

TB-LMTO METHOD FOR EMBEDDED CLUSTER

Václav Drchal

Institute of Physics ASCR, Praha, Czech Republic



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in collaboration with

Josef Kudrnovský and Peter Weinberger

MOTIVATION

- electronic and magnetic structure of impurities, finite clusters, complexes, etc.
- formation energies of impurities
- formation energies of complexes
- structural stability: effective interatomic interactions (Ising type Hamiltonian)
- effective exchange interactions (Heisenberg Hamiltonian)
- parameters of Bruno, Zingales, and Wang model

OUTLINE

- TB-LMTO method
- Embedding of a cluster
- Electrostatic energy and potential
- Total energy of a cluster
- Applications
 - magnetism of non-magnetic impurities in oxides
 - impurity formation energy
 - parameters of BZW model
- Conclusions and outlook

TB-LMTO method

$$H = C + \sqrt{\Delta}S\sqrt{\Delta}, \quad G(z) = (z - H)^{-1} = \lambda(z) + \mu(z)g(z)\mu(z)$$

$$g(z) = (P(z) - S)^{-1}, \quad \lambda(z) = \frac{\gamma - \alpha}{\Delta + (\gamma - \alpha)(z - C)}$$

$$\mu(z) = \frac{\sqrt{\Delta}}{\Delta + (\gamma - \alpha)(z - C)}, \quad P(z) = \frac{z - C}{\Delta + (\gamma - \alpha)(z - C)}$$

S ... matrix of screened structure constants

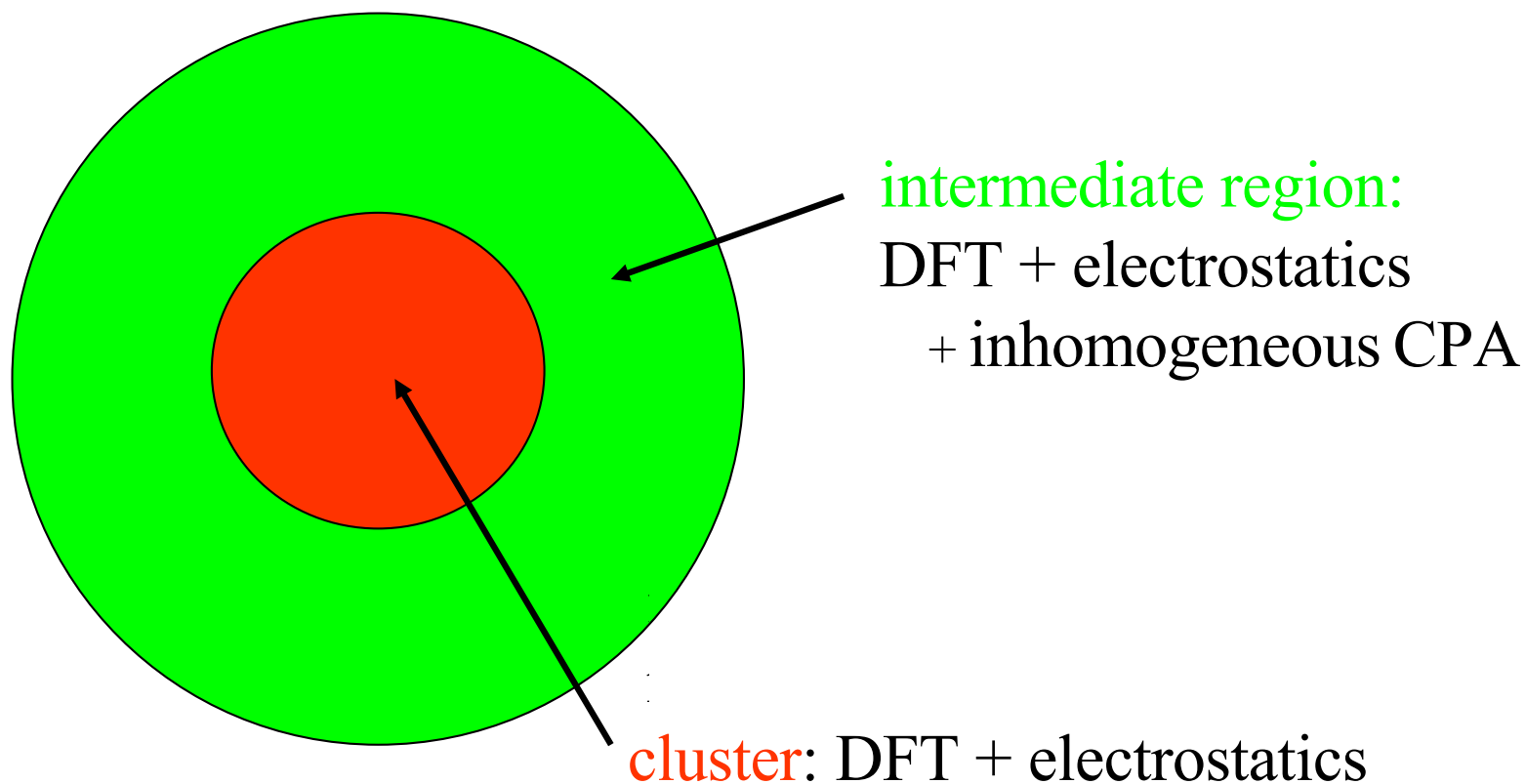
C, Δ, γ ... potential parameters, site-diagonal matrices

