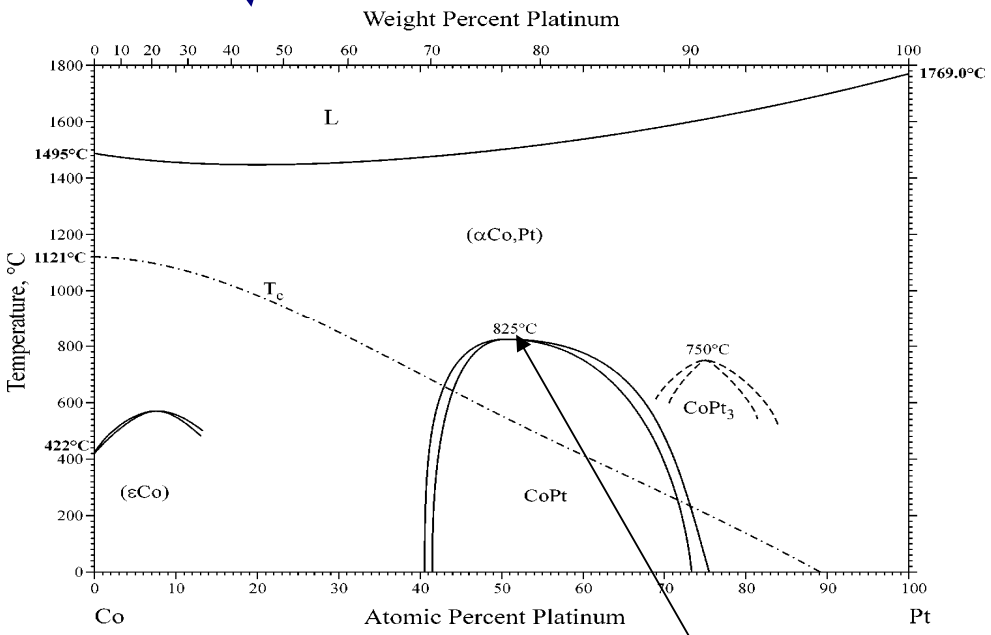
Goal: accurate determination of the phase behaviour of nano-clusters of (late) transition metal (TM) alloys: how does it change w.r.t. bulk phase behaviour ?

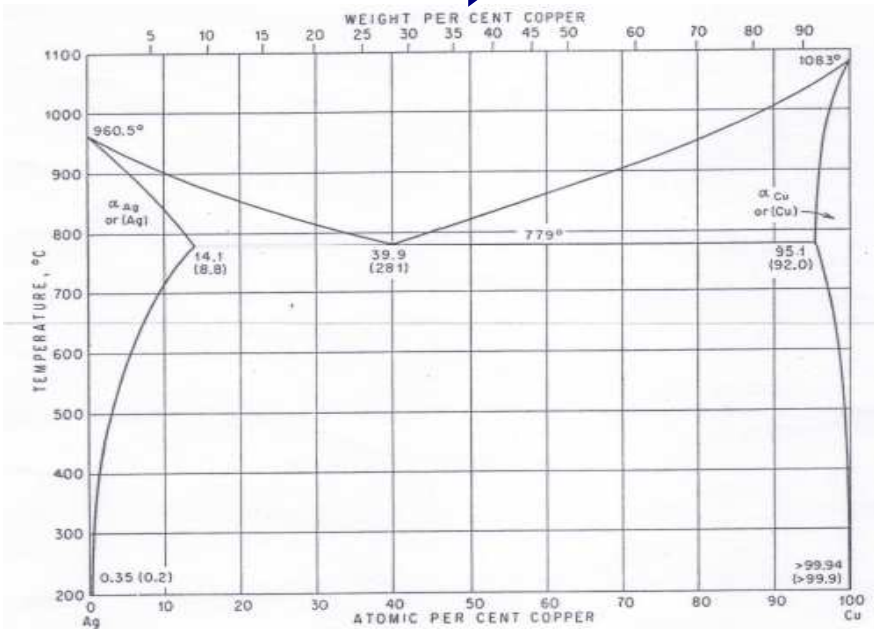


ordering.....or..... demixing

which of the two is the most stable ?

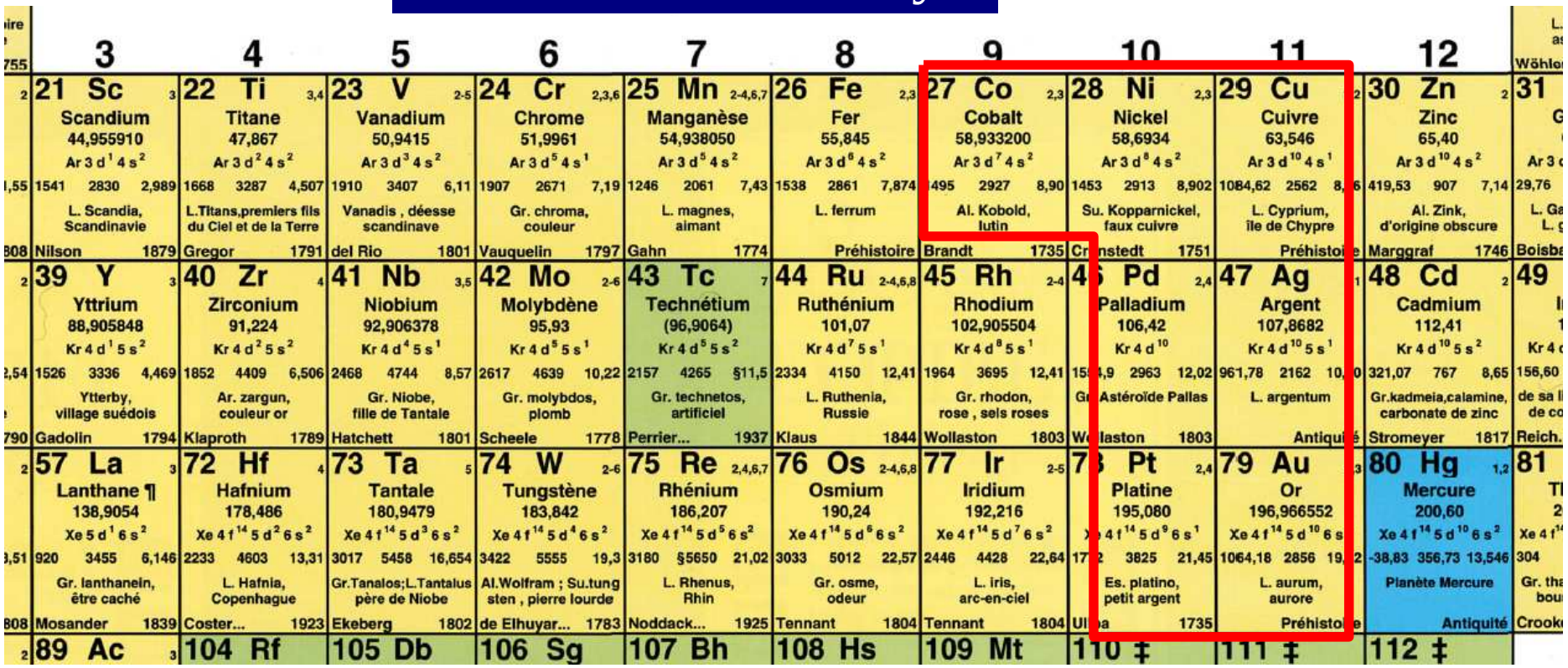






What the critical temperature T_c ? How does it change w.r.t. the bulk value ?

Transition metal alloys



Trends: { hcp demixing

bcc ordering

hcp,fcc demixing

Exceptions: e.g. CoPt shows ordered phases experimentally

To determine the phase behaviour for 'nano'-cluster alloys we want to do Semi-grand Canonical Monte Carlo simulations, including two types of events:

----> atomic displacements for geometrical relaxation and equilibration

----> change of chemical identity of a particle for given chemical potential

very time consuming simulations !!

Wanted:

$$E(\{\mathbf{r}\}) = E(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 ..... \mathbf{r}_N) \quad \Rightarrow \quad \mathbf{F}_i = -\frac{dE}{d\mathbf{r}_i}$$

Expression should be:

> 'sufficiently' accurate

> computationally fast

> linear scaling, i.e. computation time ~ N (number of atoms)

Methods

Empirical Potentials

Advantages:
- simple, fast
- linear scaling

Disadvantages:
- transferability
- no electronic structure
- physical grounds

Examples:
Embedded Atom Methods
Bond Order Potentials
Stillinger and Weber

Tight Binding (TB) Models

Advantages:
- electronic structure
- improved accuracy
- faster then ab-initio

Disadvantages:
- no self-consistency
- bad scaling (N^3)

Ab-initio Models

Advantages:
- electronic structure
- reliable (!?)

Disadvantages:
- complexity
- slow
- bad scaling

Allows for systematic approximations with:
- limited loss of accuracy
- linear scaling (!!!)

via the so-called moment methods:
- second moment approximation (SMA)
- fourth moment approximation (FMA)
- ....etc

Tight Binding

Total energy:

repulsive energy *attractive or band energy*

$$E = E_{rep} + E_{band} = \frac{1}{2}\sum_{i=1}^{N_{at}}\sum_{j} V(r_{ij}) + \int_{-\infty}^{E_F} (E-\epsilon) n(E)\, dE$$

Density of states:

$$n(E) = \sum_{\lambda} \delta(E - E_\lambda) = \sum_{\epsilon} < \psi_\epsilon | \delta(E - H_{TB}) | \psi_\epsilon >$$

Tight binding hamiltonian matrix:

atomic orbital

$$[H_{TB}]_{ij}^{\alpha\beta} = < \psi_{i\alpha} | T + V_{eff} | \psi_{j\beta} > = < \psi_{i\alpha} | T + \sum_{i'} V_{i'}^{at} | \psi_{j\beta} >$$

$$\simeq \epsilon_{i\alpha}\delta_{ij}\delta_{\alpha\beta} + < \psi_{i\alpha} | V_i^{at} | \psi_{j\beta} > = \epsilon_{i\alpha}\delta_{ij}\delta_{\alpha\beta} + \beta_{ij}^{\alpha\beta}$$

Wave function linear combination of atomic orbital:

$$\psi(\mathbf{r}) = \sum_{i=1}^{N_{at}}\sum_{\alpha} c_{i\alpha}\psi_{i\alpha}(\mathbf{r}) = \sum_{i=1}^{N_{at}}\sum_{n,l,m} c_i^{nlm} R_{nl}(|\mathbf{r} - \mathbf{r}_i|) Y_{lm}(\theta, \phi)$$

Tight Binding hamiltonian matrix blocks for spd-basis set:

$$\vec{\vec{H}}_{TB,ij} = \vec{\vec{\epsilon}}_{ij}\delta_{ij} + \vec{\vec{\beta}}_{ij}$$

diagonal matrix block;
ε_λ=free atom orbital level (λ=s,p,d)

$$\begin{pmatrix} \varepsilon_s & & & & & & & & \\ & \varepsilon_p & & & & & & & \\ & & \varepsilon_p & & & & 0 & & \\ & & & \varepsilon_p & & & & & \\ & & & & \varepsilon_d & & & & \\ & & & & & \varepsilon_d & & & \\ & & & & & & \varepsilon_d & & \\ & & & & & & & \varepsilon_d & \\ & & 0 & & & & & & \varepsilon_d \end{pmatrix}$$

off-diagonal matrix block for r_{ij} // z-axis;
probabilities of electron hopping from $|i\alpha\rangle$ to $|j\beta\rangle$

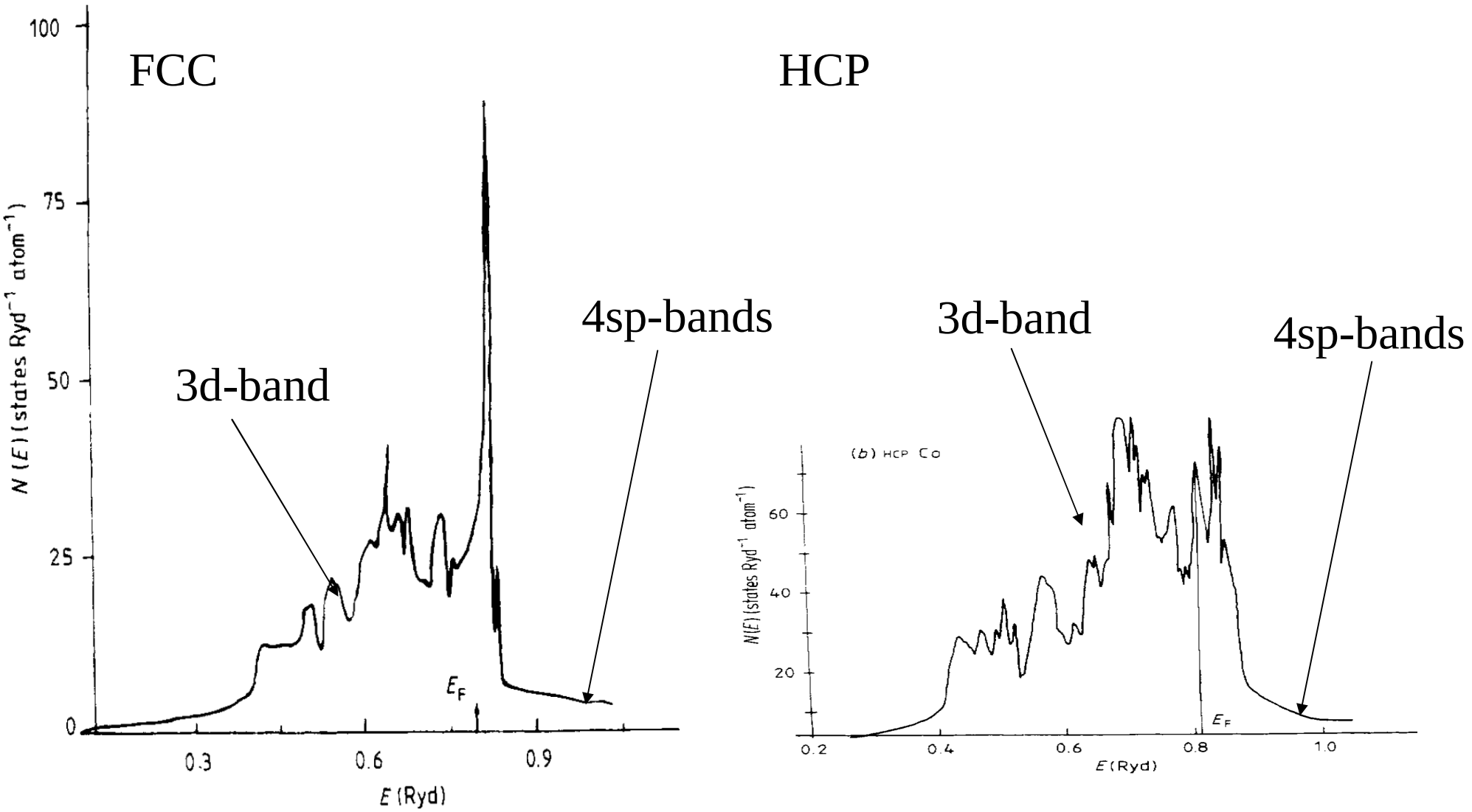
$$\begin{pmatrix} ss\sigma & 0 & 0 & sp\sigma & 0 & 0 & 0 & 0 & sd\sigma \\ 0 & pp\pi & 0 & 0 & 0 & 0 & pd\pi & 0 & 0 \\ 0 & 0 & pp\pi & 0 & 0 & pd\pi & 0 & 0 & 0 \\ -sp\sigma & 0 & 0 & pp\sigma & 0 & 0 & 0 & 0 & pd\sigma \\ 0 & 0 & 0 & 0 & dd\delta & 0 & 0 & 0 & 0 \\ 0 & 0 & -pd\pi & 0 & 0 & dd\pi & 0 & 0 & 0 \\ 0 & -pd\pi & 0 & 0 & 0 & 0 & dd\pi & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & dd\delta & 0 \\ sd\sigma & 0 & 0 & -pd\sigma & 0 & 0 & 0 & 0 & dd\sigma \end{pmatrix}$$

canonical rules for hopping integrals:

$$\begin{aligned} \beta_{dd\sigma} &= \beta_{dd\sigma,0} \exp\left(-q\left(\frac{r}{r_{eq}} - 1\right)\right) \\ \beta_{dd\pi} &= \beta_{dd\sigma}/2 \\ \beta_{dd\delta} &= 0 \end{aligned}$$

for pure d-band description
only 2 free hopping parameters: q, $\beta_{dd\sigma,0}$

