TB-LMTO METHOD FOR EMBEDDED CLUSTER

Václav Drchal

Institute of Physics ASCR, Praha, Czech Republic

Grant Agency of ASCR: project IAA100100616

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

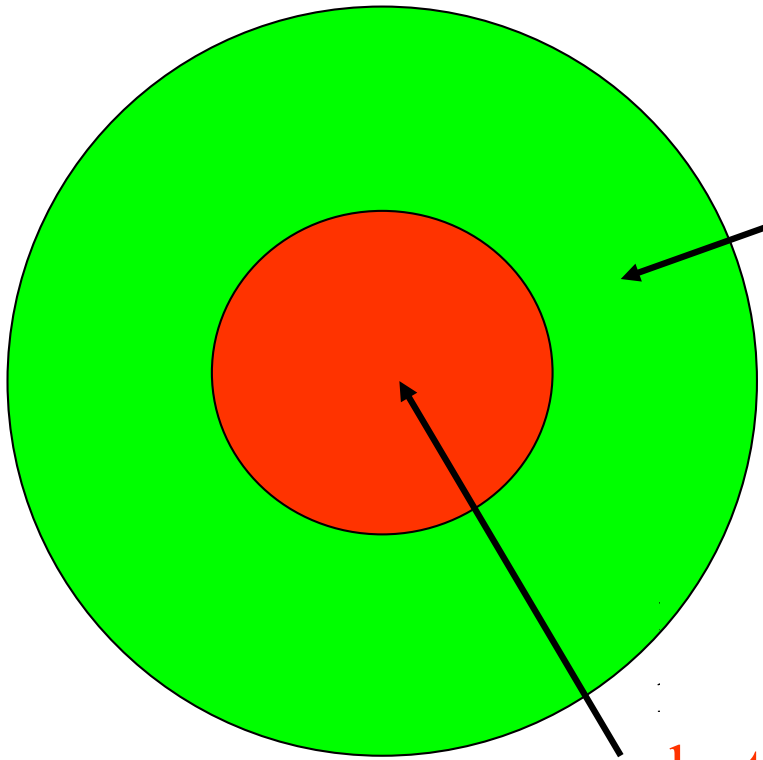
C, Δ, γ ... potential parameters, site-diagonal matrices

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

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

EMBEDDING

reference system: fixed



intermediate region:
DFT + electrostatics
+ inhomogeneous CPA

cluster: DFT + electrostatics

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

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

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

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

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

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

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

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

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

TOTAL ENERGY

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

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

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

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

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 suffi cient to calculate the DOS on cluster atoms

Tr log G

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

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

$$Tr\log(z-H) \quad = \quad Tr_I \log\left(z\Pi_I - H_{II} - H_{IH}\frac{\Pi_H}{z-H}H_{HI}\right) + Tr_H\log(z-H_{HH})$$

terms $Tr_H \log(z-H_{HH})$ 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 Tr log G(z)
- calculate $E_I^{\rm band} = \int^{E_F} dE\, E\, n_I(E)\,, \quad n_I(E) = -\frac{1}{\pi}\,{\rm Im}\, Tr_I\, G(E+i0)$

REMARKS

- reference system:
  - ideal crystal
  - disordered alloy
  - semi-infi nite 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 ZrO_2

