

## Application of DFT – Cellular Method to Alkaline Metals: Lithium

*Andrzej Koleżnyński and Wiesław S. Ptak*

*Department of Ceramics, Academy of Mining and Metallurgy,  
Al. Mickiewicza 30, 30-059 Kraków (Poland)*

*Jerzy Mrugalski*

*Satellite Data Receiving and Processing Center, Institute of Meteorology  
and Water Management, P. Borowego 14, 30-215 Kraków (Poland)*

*Katarzyna Tkacz-Smiech*

*Institute of Physics, Pedagogical University,  
Podchorążych 2, 30-084 Kraków (Poland)*

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A Kohn-Sham scheme following method of binding energy calculation for alkaline metals is proposed. The main idea of the method consists of introducing the interatomic distance dependent positive crystal field, and determining the charge density and potential term. The obtained results show good agreement between the calculated and experimental binding energies, and relatively large error in the equilibrium interatomic distance calculation.

### INTRODUCTION

Most of the methods applied in physics of metals originate directly from wave mechanics. On the other hand, it is becoming more and more obvious that many of the problems of solid state can be, with good results, interpreted in terms of electron density, independently of wave function.

Successful attempts to describe a many-electron system, using electron density, were started in the late 1920's by Thomas<sup>1</sup> and Fermi<sup>2</sup> and expanded by Dirac<sup>3</sup> and by Hartree-Fock.<sup>4</sup>

A strong mathematical foundation for electronic charge density as a key magnitude in the description of the properties of non-uniform electron gas was given in

1964 in the Hohenberg-Kohn<sup>5</sup> theorem, which stated that electron density determines all the properties of nondegenerated electron gas.

Over 35 years long development of density functional theory (DFT) has shown that electron density is a very appealing tool in solving many particle problems.<sup>6</sup>

In this paper, a method of calculation of the binding energy of atoms in metallic crystal is presented. The proposed method has been elaborated within DFT formalism. It has been used to calculate the binding energy for lithium crystal. Atomic units are used throughout the paper.

### A MODEL FOR BINDING ENERGY CALCULATION

We consider a metal as a model system of valence electrons moving in an external, periodical potential due to atomic cores. In calculation of the binding energy  $E_b$ , defined as the difference between the electronic energy  $E$  of an atom in a solid and the electronic energy of an isolated neutral atom  $E_{at}$ :

$$E_b = E - E_{at} \quad (1)$$

the cellular method has been used.

According to the method, every cell is represented by a ball («muffin-tin») with an atomic core placed in the center. Such a ball may be considered as an approximation for the Wigner-Seitz cell. The total electron density  $\rho_{mt}(\vec{r})$  in the muffin-tin cell is contributed by the densities due to all atoms in the system:

$$\rho_{mt}(\vec{r}) = \rho_{at}^0(\vec{r}) + \sum_{i(1)=1}^{P(1)} \rho_{at}(\vec{r} + \vec{R}_{i(1)}) + \sum_{i(2)=1}^{P(2)} \rho_{at}(\vec{r} + \vec{R}_{i(2)}) + \dots; \quad (2)$$

$$|\vec{r}| \leq R_{mt}$$

where  $\rho_{at}^0$  is the electron density of the atom centrally placed in the cell; the respective sums refer to successive coordinate spheres surrounding the central atom, the number  $P(1)$  denotes coordination number of the 1-st sphere.

The electron density of the central atom  $\rho_{at}^0$  and the contribution related to the first coordination sphere are most substantial in the present calculations.

The following notation has been used in Eq. (2):

$R_{mt}$  – radius of the MT cell.

$\vec{R}_i$  – radius vector of  $i$ -th atom in the coordinate system of the origin at the position of the atomic core centrally placed in the cell.

The one-atom electronic density  $\rho_{at}$  is represented by the solution of Kohn-Sham equations<sup>7</sup> for the set of electrons moving independently within the Fues-Kratzer potential.<sup>8,9</sup> It is the sum of one-electron densities and, in the spherical polar coordinates, assumes the shape:

$$\rho_{at} = \sum_{1/N_{at}} \rho_{at,k} = \sum_{1/N_{at}} N_k r^{2n(k)-2} \exp(-2 Z_k^{eff} r) \cdot Y_{l(k)}^{m(k)}(\Theta, \varphi), \quad (3)$$

where  $N_{\text{at}}$  denotes the number of electrons in the atom;  $N_k$  is a factor normalizing the  $k$ -th density contribution to one;  $n, l, m(k)$  are quantum numbers for  $k$ -th electron.

The parameter  $Z_k^{\text{eff}}$  in Eq. (3), which by analogy to the model density in an isolated atom<sup>8-10</sup> may be considered as an effective charge for the  $k$ -th electron, includes a deformation of the electron density distribution for the atom in the crystal lattice and coulomb repulsion and exchange correlation effects. According to the proposed model, it assumes the form of the atomic - distance - dependent function  $Z_k^{\text{eff}}(R_{ij})$ :

$$Z_k^{\text{eff}} = (2I_k)^{1/2}[1 + \exp(-A_k R_{ij})]; \quad i, j = 0, 1, 2, \dots, \quad i \neq j \quad (4)$$

where  $I_k$  is the  $k$ -th ionization energy expressed in atomic units.