$P(z)$... potential function, site-diagonal matrix

$G(z)$... GF, $g(z)$... auxiliary GF

EMBEDDING

reference system: fixed



reference system: **infinite homogeneous crystal**, superscript 0

cluster C ... Π_C , transition region T ... Π_T

inhomogeneous region $I = C \cup T$... $\Pi_I = \Pi_C + \Pi_T$

homogeneous region H ... Π_H

$$g^0 = (P^0 - S)^{-1}, \quad g_{II}^0 = \frac{\Pi_I}{P_{II}^0 - S_{II} - S_{IH} \frac{H}{P^0 - S} S_{HI}}$$

$$g = (P - S)^{-1}, \quad g_{II} = \frac{\Pi_I}{P_{II} - S_{II} - S_{IH} \frac{H}{P - S} S_{HI}}$$

embedding potential: $\Gamma_{II} = S_{II} - S_{IH} \frac{H}{P^0 - S} S_{HI} = \frac{\Pi_{II}}{P_{II}^0 - \frac{\Pi_I}{g_{II}^0}}$

(note that $P_{HH} = P_{HH}^0$)

Madelung potential and Madelung energy

Madelung matrix

$$M_{ij} = \begin{cases} e^2/R_{ij} & \text{for } i \neq j \\ 0 & \text{for } i = j \end{cases}$$

reference system

$$v_i^0 = \sum_j M_{ij} q_j^0, \quad E^0 = \frac{1}{2} \sum_{ij} M_{ij} q_i^0 q_j^0 = \frac{1}{2} \sum_i v_i^0 q_i^0$$

system with embedded cluster

$$\varepsilon_i = q_i - q_i^0, \quad \varepsilon_i \neq 0 \quad \text{only for } i \in I,$$

$$v_i = v_i^0 + \sum_j M_{ij} \varepsilon_j, \quad \varphi_i = \sum_j M_{ij} \varepsilon_j,$$

$$E^{\text{Mad}} = \frac{1}{2} \sum_{ij} M_{ij} q_i q_j = E^0 + \frac{1}{2} \sum_i \varepsilon_i (2v_i^0 + \varphi_i)$$

TOTAL ENERGY

$$E^{\text{tot}} = E^{\text{band}} + E^{\text{core}} + E^{\text{dc}} + E^{\text{xc}} + E^{\text{Mad}}$$

$$n(E) = -\frac{1}{\pi} \text{Im Tr } G(E + i0), \quad G(z) = (z - H)^{-1}$$

$$E^{\text{band}} = \int^{E_F} dE E n(E) = \frac{1}{2\pi i} \int_{C_R} dz z \text{Tr } G(z)$$

$$C_R = \{z : z = E_F - R + R e^{i\phi}, \phi \in (0, 2\pi)\}$$

H_0 ... reference medium, V ... perturbation by cluster

$$G_0(z) = (z - H_0)^{-1}, \quad G(z) = (z - H_0 - V)^{-1}$$

although V is limited to a small subspace, it changes $G(z)$ in the whole space and therefore it need not be sufficient to calculate the DOS on cluster atoms

Tr log G

$$E^{\text{band}} = E_F N_{el} + \frac{1}{2\pi i} \int_{C_R} dz z \text{Tr} \log(z - H)$$

two subspaces: Π_I ... cluster, Π_H ... rest of the system, $\Pi_I + \Pi_H = 1$

$$\text{Tr} \log(z - H) = \text{Tr}_I \log \left(z \Pi_I - H_{II} - H_{IH} \frac{\Pi_H}{z - H} H_{HI} \right) + \text{Tr}_H \log(z - H_{HH})$$

terms $\text{Tr}_H \log(z - H_{HH})$ are identical for reference system and for the cluster and thus will mutually subtract

two problems:

1. logarithm is a multivalued function
 2. potential function in the TB-LMTO has poles
- use the trick with $\text{Tr} \log G(z)$
 - calculate $E_I^{\text{band}} = \int^{E_F} dE E n_I(E)$, $n_I(E) = -\frac{1}{\pi} \text{Im} \text{Tr}_I G(E + i0)$

REMARKS

- reference system:
 - ideal crystal
 - disordered alloy
 - semi-infinite solid
 - empty spheres
- short-ranged structure constants needed \Rightarrow TB-LMTO
- calculation proceeds in two steps:
 - embedding potential Γ_{II} and Madelung potential of reference medium for inhomogeneous region
 - selfconsistency in the inhomogeneous region
- convergence of results with size of cluster important

Magnetism of non-magnetic impurities in non-magnetic oxides

magnetism without d-electrons, or d^0 –magnetism

- vacancies at cation sites in TiO_2 , ZrO_2 , HfO_2 can induce magnetic moments on neighboring oxygen atoms
- formation energy of such vacancies is very high
- substitution of TM atom by an atom of alkali metal Li, Na, K, Rb ... or alkaline earths Be, Mg, Ca, ...

Results for ZrO₂

fluorite structure, cluster 59 sites

shell	n	atom
0	1	Zr, Vac, K, etc.
1	8	O ... O(1)
2	6	empty
3	12	Zr
4	24	O ... O(2)
5	8	E

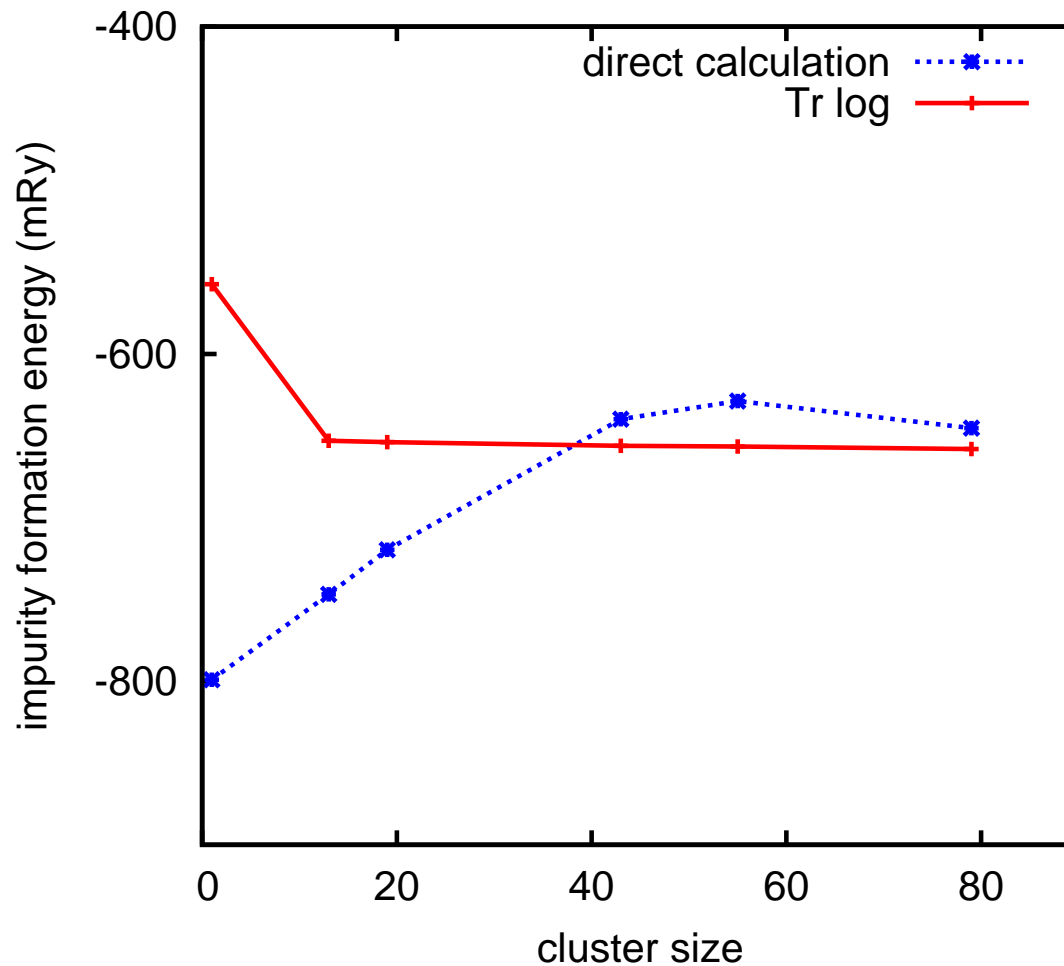
Results for ZrO₂

comparison with FPLAPW calculations for XZr₇O₁₆ (12.5 % X) and XZr₃₁O₆₄ (3.125 %), where X=Vac, K, etc.