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 ZrO_2

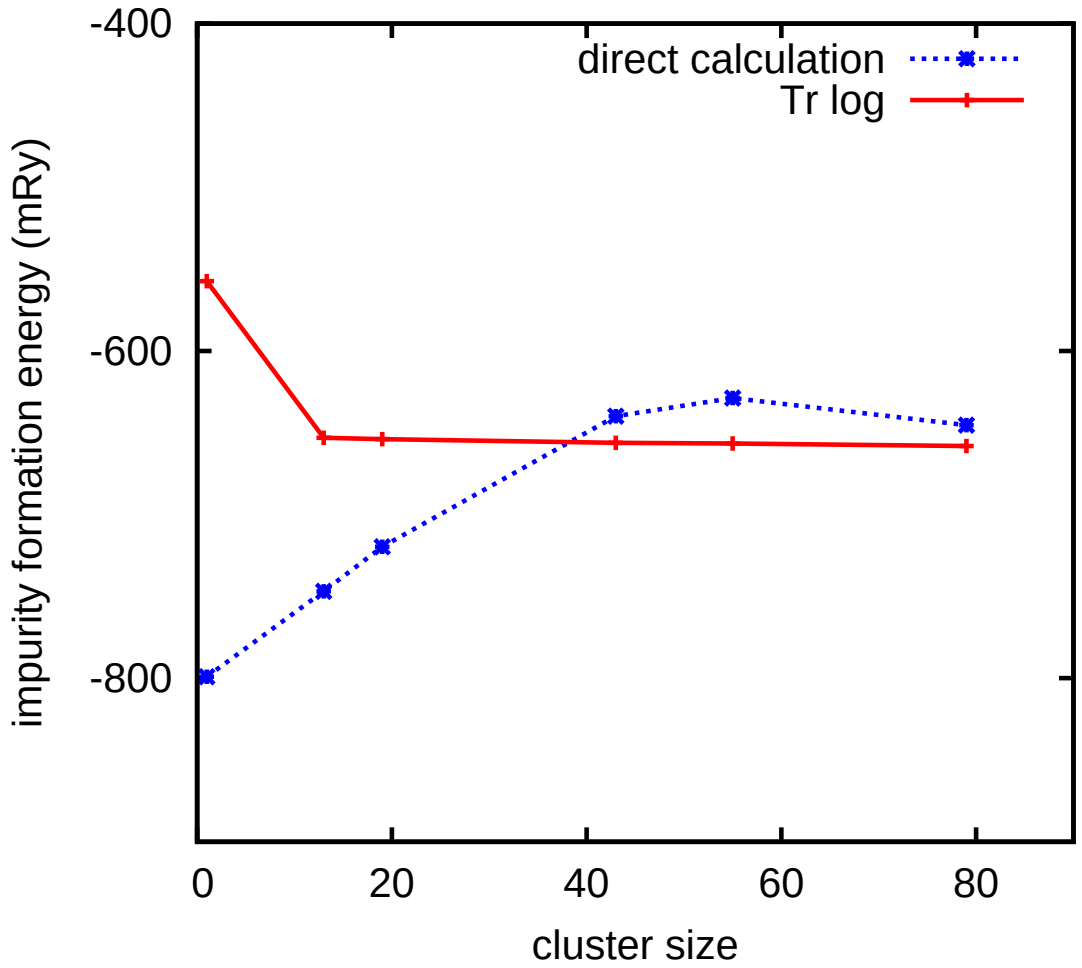
comparison with FPLAPW calculations for XZr_7O_{16} (12.5 % X) and $XZr_{31}O_{64}$(3.125 %), where X=Vac, K, etc.

	cluster $M[\mu_B]$	12.5 % $M[\mu_B]$	3.125 % $M[\mu_B]$
Vac	0.005	0.00	0.00
O(1)	0.421	0.40	0.41
O(2)	0.027	0.06	0.03
total	3.927	3.86	3.99

	cluster $M[\mu_B]$	12.5 % $M[\mu_B]$	3.125 % $M[\mu_B]$
K	0.158	0.10	0.08
O(1)	0.244	0.30	0.24
O(2)	0.023	0.05	0.03
total	2.616	3.00	2.80