Typical examples of the density of states for a transition metal



Cohesive energy of TMs dominated by d-band filling

Graphs from: N.I. Kulikov and E.T. Kulatov, J. Phys F: Met. Phys 12, 2267 (1982)

Tight Binding and moments method

repulsion

attraction, band energy

Total energy: $$E = \sum_{i=1}^{N} E_i = \sum_{i=1}^{N} \left(\sum_j A e^{-p r_{ij}} + 2 \sum_\lambda \int_{-\infty}^{E_{f,i}} (E - \epsilon_i) n_{i,\lambda}(E) dE \right)$$

Local density of λ-states (λ=s,p,d..):

$$n_{i\lambda}(E) = -\frac{1}{\pi} \lim_{\eta \to 0} Im \sum_\epsilon \sum_m \frac{| < \psi_{i\lambda m} | \psi_\epsilon > |^2}{z - E_\epsilon} = -\frac{1}{\pi} \lim_{\eta \to 0} Im \sum_m \left\langle \psi_{i\lambda m} \left| \frac{1}{zI - H_{TB}} \right| \psi_{i\lambda m} \right\rangle$$

moments expansion

$$\sum_{n=0}^{\infty} \frac{\sum_m < \psi_{i\lambda m} | H_{TB}^n | \psi_{i\lambda m} >}{z^{n+1}} = \sum_{n=0}^{\infty} \frac{\mu_n^{i\lambda}}{z^{n+1}}$$

continued fraction expansion

$$-\frac{1}{\pi} \lim_{\epsilon \to 0} \cfrac{1}{z - a_1^{i\lambda} - \cfrac{b_1^{i\lambda}}{z - a_2^{i\lambda} - \cfrac{b_2^{i\lambda}}{z - a_3^{i\lambda} - \ldots}}}$$

moments

$$\mu_n^{i\lambda} \quad (n = 0, 1, 2...)$$

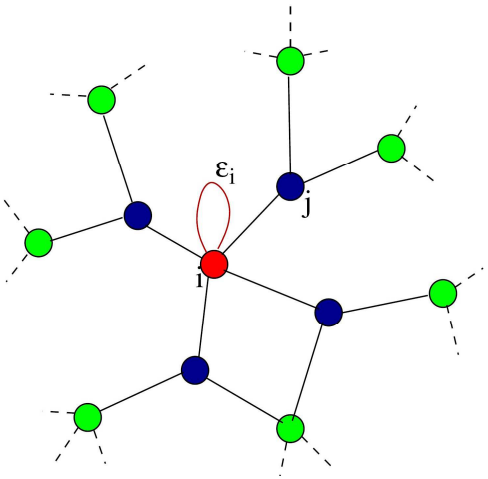
one-to-one correspondence

continued fraction coefficients

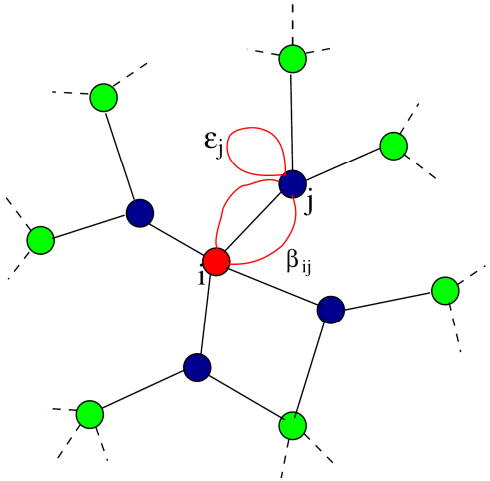
$$a_n^{i\lambda} \ , \ b_n^{i\lambda} \quad (n = 1, 2...)$$

Computation of the n-th moment for atom i involves

all closed paths of n steps beginning and ending on atom i



$$\mu_1 = \epsilon_i$$

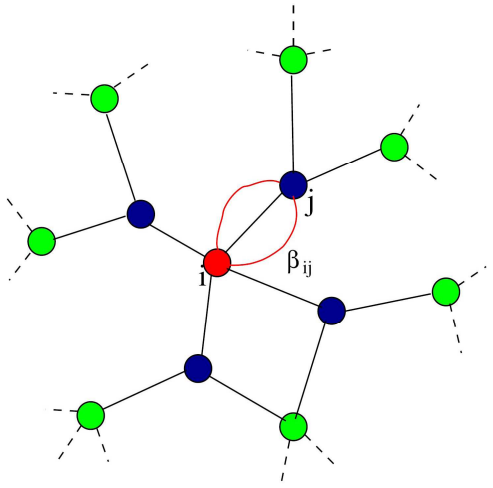


$$\mu_3 = .. + \epsilon_i \beta_{ij} \beta_{ji} + \beta_{ij} \epsilon_j \beta_{ji} + ..$$

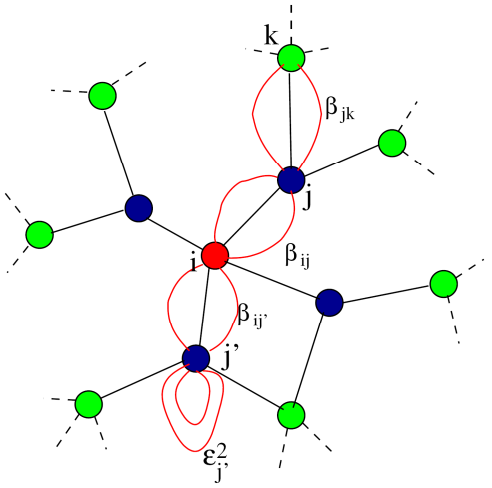
central atom i

nearest neighbour

next nearest neibour



$$\mu_2 = \epsilon_i^2 + \beta_{ij} \beta_{ji} + ..$$



$$\mu_4 = .. + \beta_{ij} \beta_{jk} \beta_{kj} \beta_{ji} + .. \beta_{ij} \epsilon_j^2 \beta_{ji} + ...$$

Second Moment Approximation (SMA)

Termination of the continued fraction expansion by taking:

$$\begin{cases} a_n^{i\lambda} = a_1^{i\lambda} \\ b_n^{i\lambda} = b_1^{i\lambda} \end{cases} \forall n > 2$$

Consequently:

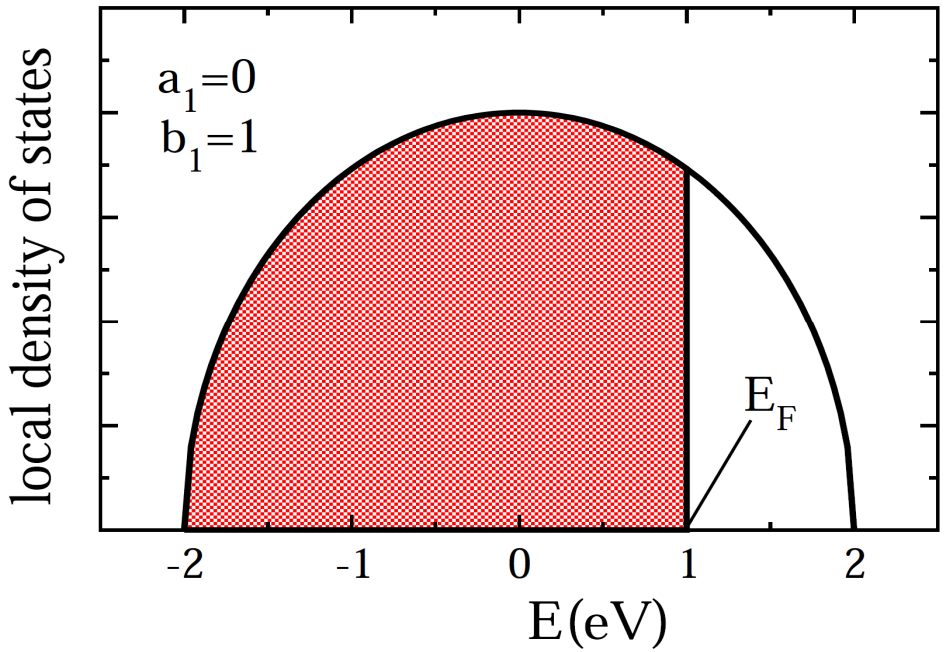
$$n_{i,\lambda}(E) = -\frac{1}{2\pi} \lim_{\epsilon \to 0} Im \frac{(z - a_1) - i\sqrt{4b_1^{i\lambda} - (E - a_1^{i\lambda})^2}}{b_1^{i\lambda}}$$

- Energy band for:

$$a_1^{i\lambda} - 2\sqrt{b_1^{i\lambda}} \leq E \leq a_1^{i\lambda} + 2\sqrt{b_1^{i\lambda}}$$

- Fermi energy follows from:

$$Z_i = \int_{-\infty}^{E_F} n(E) dE$$



Simplication for pure d-band description for transition metals

Using: $\epsilon = a_1 = \epsilon_d \longrightarrow$ E=0 for isolated atom

and the variable change: $E' = \dfrac{E - a_1^{i\lambda}}{\sqrt{b_1^{i\lambda}}}$

leads to:

$$Z_i = \int_{E_{b,min}}^{E_F} \frac{\sqrt{4b_1^{i\lambda} - (E - a_1^{i\lambda})^2}}{b_1^{i\lambda}} dE = \int_{-2}^{E'_F} \sqrt{2 - E'^2} dE' = C(N_{el,i})$$

$$E_{band} = \int_{E_{b,min}}^{E_F} (E - \epsilon) \frac{\sqrt{4b_1^{i\lambda} - (E - a_1^{i\lambda})^2}}{b_1^{i\lambda}} dE = \sqrt{b_1^{i\lambda}} \int_{-2}^{E'_F} E' \sqrt{2 - E'^2} dE' = C'(N_{el,i}) \sqrt{b_1^{i\lambda}}$$

where: $\sqrt{b_1^{i\lambda}} = \sqrt{\mu_2^{i\lambda} - \mu_1^{i\lambda}\mu_1^{i\lambda}} = \sqrt{< \vec{\psi}_i | \sum_j \vec{\beta}_{ij} \vec{\beta}_{ji} | \vec{\psi}_i >}$

Next, forget about angular dependence in the d-band hopping integrals
(i.e. treat the d-band as an s-band), then:

$$E_{band} = C'(N_{el,i}) \sqrt{\sum_j \left(\beta'_0 \exp\left(-q' r_{ij}\right)\right)^2}$$

→ Finnis-Sinclair
Embedded atom
SMA

Fourth Moment Approximation (FMA)

Termination of the continued fraction expansion by taking:

$$\begin{cases} a_n^{i\lambda} = a_2^{i\lambda} \\ b_n^{i\lambda} = b_2^{i\lambda} \end{cases} \quad \forall n > 2$$

Consequently:

$$n_{i,\lambda}(E) = -\frac{1}{\pi} \lim_{\epsilon \to 0} Im \frac{A_0 + A_1 z - i b_1 \sqrt{4 b_2^{i\lambda} - (E - a_2^{i\lambda})^2}}{B_0 + B_1 z + B_2 z^2}$$

- energy band for:

$$a_2^{i\lambda} - 2\sqrt{b_2^{i\lambda}} \leq E \leq a_2^{i\lambda} + 2\sqrt{b_2^{i\lambda}}$$

- possibly pole contribution when

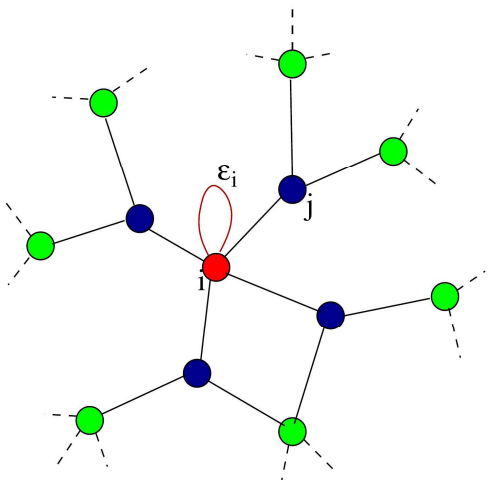
$$B_0 + B_1 E + B_2 E^2 = 0$$

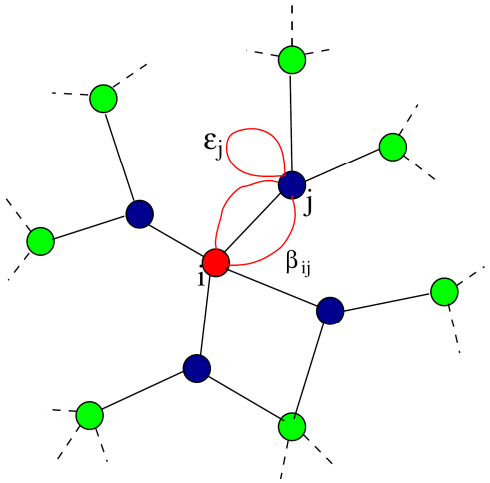
$n_{i,\lambda}(E)$ and $En_{i,\lambda}(E)$ still analytically integrable*