The adjustment parameter  $A_k$  is much higher when describing any of the core electrons than in the case of valence electrons:

$$A_{1 \leq k \leq N_{\text{valence}}} \ll A_{N_{\text{valence}} < k \leq N_{\text{core}}}$$

This means that the influence of the crystal lattice on the charge density distribution in the atomic core is very weak.

The total electronic energy in the muffin-tin cell is a functional of the electron density  $\rho_{\text{mt}}$ :

$$E = E[\rho_{\text{mt}}(\vec{r})] = \int_{\substack{\text{MT cell} \\ \text{volume}}} d\tau \varepsilon(\rho_{\text{mt}}; \vec{r}). \quad (5)$$

The function  $\varepsilon(\rho_{\text{mt}}; \vec{r})$  in the above expression represents energy density and is a sum of one-electron contributions referred to the central atom:

$$\varepsilon(\rho_{\text{mt}}; \vec{r}) = \sum_{1/N_{\text{at}}^0} \varepsilon(\rho_{\text{at},k}; \vec{r}) \quad (6)$$

The component  $\sum \varepsilon(\rho_{\text{at},k}^0; \vec{r})$ , which represents the energy of the set of noninteracting electrons subjected to the potential field of the screened nucleus, is a sum of kinetic and potential energy:

$$\varepsilon(\rho_{\text{at},k}^0; \vec{r}) = -\frac{1}{2} \rho_{\text{at},k}(\vec{r})^{1/2} \nabla^2 \rho_{\text{at},k}(\vec{r})^2 + V_k^{\text{ext}}(\vec{r}) \cdot \rho_{\text{at},k}(\vec{r}) \quad (7)$$

The relation between the parameter of the potential and the effective charge in the density is of an analogous character to the relation between the charge in hydrogen-like function and in the respective potential.

In our considerations, an isolated atom is treated as a single muffin-tin cell covering the whole space ( $R_{\text{mt}} \rightarrow \infty$ ). The electronic energy of the free atom, calculated according to Eq. (5), consists of only one-electron terms (see Eq. (7), and is simply a sum of ionization energies<sup>9,11</sup>

$$E_{\text{at}} = - \sum_{1/N_{\text{at}}} I_k, \quad (8)$$

so it is equal to the »experimental« energy of an isolated atom.

## RESULTS

The proposed method has been used for the binding energy calculation for lithium crystal. In calculations, the spherical symmetry of the electron density distribution, due to the non directional character of metallic bond, has been assumed. The binding energy has been determined as a function of the distance between atomic cores in the metal and calculated for the temperature of 0 K and with regard to the bottom of a potential well. The results of calculations are presented in Table I, together with the respective literature data (experimental and theoretical). Furthermore, Figure 1 shows the shape of the dependence between the distance of the atoms in the crystal lattice and the energy determined according to the proposed model.

The following symbols are used for figures:

$E_M$  – minimal binding energy,

$R_M$  – equilibrium atom cell radius,

$Z_{\text{eff}M}$  – effective charge for minimal binding energy,

$N$  – population calculated for equilibrium cell radius.

TABLE I

*Effective charge, atomic cell radius and binding energy calculated for lithium according to the one- and two-parameter models, in comparison with the respective literature data.*

metallic crystal	Number of parameters	Effective charge $Z_{\text{eff}M}/\text{a.u.}$	Cell radius $R_M/\text{a.u.}$		Binding energy $E_M/\text{a.u.}$	
			This work	Experimental <sup>a)</sup>	This work	Experimental <sup>b)</sup>
Li	1: $A = 0.311$	0.785	4.50	2.855	-0.058	-0.058
	2: $A = 0.125$ $B = 1.73$	0.922	2.85	2.855	-0.058	-0.058

a) C. Kittel, *Introduction to Solid State Physics*, John Wiley and Sons, New York, 1966.

b) G. E. R. Schulze, *Metallphysik*, Akademie-Verlag, Berlin, 1974.

## DISCUSSION

The main idea of the proposed method is the existence of a local, crystal positive field, dependent on the interatomic distance. The field is approximated by the effective charge of atomic core, expressed as a function of the cell radius  $Z_{\text{eff}}(R)$ . The field, according to the main H-K theory assumptions must lead to an increase in electronic density and to the dependence of total energy on the distance between atoms. The crucial problem of the calculations concerns the shape of the function  $Z_{\text{eff}}(R)$ . The one-parametric exponential function Eq. (4) does not allow fitting the binding energy at the proper value of interatomic distance. Therefore, we have tried to apply the two parametric function:



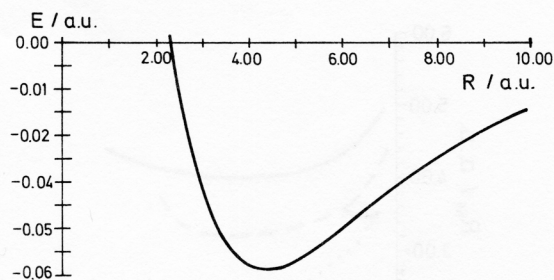


Figure 1. The binding energy fitted to the experimental value for the one-parameter model in the function of the atomic cell radius for lithium crystal.  $A = 0.311$ ,  $R_M = 4.5$ ,  $E_M = -0.058$ ,  $Z_{\text{eff}} = 0.785$ ,  $N = 0.833$ .