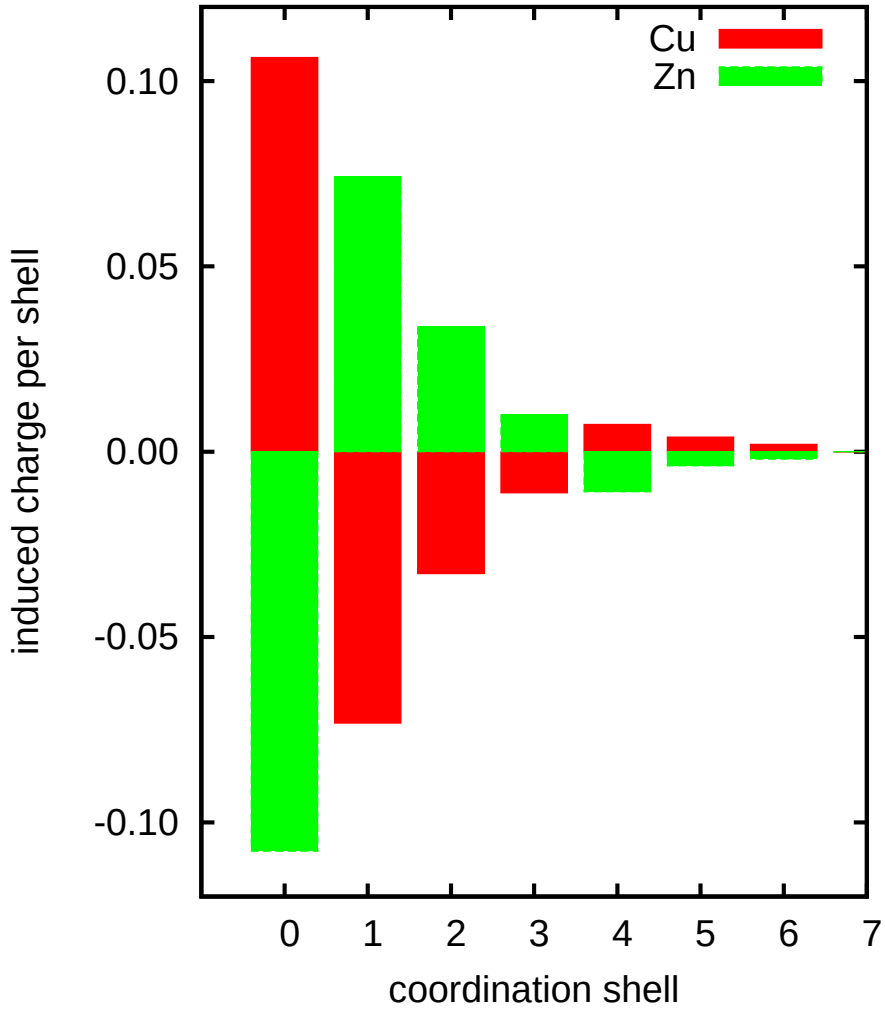
Zn impurity in fcc-Cu

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



Impurity-induced charges

charge induced in the neighborhood of Cu and Zn atom in bcc-$Cu_{50}Zn_{50}$ alloy



Model of Bruno, Zingales, and Wang

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

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

q_i ... net charge

b_i ... bare charge

a_i ... strength of electron-electron interaction

minimization of energy:

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

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

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

qV-relation

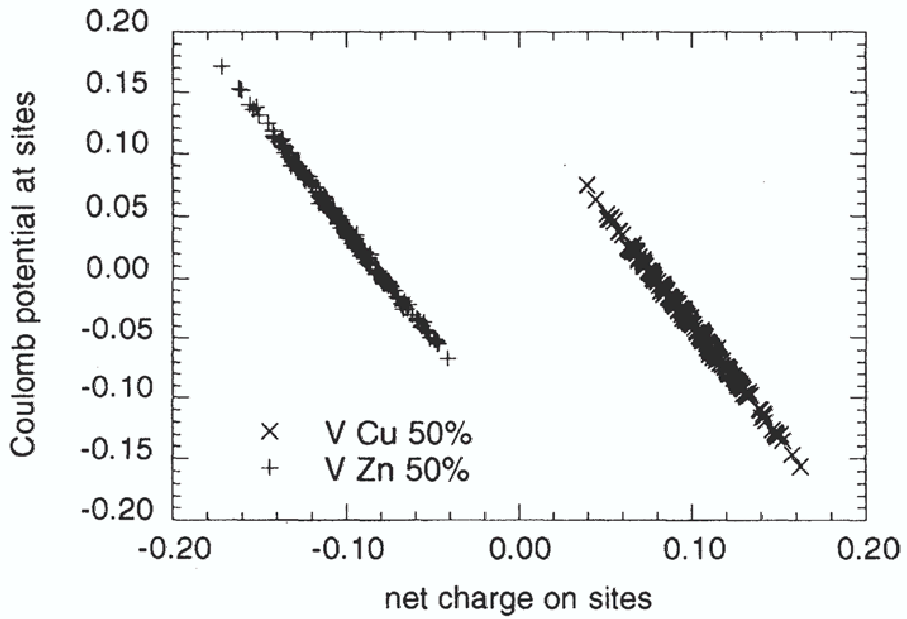


FIG. 1. The Coulomb potential V^i versus the charges q^i on the 432 sites in the cell for a 50% Cu-Zn alloy with the bcc crystal structure. The plus signs are the data points for sites that have a Zn atom on them and the crosses are for Cu. The potentials and charges are in dimensionless atomic units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

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

- 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 $V^{\rm ext}$ on the site at origin

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

	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.