* *Analytic solution from:*
G. Allan, M.C. Desjongueres and D. Spanjaard – Solid State Communications, Vol. 50, no. 5 (1984)

Computation of the n-th moment for atom i involves

all closed paths of n steps beginning and ending on atom i





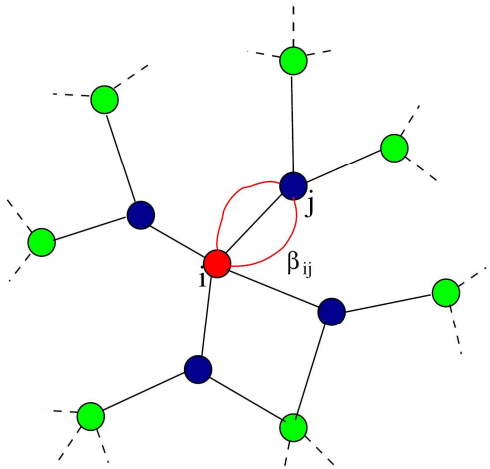
central atom i

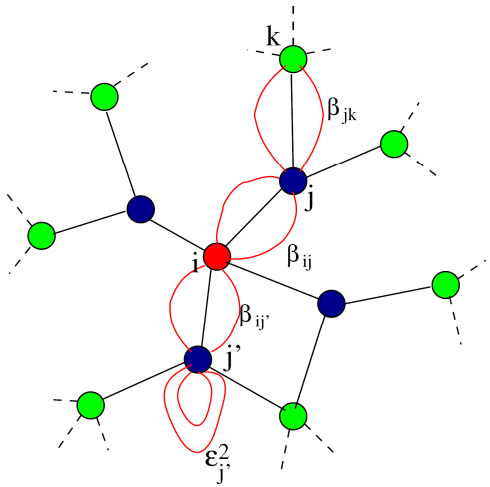
nearest neighbour

next nearest neibour

$$\mu_1 = \epsilon_i$$

$$\mu_3 = .. + \epsilon_i\beta_{ij}\beta_{ji} + \beta_{ij}\epsilon_j\beta_{ji} + ..$$





$$\mu_2 = \epsilon_i^2 + \beta_{ij}\beta_{ji} + ..$$

$$\mu_4 = .. + \beta_{ij}\beta_{jk}\beta_{kj}\beta_{ji} + ..\beta_{ij}\epsilon_j^2\beta_{ji} + ...$$

NB: SMA does not take into account diagonal disorder, FMA does !!!

In SMA mixing behaviour has to be adjusted by β_{ij}^{AB}

Monitoring mixing properties and surface segregation

Cluster expansion in the spirit of a TB description:

$$E = NV_0 + \sum_{\mathbf{n}} \sum_{i} p_i^{\mathbf{n}} V_{1,i}^{\mathbf{n}} + \sum_{\mathbf{n},\mathbf{m}} \sum_{<ij>} p_i^{\mathbf{n}} p_j^{\mathbf{m}} V_{2,ij}^{\mathbf{nm}} + ...$$

with:

$$p_i^{\mathbf{n}} = \begin{cases} 1 & \text{if the atom at site } \mathbf{n} \text{ is of type } i \\ 0 & \text{else} \end{cases}$$

For a perfect, bulk lattice, we obtain:

$$E = C + N_{AB} V_E + ...$$

with:

$$V_E = V_{2,AB} - \frac{1}{2}\left(V_{2,AA} + V_{2,BB}\right) \longrightarrow \text{excess energy parameter}$$

$$V_E > 0 \longrightarrow \text{demixing}$$

$$V_E < 0 \longrightarrow \text{ordering}$$

Parameter space

Excess energy depends on:

$$V_E = V_E(\Delta\epsilon, \Delta\beta, \beta_{av}, N^d_{e,av}, x_B)$$

with:

$$\begin{aligned}
\Delta\epsilon = \epsilon_A - \epsilon_B &= \text{diagonal disorder} \\
\Delta\beta = \beta_{AA} - \beta_{BB} &= \text{off-diagonal disorder} \\
\beta_{av} = (\beta_{AA} + \beta_{BB})/2 &= \text{average off-diagonal term} \\
N^d_{e,av} = (1 - x_A)N^d_A + x_B N^d_B &= \text{band filling} \\
x_B = 1 - x_A &= \text{composition} \\
(\beta_{AB} = \sqrt{\beta_{AA}\beta_{BB}} &= \text{Sheba rule})
\end{aligned}$$

Using canonical rules:

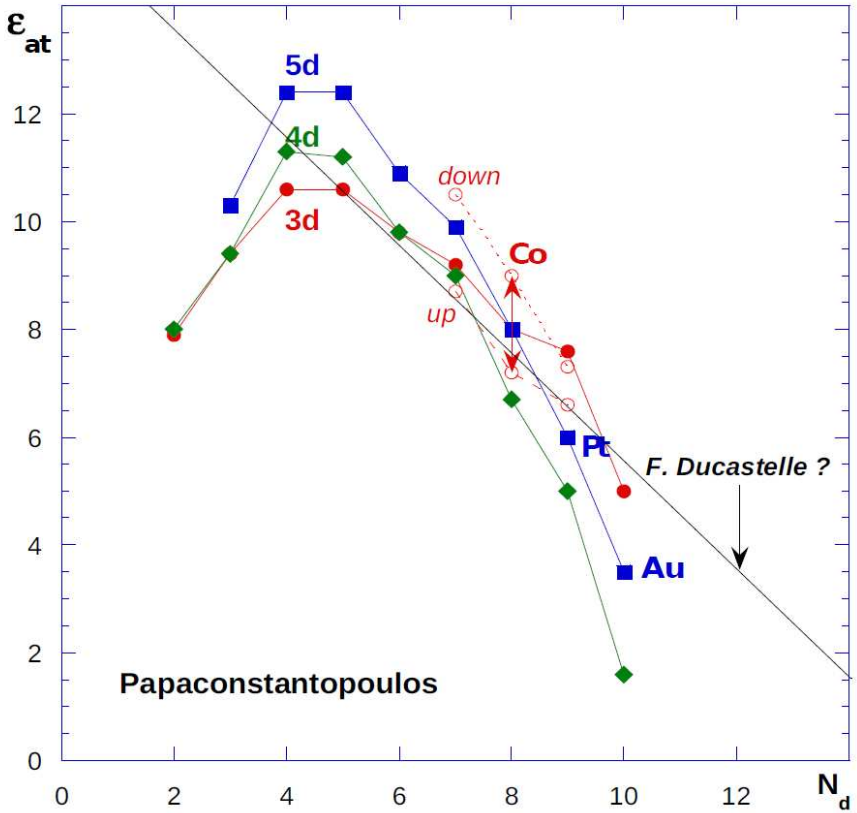
$$\beta_{dd\sigma} = -2\beta_{dd\pi} \text{ and } \beta_{dd\delta} = 0$$

the d-band width W is equal to :

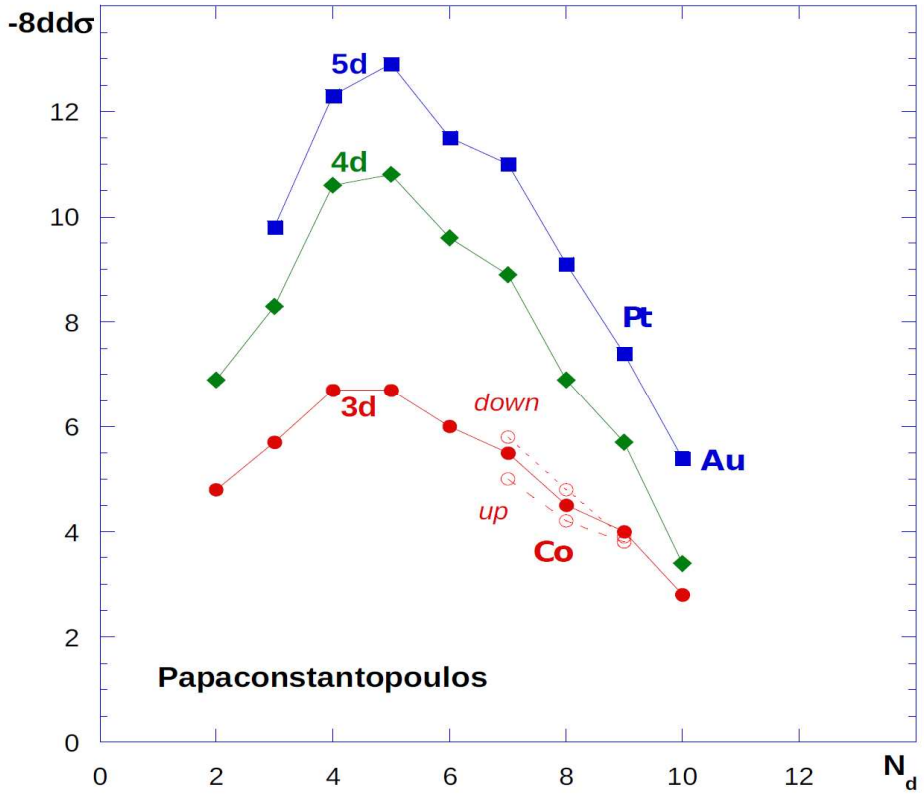
$$W = 8|\beta_{dd\sigma}|$$

Range of parameter values

variation of ε



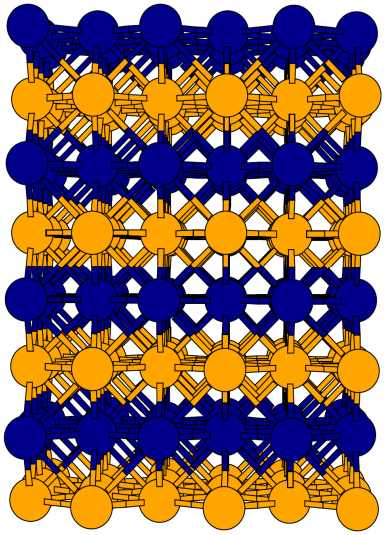
variation of W



..... according to Papaconstantopoulos

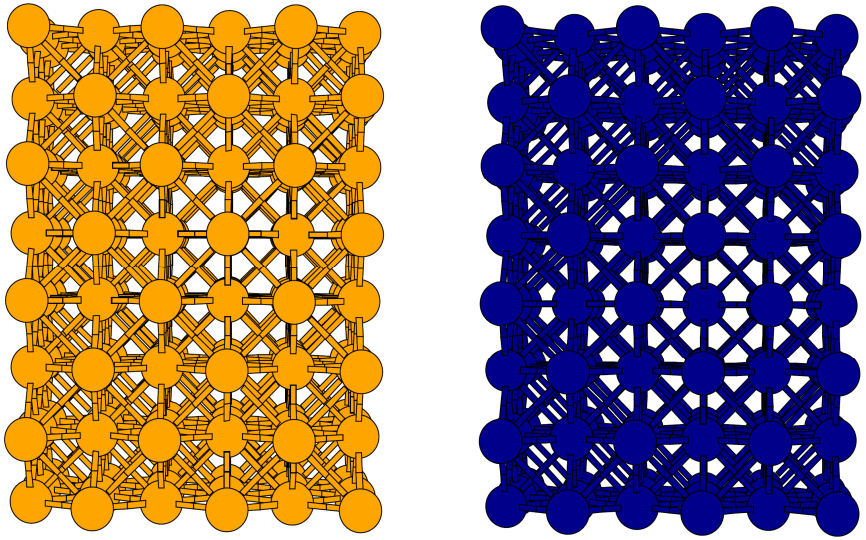
Computation of excess parameter V_E from reference lattice systems

AB

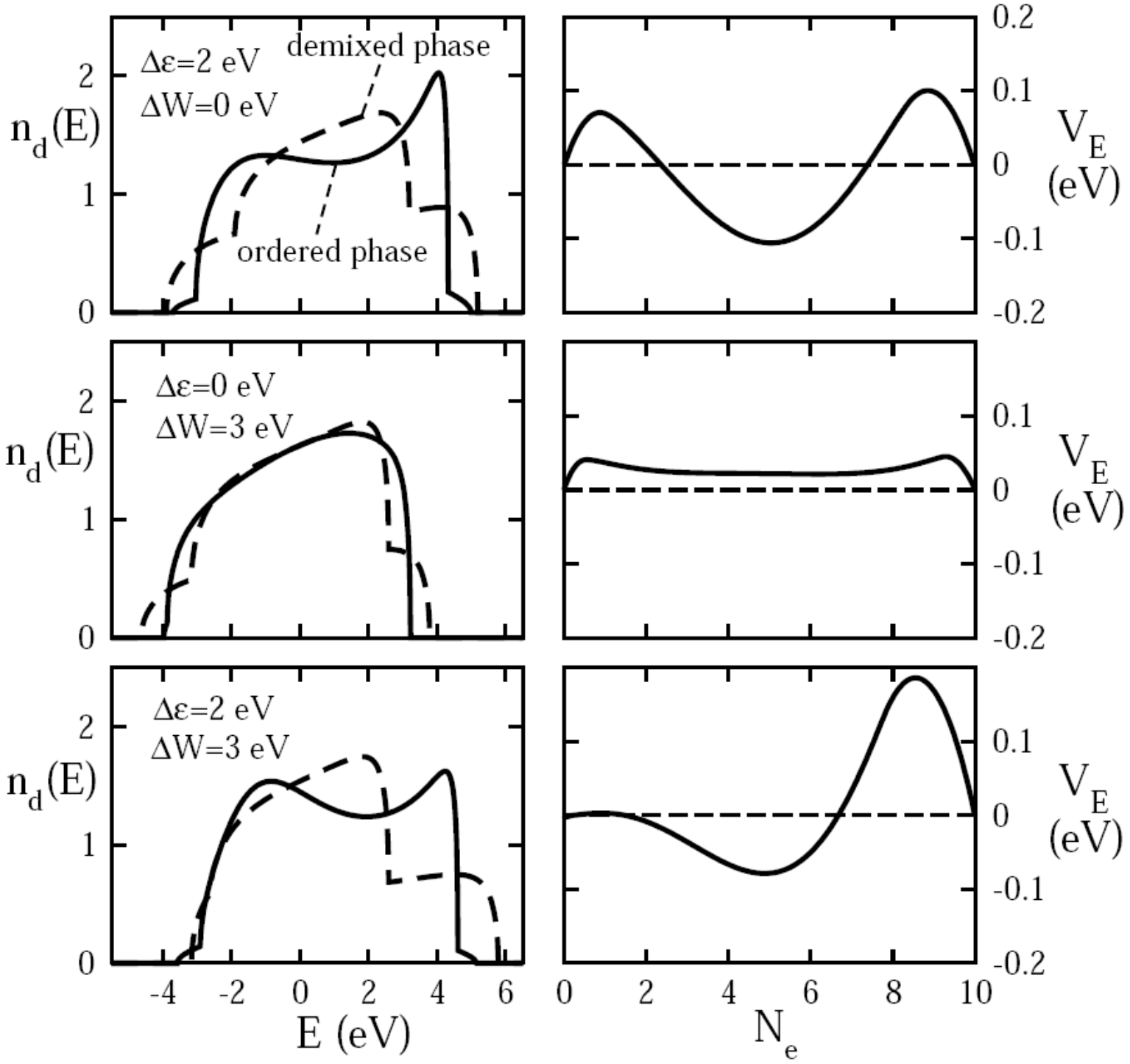


($L1_0$)