	cluster	12.5 %	3.125 %		cluster	12.5 %	3.125 %
	$M[\mu_B]$	$M[\mu_B]$	$M[\mu_B]$		$M[\mu_B]$	$M[\mu_B]$	$M[\mu_B]$
Vac	0.005	0.00	0.00	K	0.158	0.10	0.08
O(1)	0.421	0.40	0.41	O(1)	0.244	0.30	0.24
O(2)	0.027	0.06	0.03	O(2)	0.023	0.05	0.03
total	3.927	3.86	3.99	total	2.616	3.00	2.80

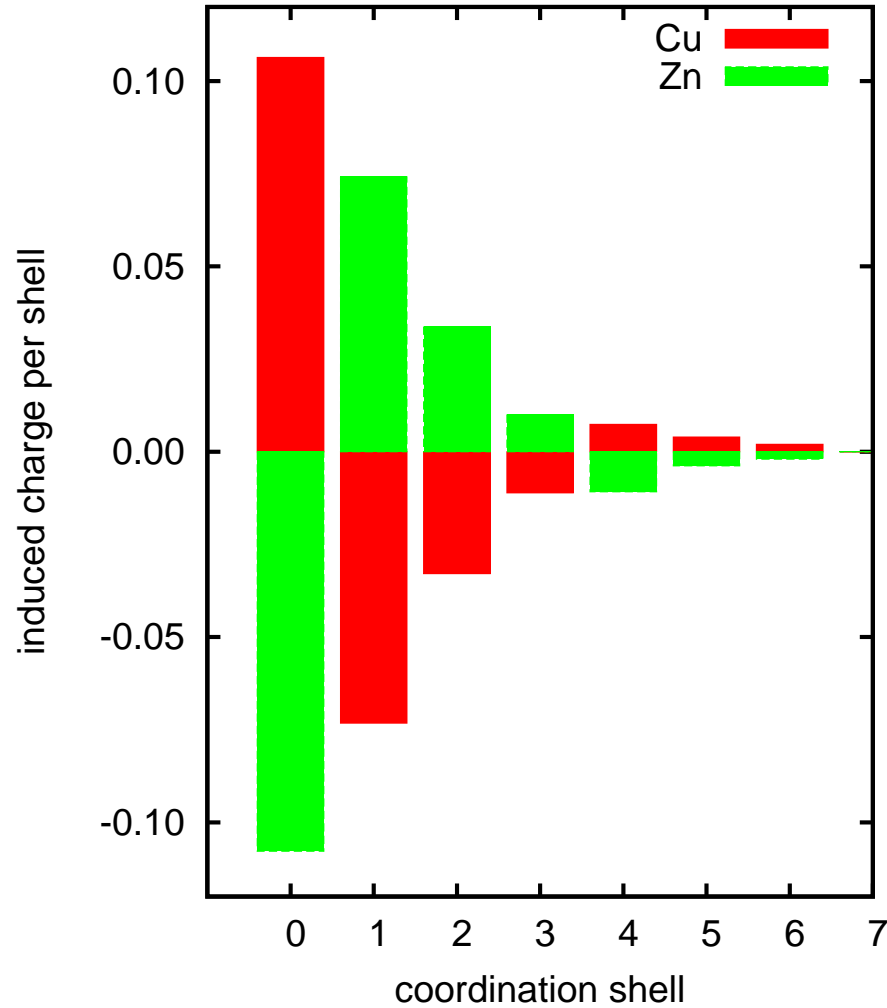
Zn impurity in fcc-Cu

impurity formation energy $\Delta E = \left(E[Cu_{N-1}Zn] + \epsilon[Cu] \right) - \left(E[Cu_N] + \epsilon[Zn] \right)$