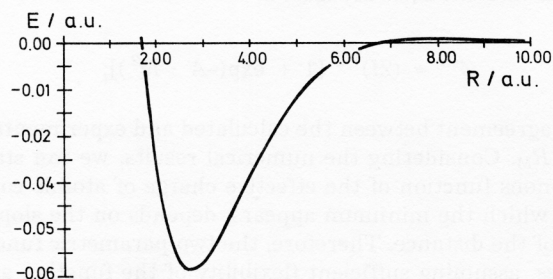


Figure 2. The binding energy as in Figure 1, but for the two-parameter model.  $A = 0.125$ ,  $B = 1.73$ ,  $R_M = 2.85$ ,  $E_M = -0.058$ ,  $Z_{\text{eff}} = 0.922$ ,  $N = 0.606$ .

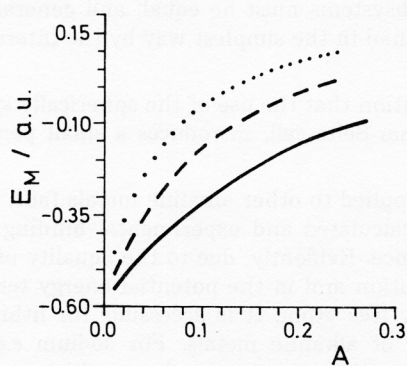


Figure 3. Relation of the minimal binding energy  $E_M$  to parameter  $A$  of the model, calculated for three different values of  $B$  parameter: solid line –  $B = 1$ , dashed line –  $B = 1.5$ , dotted line –  $B = 2$ .

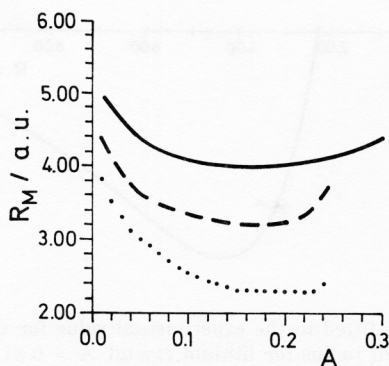


Figure 4. Relation of the atomic cell equilibrium radius  $R_M$  to the parameter  $A$  of the model, calculated for different values of  $B$ , as in Figure 2.

$$Z^{\text{eff}} = (2I)^{1/2} [1 + \exp(-A \cdot R^B)];$$

which gives a good agreement between the calculated and experimental values for both quantities,  $E_M$  and  $R_M$ . Considering the numerical results, we can state that the total energy is a monotonous function of the effective charge of atomic core, but the interatomic distance, at which the minimum appears, depends on the slope of the effective charge in function of the distance. Therefore, the two-parametric function is necessary to adopt both values, assuming sufficient flexibility of the function and its proper behavior at infinity. In this case, the first parameter ( $A$ ) governs mainly the values of the effective charge, the second ( $B$ ) determines the slope of the effective charge near the minimum. The crystal field which depends on the effective charge of atomic core follows our idea of the chemical potential of atomic core.<sup>12</sup> If the atomic cores and valence band electrons in metals are treated as two subsystems in equilibrium, the chemical potentials of subsystems must be equal, and generally must depend on the positive field of cores defined in the simplest way by the interatomic distance dependent effective charge.

It is necessary to mention that the use of the spherically symmetric cell, as an approximation for the Wigner-Seitz cell, introduces a small percent error into the calculation of energy.

The same approach applied to other alkaline metals fails. It is possible to achieve agreement between the calculated and experimental binding energies, but with too large an interaction distance. Evidently, due to the equality of the effective charge in electronic density distribution and in the potential energy term, we treat the atomic cell in crystal as a nearly free atom. It is accessible for lithium but was a poor approximation for the rest of alkaline metals. For sodium *e.g.*, the fit of energy is achieved for the interatomic distance at under 7 a.u., which is approximately two times bigger than the experimental value. We expect that the subsequently introduced quantum defect approach<sup>9</sup> will improve the results.

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## SAŽETAK

**Primjena celularnog DFT postupka na alkalijske metale: litij**

*Andrzej Koleżyński, Jerzy Mrugalski, Wiesław S. Ptak  
i Katarzyna Tkacz-Smiech*

Predložen je postupak za proračun svojstava alkalijskih metala u kojemu se kombinira Kohn-Shamova shema s metodom energija vezanja. Glavna ideja postupka sastoji se u uvodenju kristalnog polja ovisnoga o međuatomske udaljenostima. Postignuti rezultati pokazuju dobro slaganje između izračunanih i eksperimentalnih energija vezanja, ali i relativno velike pogreške u proračunu ravnotežnih međuatomske udaljenosti.