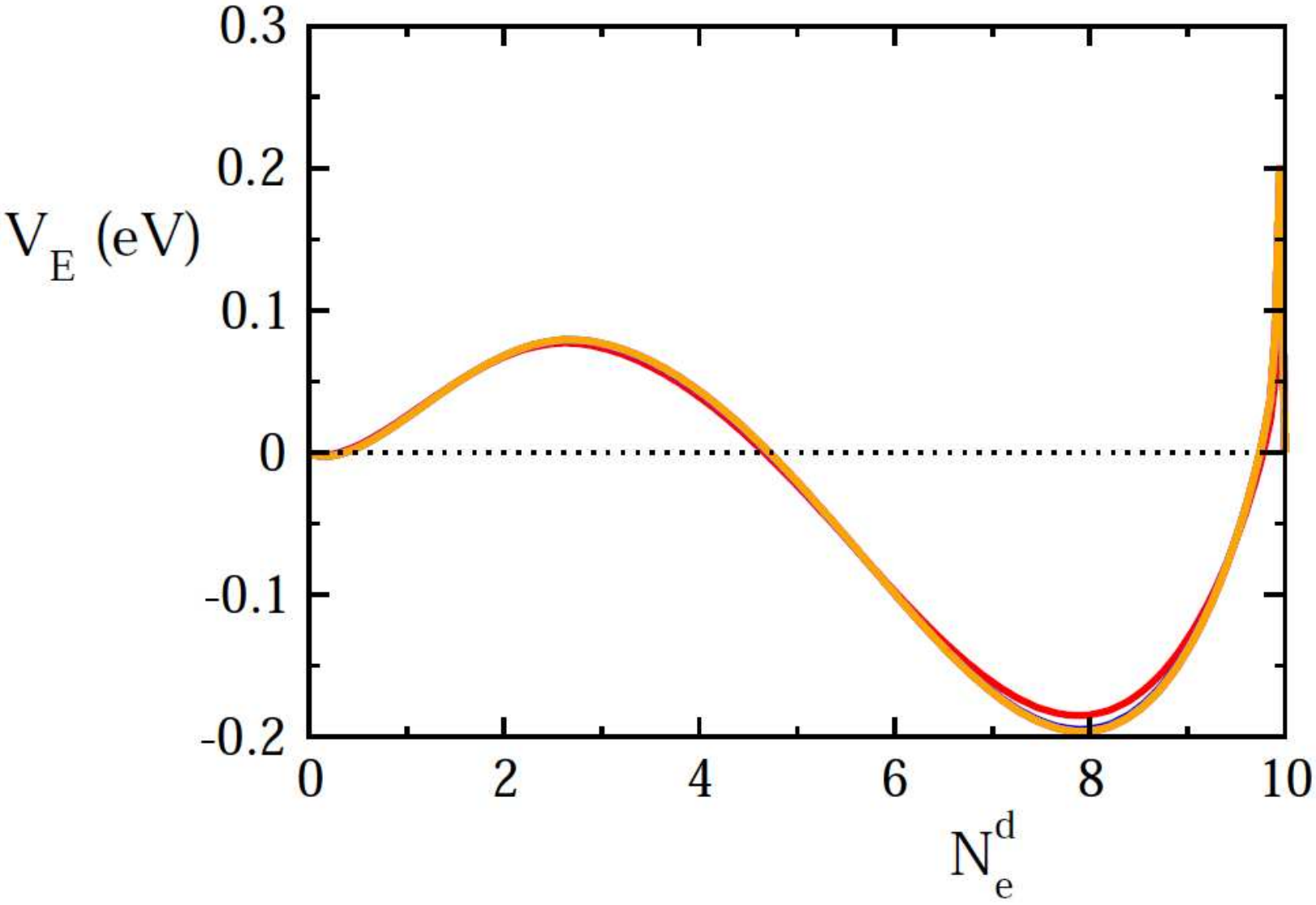
½ A + ½ B

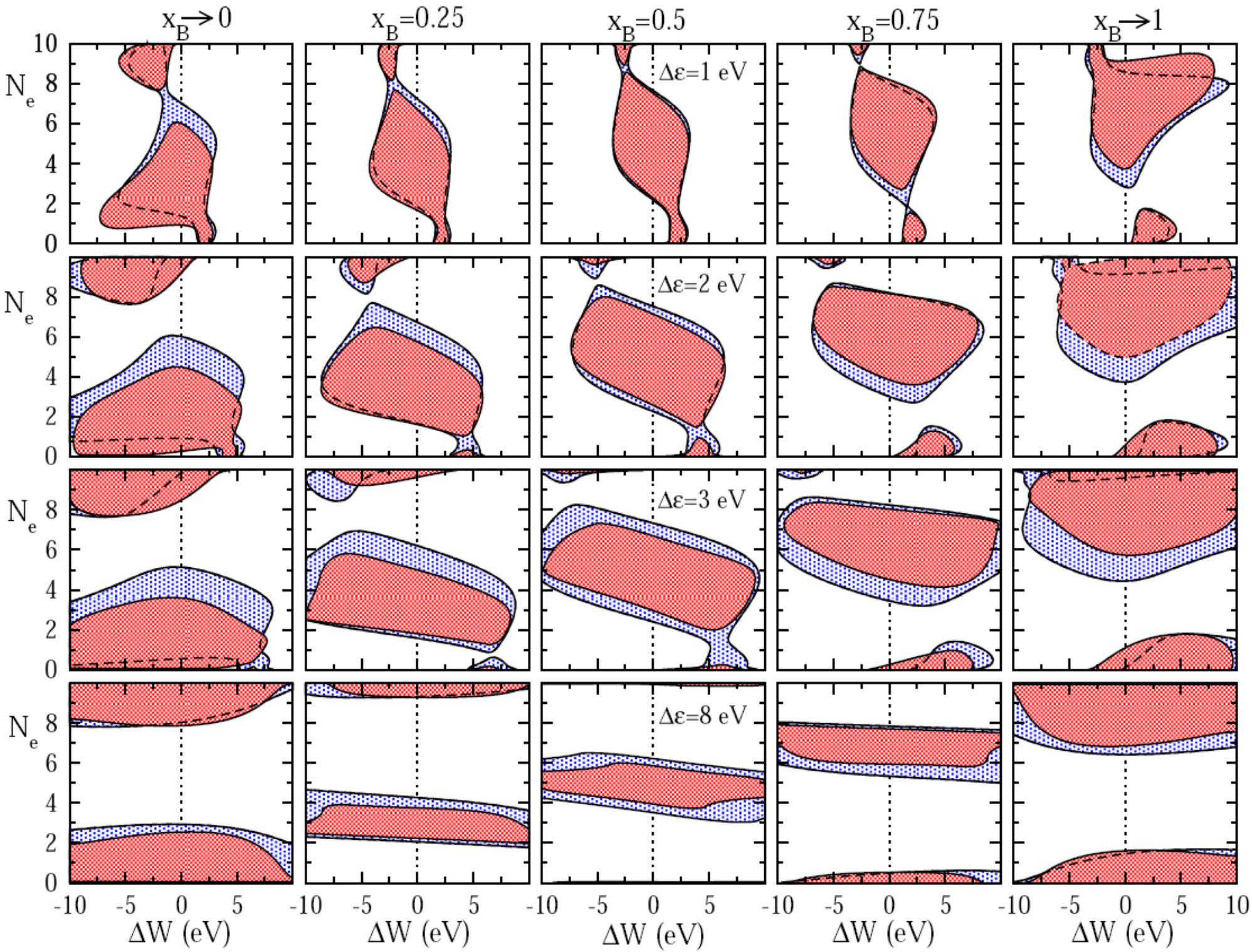


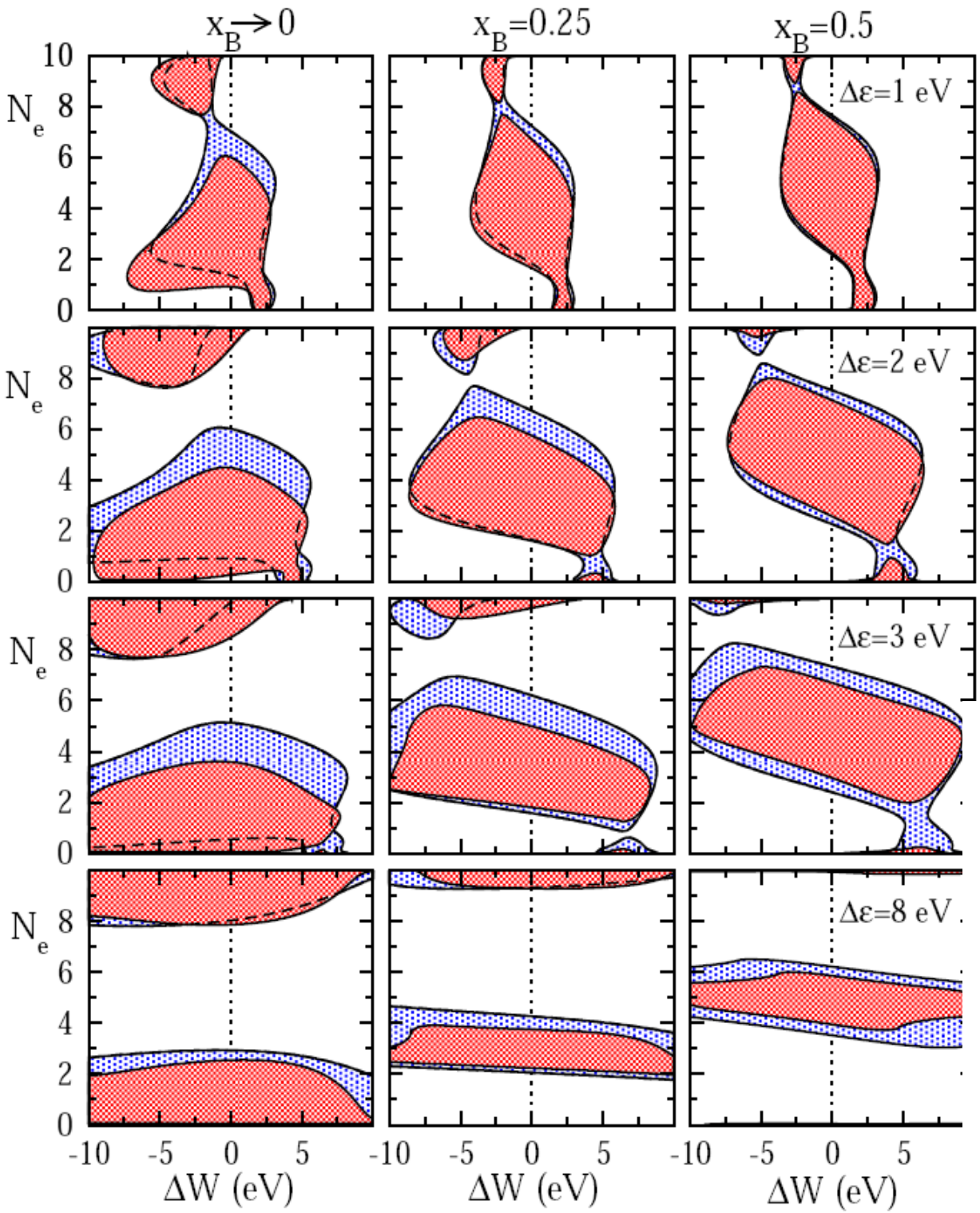
$$
\begin{aligned}
V_E &= \frac{\Delta E_{coh}}{N_{AB}} \\
&= \frac{N}{N_{AB}} \sum_{i=A,B} x_i \left(\int_{-\infty}^{E_{f,AB}} (E-\epsilon_i) n^d_{AB,i}(E) dE - \int_{-\infty}^{E_{f,A+B}} (E-\epsilon_i) n^d_i(E) dE \right) \\
&= \frac{N}{N_{AB}} \sum_{i=A,B} x_i \left(\int_{-\infty}^{E_{f,AB}} E n^d_{AB,i}(E) dE - \int_{-\infty}^{E_{f,A+B}} E n^d_i(E) dE \right)
\end{aligned}
$$


Δε=2 eV
ΔW=0 eV
demixed phase
ordered phase
n_d(E)
Δε=0 eV
ΔW=3 eV
Δε=2 eV
ΔW=3 eV
E (eV)
N_e
V_E (eV)

Calculation V_E from mixed reference system with 2 impurities, being 1-st, 2-nd, 3-rd, 4-th and 5-th neighbours




x_B→0
x_B=0.25
x_B=0.5
x_B=0.75
x_B→1
Δε=1 eV
Δε=2 eV
Δε=3 eV
Δε=8 eV
N_e
ΔW (eV)



	N_e	$\delta_{d,0}$	δ_d	δ_{nd}
CuPd	9.40	0.1	-2.7	-2.9
CuAg	9.85	3.4		-0.6
CuPt	9.25	1.0	3.5	4.6
CuAu	9.75	1.6		-2.6
CoPt	8.35	2.2	1.0	-2.9
NiPt	8.85	1.5	0.2	-3.4