Impurity-induced charges

charge induced in the neighborhood of Cu and Zn atom in bcc-Cu₅₀Zn₅₀ alloy



Model of Bruno, Zingales, and Wang

E. Bruno, L. Zingales, and Y. Wang: PRL **91** (2003), 166401.

$$E(\{q_i\}) = E^{\text{loc}}(\{q_i\}) + E^{\text{Mad}}(\{q_i\}) = \sum_i \frac{a_i}{2} (q_i - b_i)^2 + \frac{1}{2} \sum_{i,j} M_{ij} q_i q_j ,$$

q_i ... net charge

b_i ... bare charge

a_i ... strength of electron-electron interaction

minimization of energy:

$$a_i(q_i - b_i) + \sum_j M_{ij} q_j = 0, \quad V_i = \sum_j M_{ij} q_j$$

$$a_i q_i + V_i = a_i b_i = k_i \quad \dots \text{linear } q\text{-}V \text{ relation}$$

parameters a_i, b_i determined from supercell calculations or from local-field CPA

qV-relation

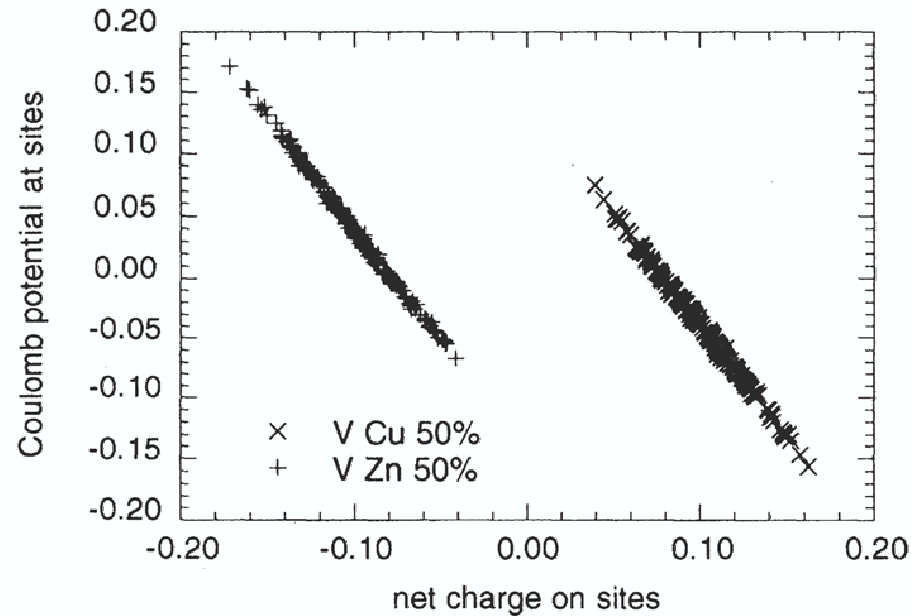


FIG. 1. The Coulomb potential V^i versus the charges q^i on the 432 sites in the cell for a 50% Cu-Zn alloy with the bcc crystal structure. The plus signs are the data points for sites that have a Zn atom on them and the crosses are for Cu. The potentials and charges are in dimensionless atomic units as described in the text.

Faulkner, Wang, and Stocks, PRB **52** (1995), 17106.

BZW model

- screened Madelung interactions M_{ij}^{scr}
- corrections to effective interatomic interactions

$$V_{ij}^{\text{scr}} = M_{ij}^{\text{scr}} (q_i^A - q_i^B)(q_j^A - q_j^B)$$

- statistics of net charges on atoms in an alloy

V. Drchal, R. Hammerling, and P. Weinberger: Phys. Rev. B **74**, 214204.

Parameters of BZW model

add external Madelung potential V^{ext} on the site at origin

$$aq + V^{\text{tot}} = k = ab, \quad V^{\text{tot}} = V^{\text{ext}} + V^{\text{induced}}$$

	TB-LMTO-CPA		KKR-CPA	
	Cu	Zn	Cu	Zn
a	1.26	1.24	1.84	1.82
b	0.0711	-0.0726	0.079	-0.078
k	0.0896	-0.0903	0.145	-0.144

- KKR-CPA: J.S. Faulkner, Y. Wang, and G.M. Stocks: Phys. Rev. B **55** (1997), 7492.
- TB-LMTO-CPA: present calculations

CONCLUSIONS AND OUTLOOK

- flexible, numerically medium-cost method
- electronic structure of clusters (charge distribution, LDOS)
- magnetic structure of clusters (magnetic moments)
- energetics:
 - impurity/complex formation energies
 - effective interactions
 - parameters of BZW model, etc.