Monitoring surface segregation

For a slab geometry on a lattice, using cluster expansion:

$$E = C + N_{AB}V_E + \frac{1}{2}(N_A^s - N_B^s)\Delta V^s + \ldots$$

with ΔV^s the surface segregation parameter:

$$\begin{aligned}\Delta V^s &= E_A^s(N_{e,A}^d) - E_B^s(N_{e,B}^d) \\ &= V_{1,A}^s - V_{1,A}^b - \left(V_{1,B}^s - V_{1,B}^b\right) + \frac{1}{2}(\gamma^s - \gamma^b)\left(V_{2,AA} - V_{2,BB}\right)\end{aligned}$$

$\Delta V^s > 0 \longrightarrow$ B segregates to surface

$\Delta V^s < 0 \longrightarrow$ A segregates to surface

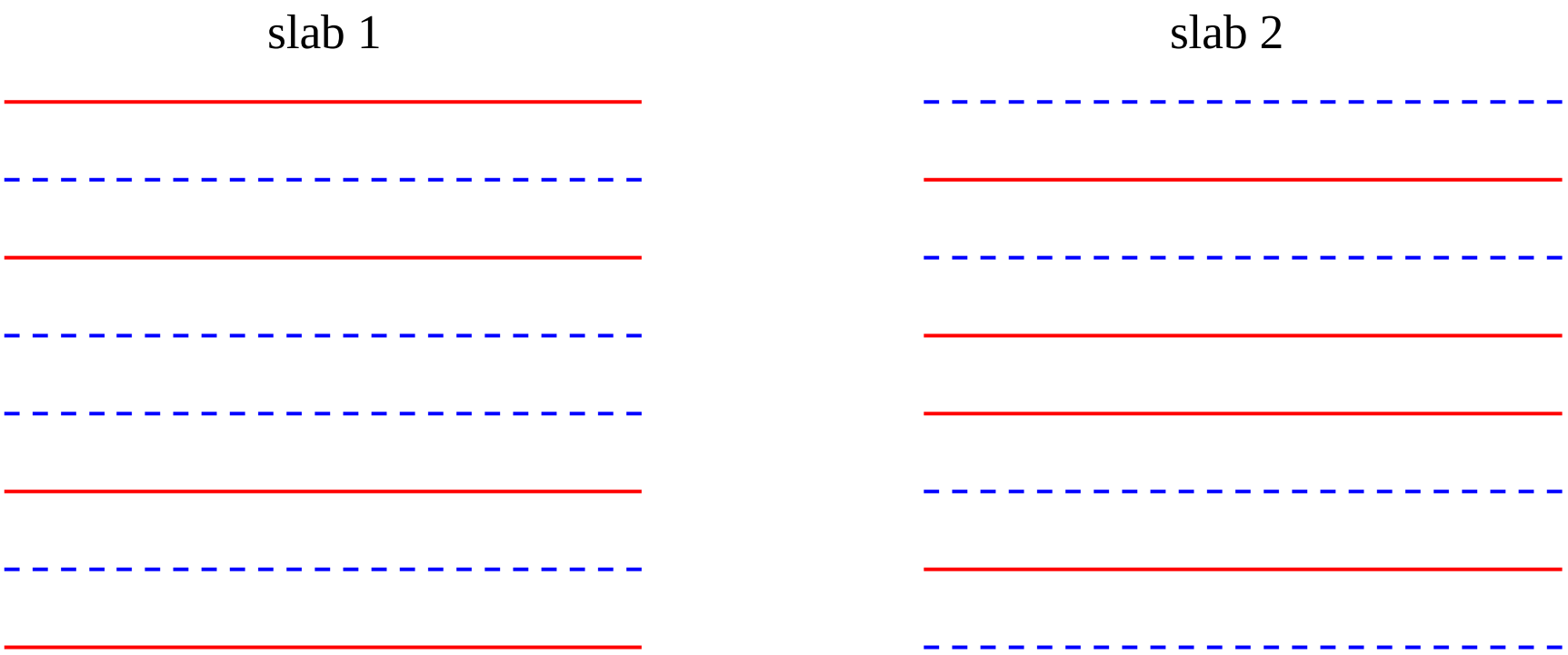
Computation of surface segregation parameter ΔV^s from lattice slabs

Method 1a

Surface segregation parameter calculated simply as:

$$\Delta V^s = \frac{1}{N^s}\left(E_{sl1} - E_{sl2}\right)$$

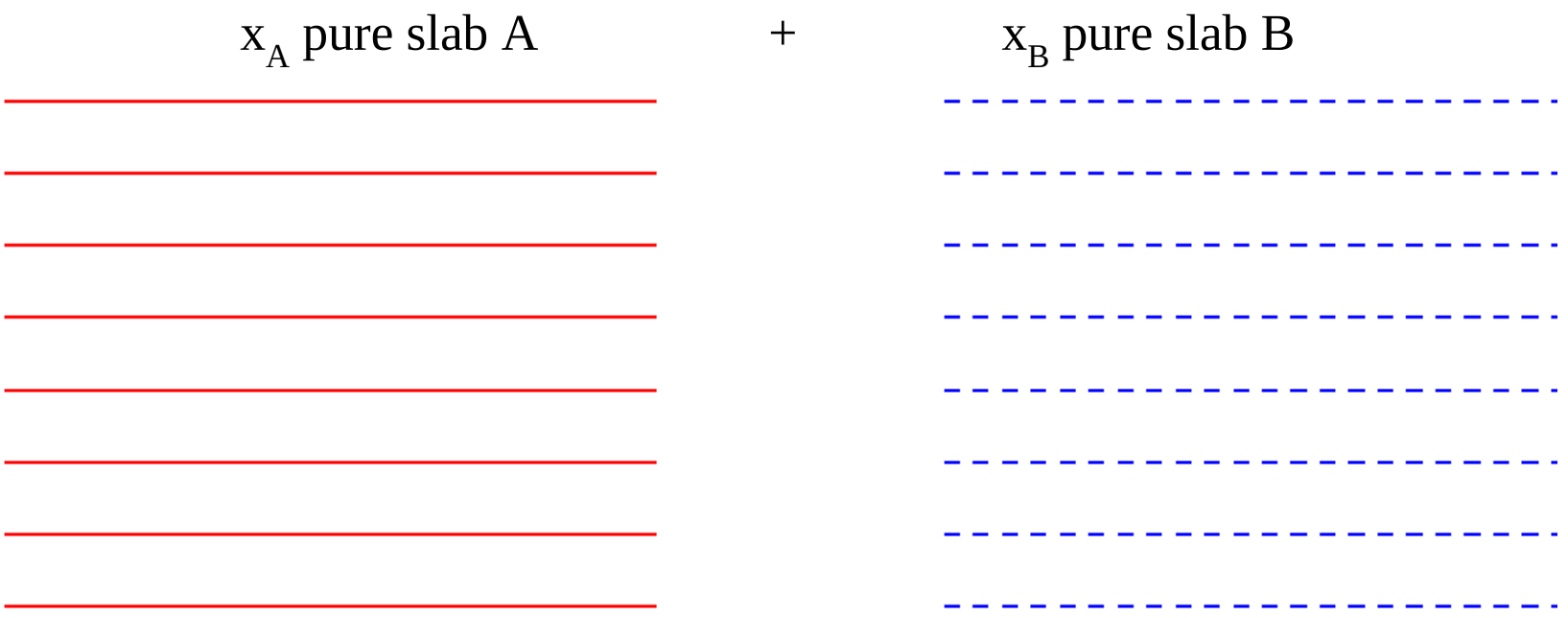
or use (method 1b):



Then, assuming $V^{sb}_{2,AB} = V^{bb}_{2,AB}$, again:

$$\Delta V^s = \frac{1}{N^s}\left(E_{sl1} - E_{sl2}\right)$$

Method 2

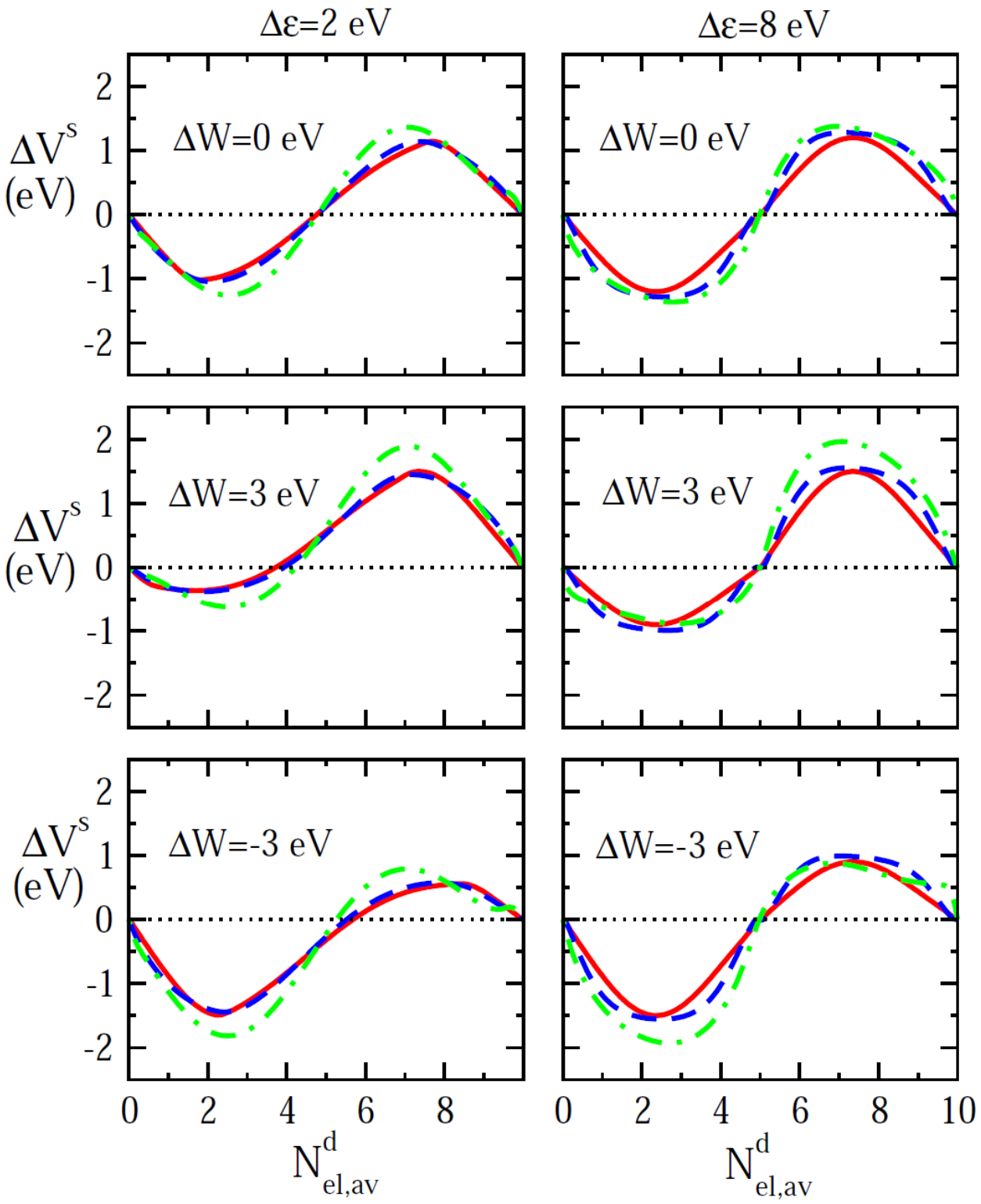


For give N^d_e, first compute charges on A and B, solving:

$$N_e^d = \int_{-\infty}^{E_{f,slA+slB}} (x_A n_{slA}(E) + x_B n_{slB}(E)) dE = x_A N_{e,A}^d + x_B N_{e,B}^d$$

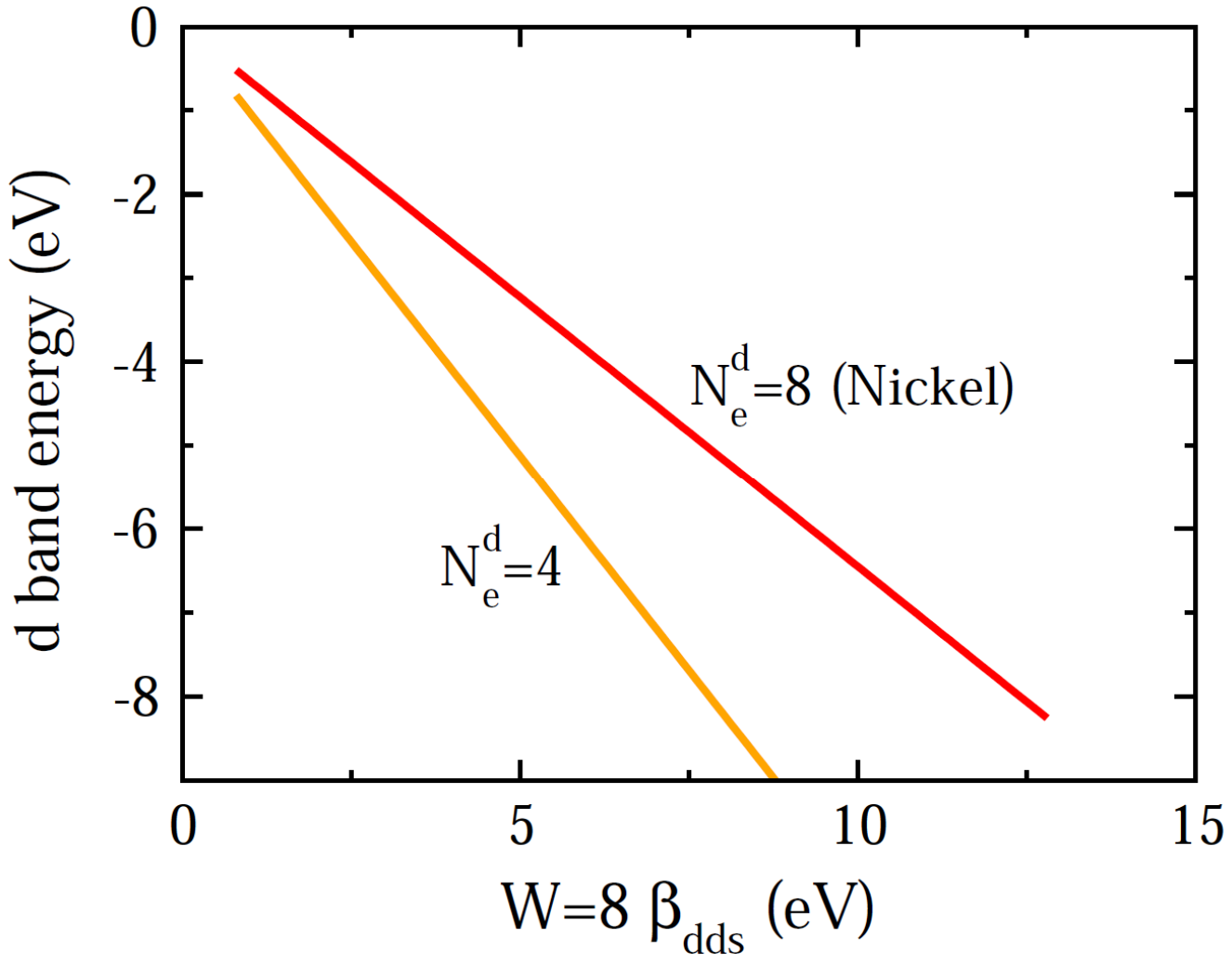
Subsequently compute:

$$\begin{aligned} \Delta V^s &= \frac{1}{N^s}\Delta E^s = \frac{1}{N^s}\left(E_A^s(N_{e,A}^d) - E_B^s(N_{e,B}^d)\right) \\ &= \frac{1}{N^s}\left(E_{slA}(N_{e,A}^d) - E_{bA}(N_{e,A}^d) - (E_{slB}(N_{e,B}^d) - E_{bB}(N_{e,B}^d))\right) \end{aligned}$$


Δε=2 eV
Δε=8 eV
ΔW=0 eV
ΔW=3 eV
ΔW=-3 eV
ΔV^s (eV)
N^d_el,av
2
1
0
-1
-2
0
2
4
6
8
10

Parametrisation of TBFMA potential

Starting with Nickel (E_{coh}=-4.46 eV, W_d=3 eV).....

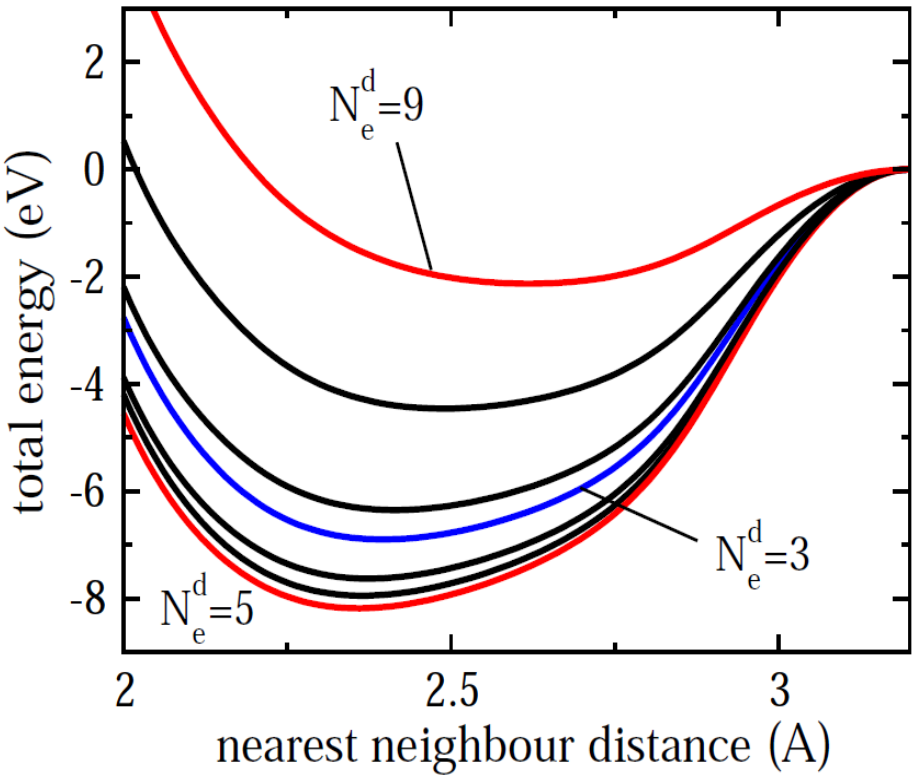


Conclusion: a d-band basis cannot give a good fit of total energy and electronic structure (d-band width W_d) at the same time ----> next step: sd-band basis set

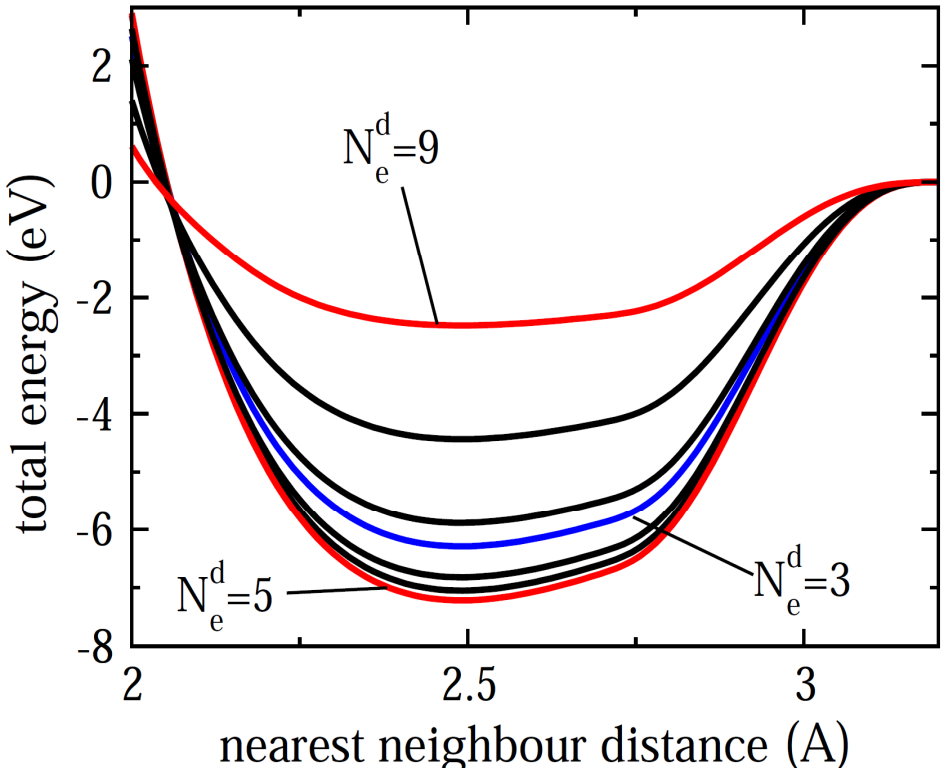
Simulations

Constructing a family of potentials from an existing TBFMA model for Ni*

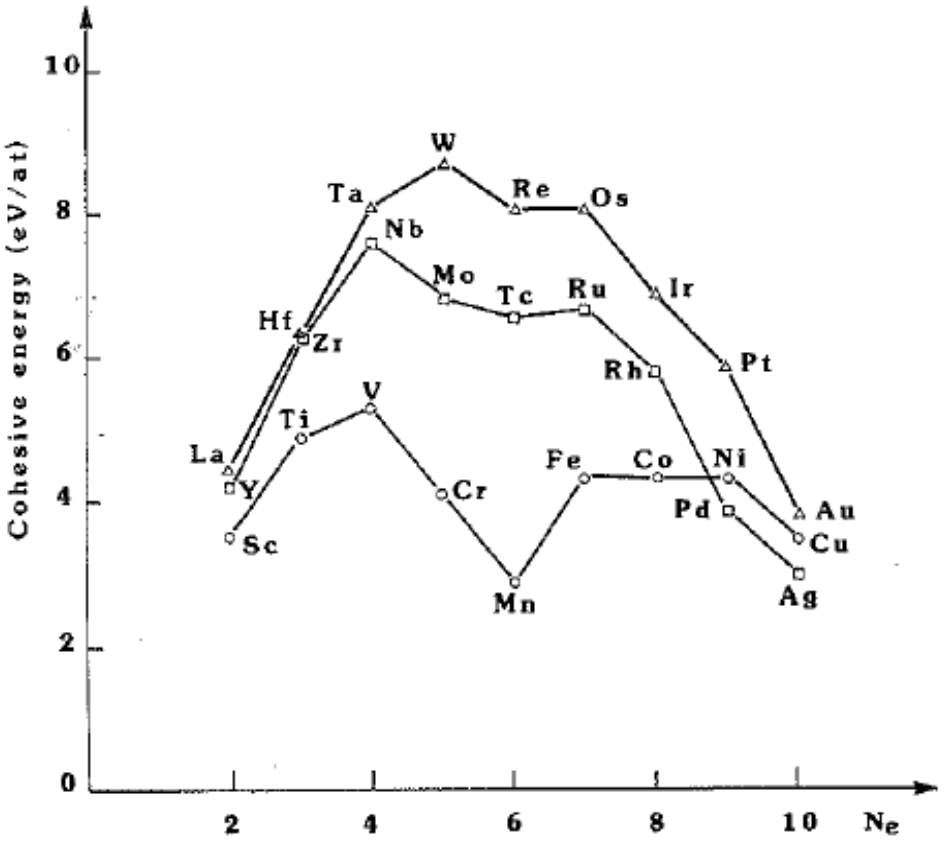
without any other change in parameters

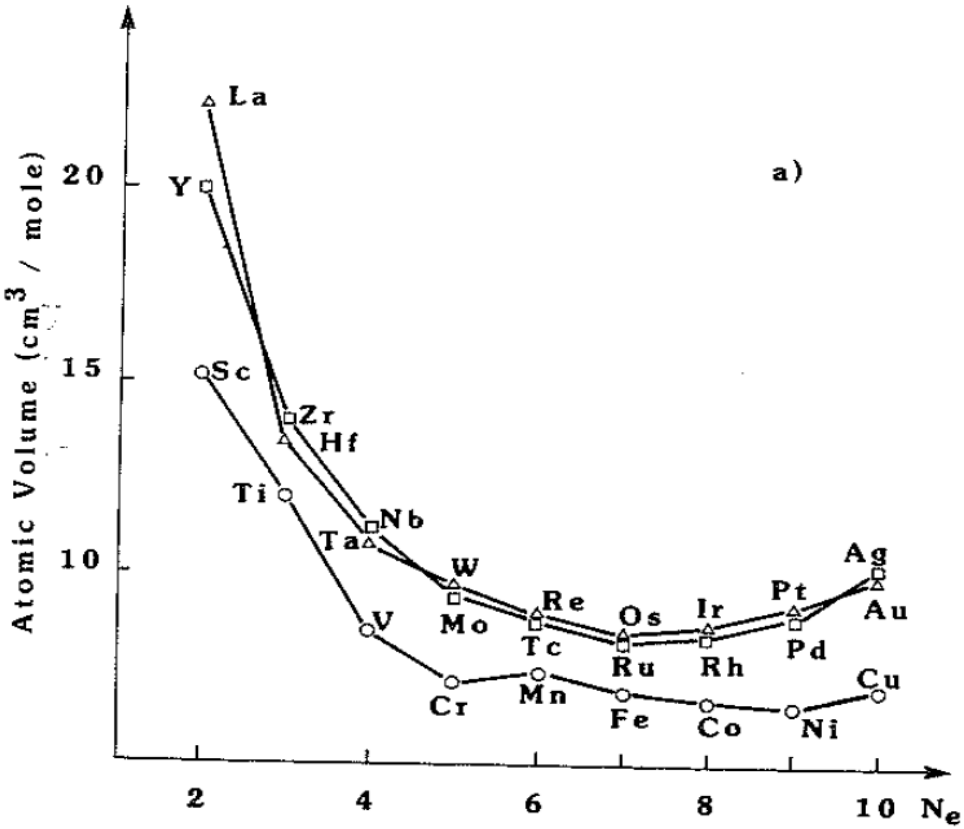


with adjustment of repulsive potential
to keep equal lattice parameters



H. Amara, J.M. Roussel, C. Bichara, J.P. Gaspard, F. Ducastelle, Phys Rev B 79 (2009) 014109



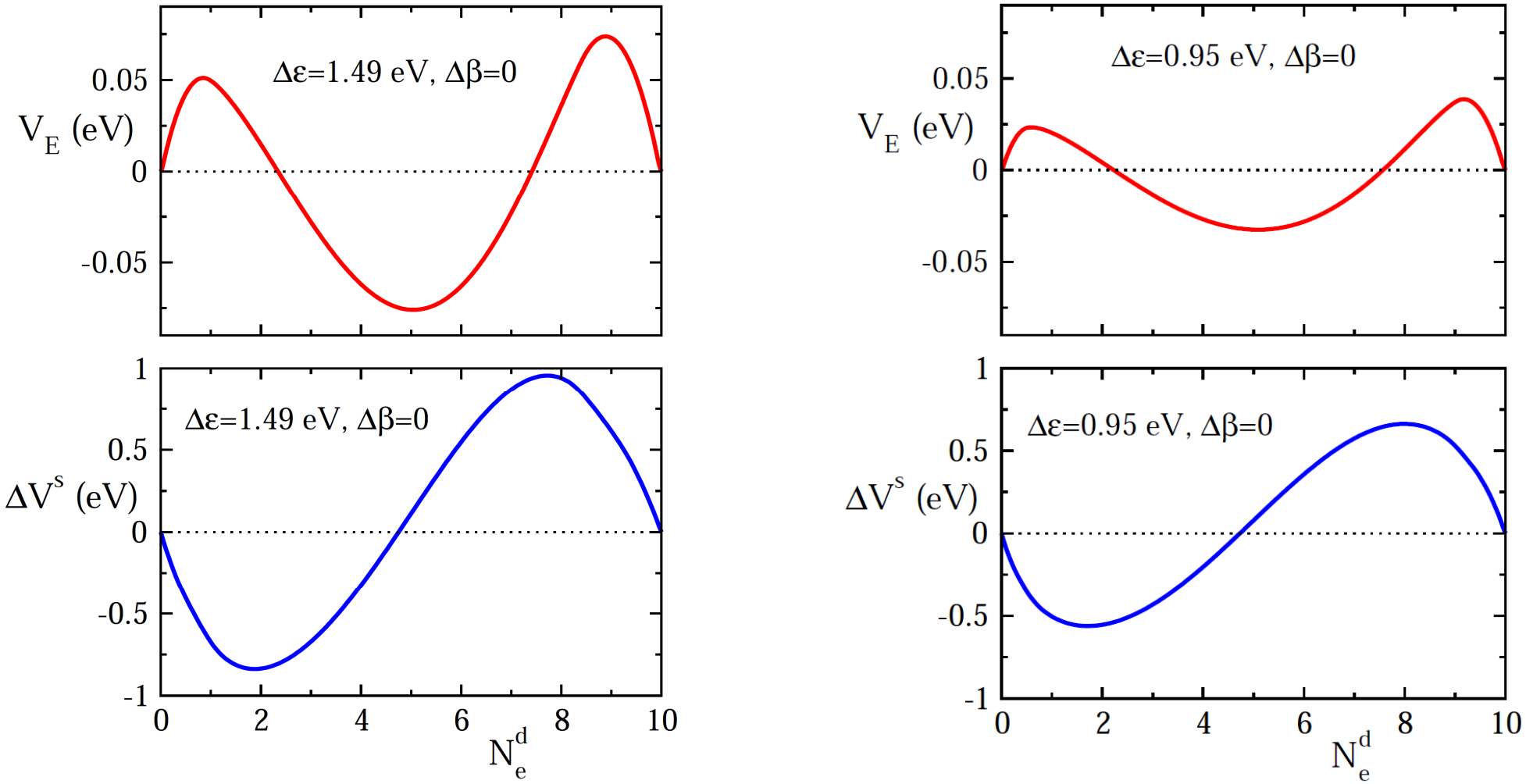


… pictures from Ducastelle in “Alloys”

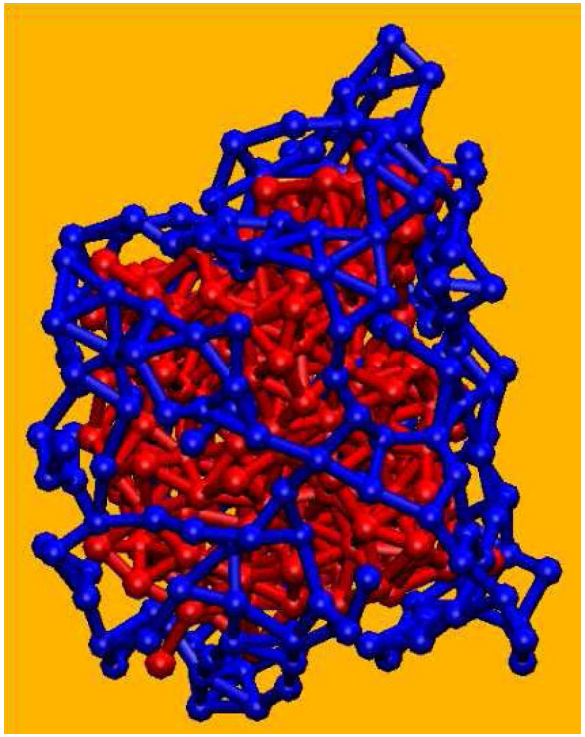
Simulations performed for two alloys from the family

	$N^d_{e,A}$	$N^d_{e,B}$	ϵ_A	ϵ_B
Alloy 1	7	9	0	-1.49
Alloy 2	4	6	0	-0.95

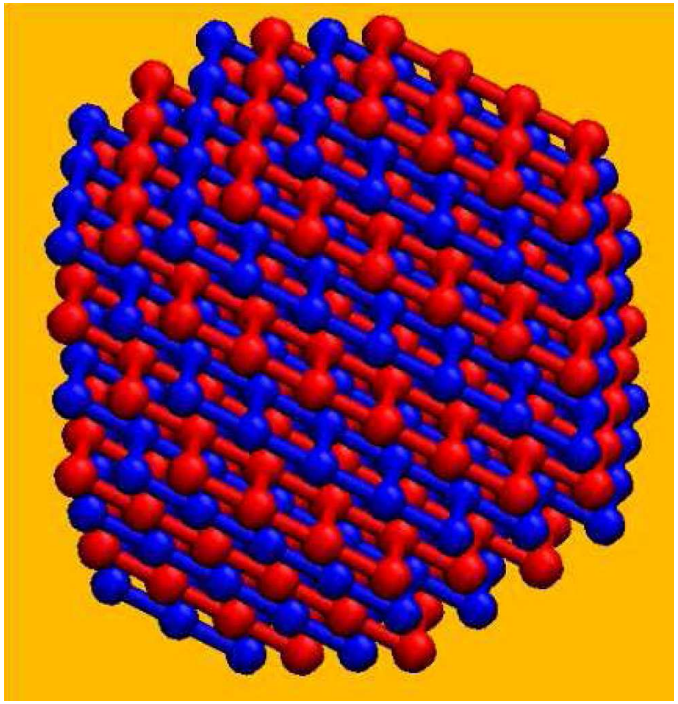
$x_A = x_B = 1/2$



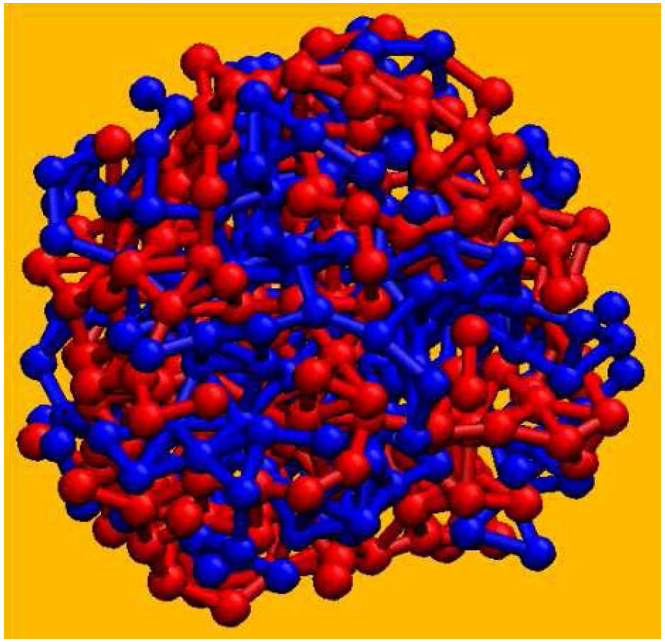
alloy 1 after melting



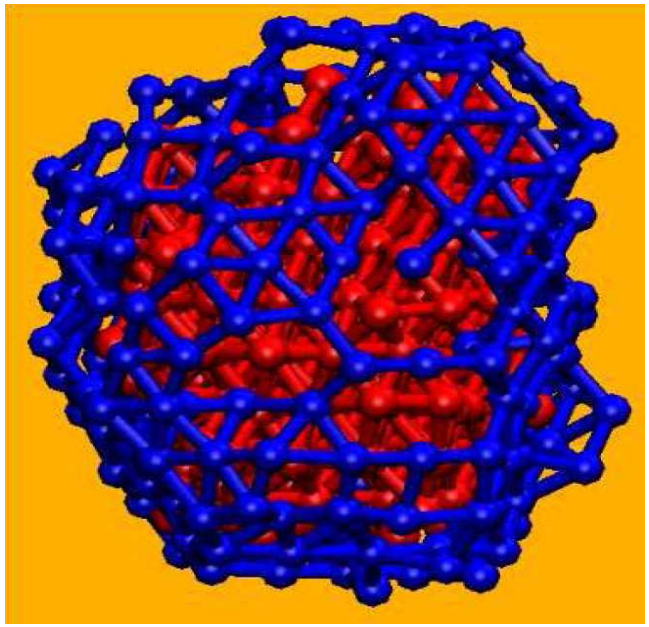
initial ordered cluster



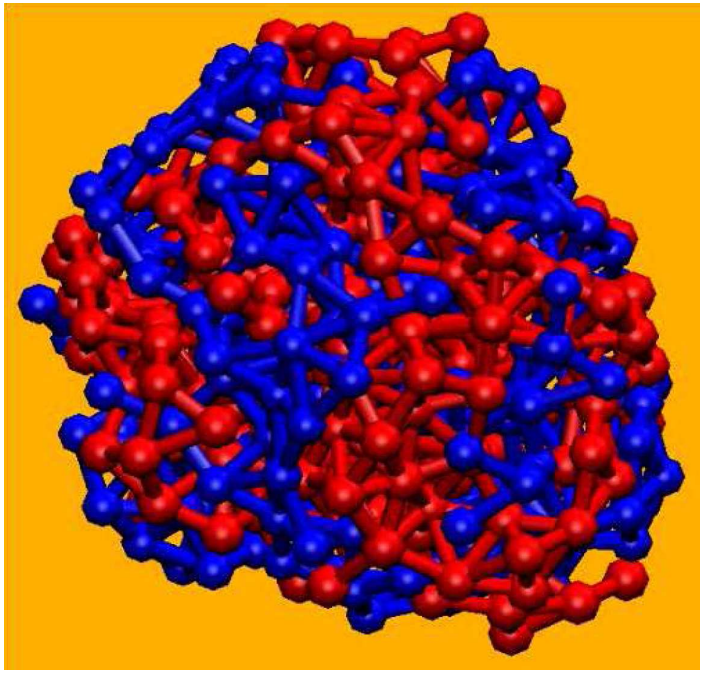
alloy 2 after melting

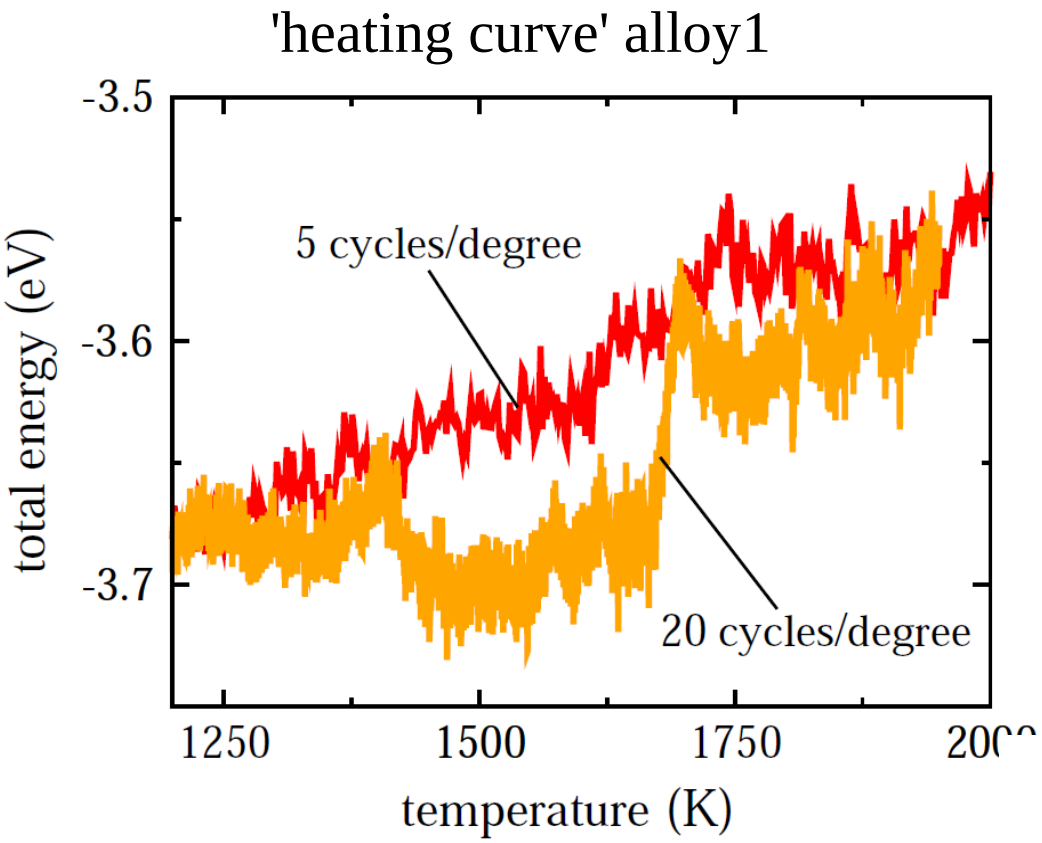


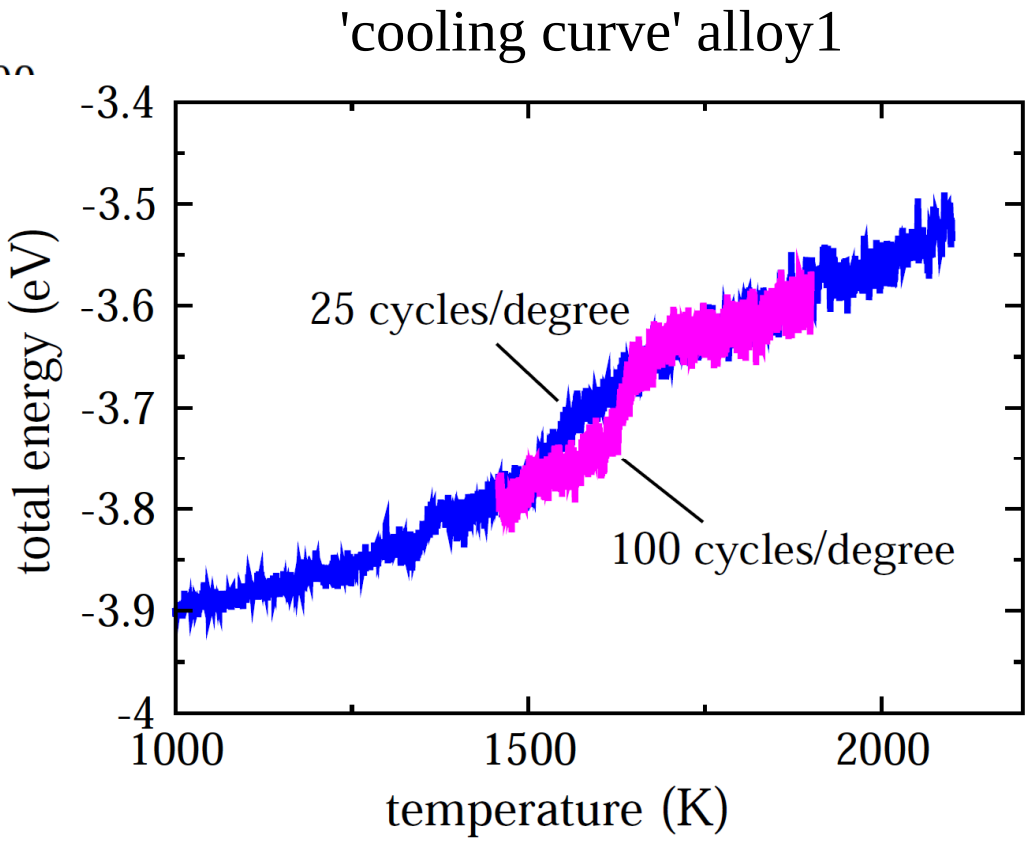
alloy 1 after recrystallisation



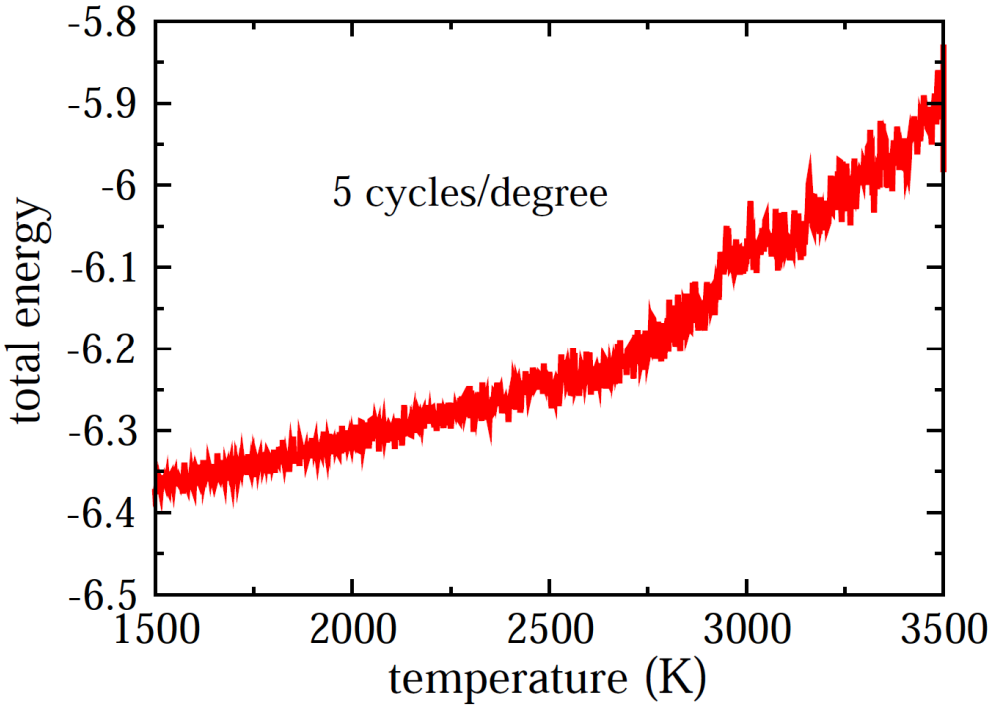
alloy 2 after recrystallisation



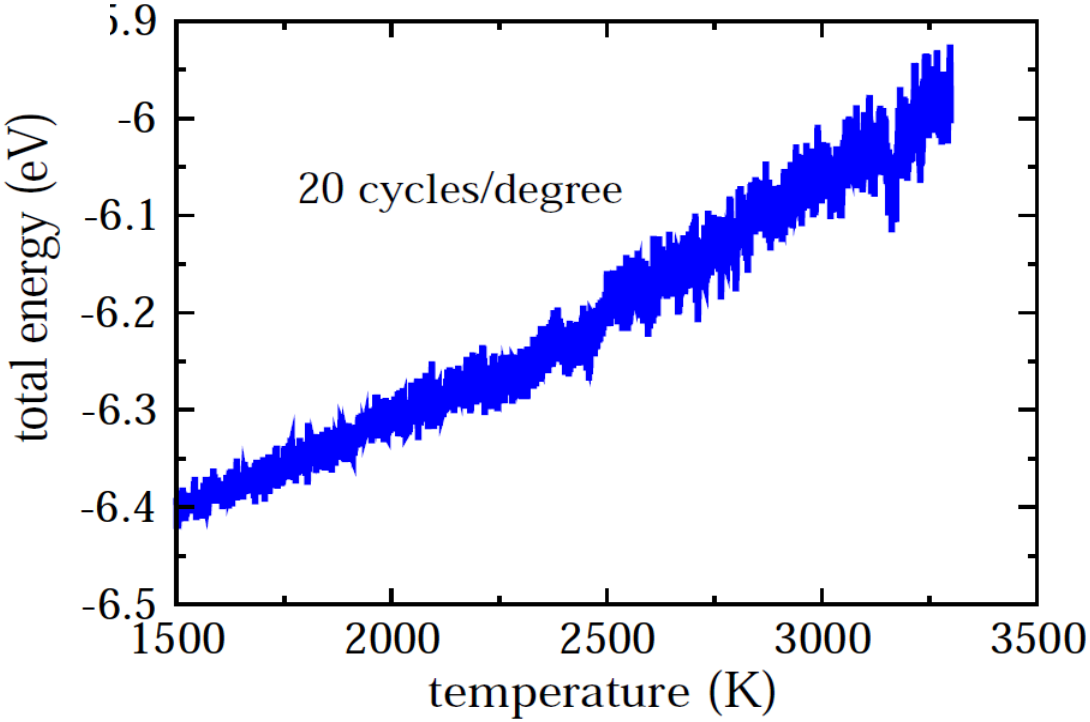

'heating curve' alloy1
-3.5
-3.6
-3.7
total energy (eV)
5 cycles/degree
20 cycles/degree
1250
1500
1750
temperature (K)


'cooling curve' alloy1
-3.4
-3.5
-3.6
-3.7
-3.8
-3.9
-4
total energy (eV)
25 cycles/degree
100 cycles/degree
1000
1500
2000
temperature (K)

'heating curve' alloy 2



'cooling curve' alloy 2



Conclusions

The fourth moment approximation includes the effects the electronic structure satisfactory by taking into account both diagonal and off-diagonal disorder.

The impact of the electronic structure on mixing properties is significant.

A significant improvement of the TBFMA description of the late transition metals seems achievable by using an sd-band basis set (instead of just d). The improvement regards the electronic structure (band width) and thus the mixing properties.

Context

The use of the Fourth Moment Approximation* (FMA) within a Tight Binding (TB) description to build an interatomic interaction model for atomistic simulations seems a significant step forward w.r.t. the Second Moment Approximation (SMA):

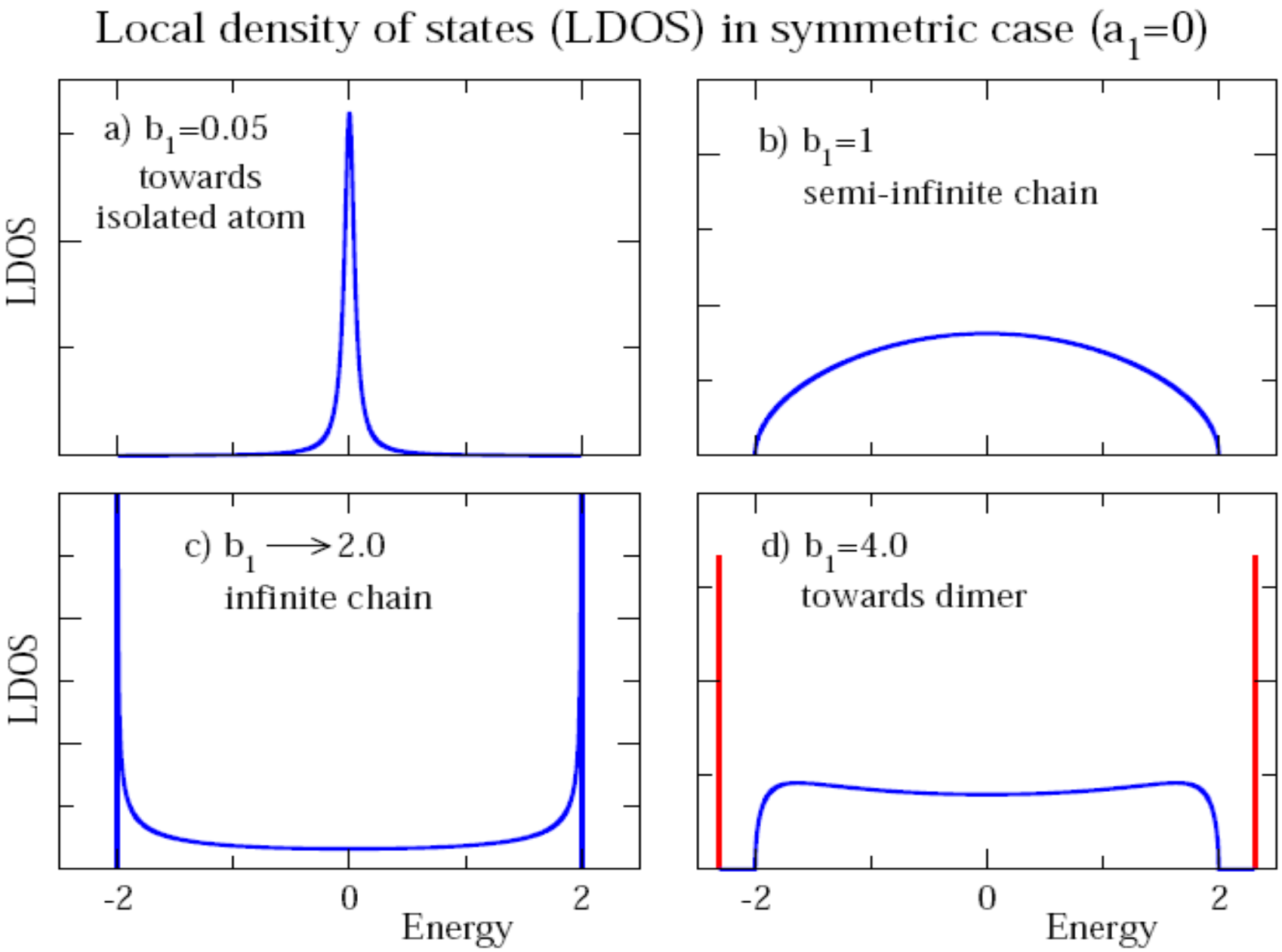
- it includes electronic structure properties
- more quantum aspects are preserved
- due to a recent effort**, simulations based on FMA are only up to one order of magnitude slower then for SMA models

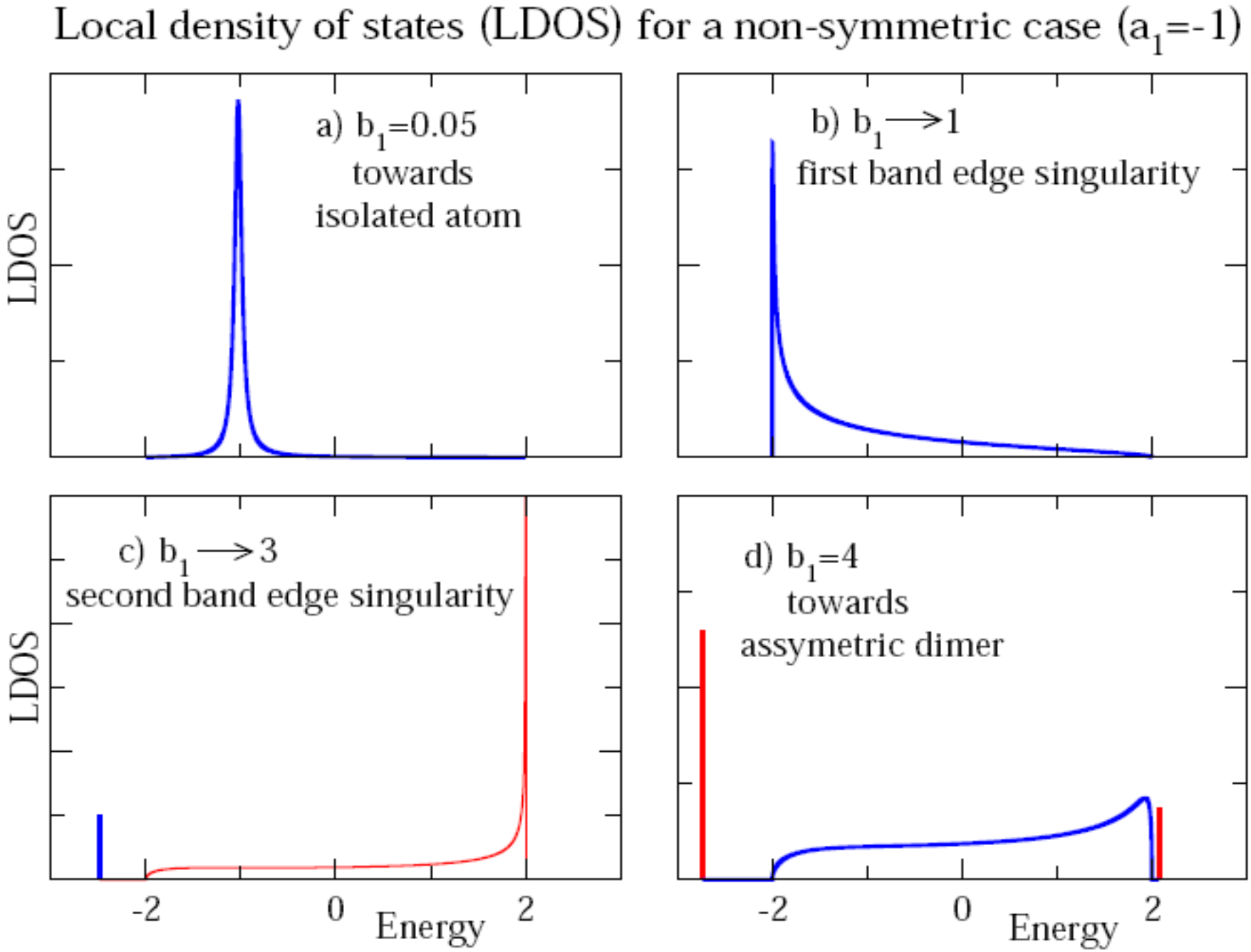
With the expected increase of accuracy of the FMA w.r.t. SMA, predictions of equilibrium properties and the critical temperature of nano clusters of (late) transition metal alloys from grand-canonical Monte Carlo simulations should become much more reliable.

As a important test for the FMA, before starting to parametrize a FMA based model for real transition metals (TMs) relevant for SimNanA, we performed a FMA based lattice model study of the trends in the bulk mixing properties and surface segregation properties.

** An example of a TBFMA model for C-Ni systems is described in:*
H. Amara, J.M. Roussel, C. Bichara, J.P. Gaspard, F. Ducastelle, Phys Rev B 79 (2009) 014109
*** J.H. Los, C. Bichara and R.J.M. Pellenq, "Tight Binding within the Fourth Moment Approximation: efficient implementation and application to ....etc", submitted to PRB*

Examples of the local densities of states for TB model within 4-th moments approximation (a2=0, b2=1)




Local density of states (LDOS) for a non-symmetric case (a_1=-1)
a) b_1=0.05
towards
isolated atom
b) $b_1 \longrightarrow 1$
first band edge singularity
c) $b_1 \longrightarrow 3$
second band edge singularity
d) b_1=4
towards
assymetric dimer
LDOS
LDOS
-2
0
2
Energy
-2
0
2
Energy