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Orbital-free Modelling Method for Materials Contained Atoms with D-Electrons

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ABSTRACT

On the example of the Tin and Cun clusters with n up to 4 it is shown that an orbital-free (OF) version of the density functional theory (DFT) may be used for multiatomic systems containing atoms with d-electrons. The equilibrium interatomic distances and binding energies are found close to known experimental and calculated data. The OF results for Ti-Cu dimer are in satisfactory agreement with the Kohn-Sham results.

Keywords : Orbital-free, Density Functional, d-atoms, Titanium, Cooper

I. INTRODUCTION

The orbital-free (OF) approach is a version of the density functional theory (DFT) [1, 2]. It is a consecutive development of the idea of Hohenberg-Kohn [1] that the basic state of a quantum system can be completely described by means of electronic density. This approach, in contrary to the Kohn-Sham (KS) method, does not use the wave functions (orbitals) and operates with the only electron density. Advantage of this approach is obvious: operating only with an electronic density instead of numerous wave functions, it allows to increase sharply the speed of calculations and to include in consideration huge number of atoms (according to authors of work [3] to one million)

A number of works (for instance [3-8]) devoted to development of the OF version of the DFT were appeared last years. All of them are based on the idea that there exist some universal functional of kinetic energy, therefore authors made attempts to find this functional and to use it for the OF calculations. However, it was recently shown [9, 10], the Hohenberg-Kohn idea about existence of the universal density functional leading to the energy minimum was not strictly proved, and it is possible to say only about approximate solutions of the problem.

Thus, there are no bases to believe that there are some common functions for kinetic functional and energy, which could be used for atoms of any type and any quantity. In our previous papers [11-15] we described an orbital-free approach for modeling of nanosystems contained atoms with s and p electrons. The key point of the approach was calculation of the kinetic energy using some fitting functions special for each type of atoms. The s-p OF approach was tested on clusters contained C, Al, Si, and O atoms and demonstrated good agreement with Kohn-Sham DFT (KS-DFT) method and experimental data. Now we describe an expansion of our method for materials contained atoms with d-electrons. As we know, till now there are no works in which development of the OF method for atoms with d-electrons is shown.

II. A GENERAL DESCRIPTION OF THE OF APPROACH

Following the common idea of our approach let us remind that DFT claims that the energy Eel of the ground state of any quantum system can be found by minimization of the some functional depending only on the electronic density of this system ρ:

$$E_{el}[\rho]=\int \varepsilon(\rho)d\boldsymbol{r}=\int V(\boldsymbol{r})\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}+ \\ +\frac{1}{2}\int \varphi(\rho)\rho(\boldsymbol{r})d\boldsymbol{r}+\int \varepsilon^{ex-c}(\rho)d\boldsymbol{r}+\int \varepsilon^{kin}(\rho)d\boldsymbol{r} \qquad (1)$$

where $V(\boldsymbol{r})$ is an external potential, $\varphi(\boldsymbol{r})=\int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}'$ is the electrostatic electron Hartree potential, ε_{ex-c} and ε_{kin} are exchange-correlation and kinetic energies (per electron).

Minimization of (1) means solving the following equation:

$$F[\rho]\equiv\frac{\delta E_{el}[\rho]}{\delta\rho}=V(\boldsymbol{r})+\varphi(\boldsymbol{r})+\mu_{kin}(\rho)+\mu_{ex-c}(\rho)=0\,, \qquad (2)$$

with a condition $\int \rho(r)d^3r = N$, where

$\mu_{kin}(\rho)=\dfrac{\delta E_{kin}[\rho]}{\delta\rho}$ and $\mu_{ex-c}(\rho)=\dfrac{\delta E_{ex-c}[\rho]}{\delta\rho}$ are so called kinetic and exchange-correlation potentials.

There are some realistic approximations for the exchange-correlation potential $\mu_{ex-c}(\rho)$ (for example [16-18]); the potential of the electron-electron repulsion $\varphi(r)$ may be calculated using Fourier transformations or Poisson equations; the external potential $V_{ext}(r)$ usually consists of atomic potentials or of pseudopotentials. The only real problem is the kinetic potential $\square_{kin}$.

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III. DESCRIPTION OF THE S-P-D CASE

The OF approach may be developed for the full-electron potentials (we are working now intensively in this direction), however we will used now a more simple pseudopotential (PP) approximation. It is appropriate to mention that all works known to us in the field of the OF approach are performed within PP approximation.

Because pseudopotentials are constructed separately for s, p, and d states, we have to divide the total density ρ for partial densities ρ_s, ρ_p, ρ_d , and to write three expressions for functionals $F_s[\rho_s,\rho]$, $F_p[\rho_p,\rho]$, and $F_d[\rho_d,\rho]$ for equilibrium conditions:

$$F_s[\rho_s,\rho]\equiv\frac{\partial E}{\partial\rho_s}=-V_s(r)+\varphi(r)+\mu^s_{kin}(\rho_s)+\mu_{ex-c}(\rho)=0\,, \qquad (3)$$

$$F_p[\rho_p,\rho]\equiv\frac{\partial E}{\partial\rho_p}=-V_p(r)+\varphi(r)+\mu^p_{kin}(\rho_p)+\mu_{ex-c}(\rho)=0\,, \qquad (4)$$

$$F_d[\rho_d,\rho]\equiv\frac{\partial E}{\partial\rho_d}=-V_d(r)+\varphi(r)+\mu^d_{kin}(\rho_d)+\mu_{ex-c}(\rho)=0\,, \qquad (5)$$

where $V_s(\boldsymbol{r})$, $V_p(\boldsymbol{r})$ and $V_d(\boldsymbol{r})$ are sums of *s, p,* and *d* components of atomic pseudopotentials.

The electrostatic potential $\varphi(r)$ and the exchange-correlation potential $\mu_{ex-c}(\rho)$ are calculated through the total density ρ while partial kinetic potentials $\mu^s_{kin}(\rho_s)=\dfrac{\partial E^s_{kin}}{\partial\rho_s}$, $\mu^p_{kin}(\rho_p)=\dfrac{\partial E^p_{kin}}{\partial\rho_p}$ and $\mu^d_{kin}(\rho_d)=\dfrac{\partial E^d_{kin}}{\partial\rho_d}$ depend on corresponding partial densities ρ_s, ρ_p, and ρ_d.

In our previous works [11-15] we used the following way to simulate s-p multiatomic systems: we fitted kinetic potentials for homoatomic dimers leading to their appropriate equilibrium energies and interatomic distances and then used these potentials for larger systems. Now, in the present work, we use the same way for d-systems.

To demonstrate a possibility of our OF approach to model systems with d electrons we considered clusters contained Ti and Cu atoms. Titanium is a typical element with the incomplete d-shell, while cooper is an element with filled d-shell. Thus their comparing consideration have to be very convincing and useful for developing of the OF modeling.

It is known that d-electrons are rather close to s-electrons energetically and are mixed with them in solids and molecules. The Ti atomic valence configuration is 3d24s2. In another word, the s-shell is filled completely but the d-shell is filled only partially, thus electrons can transfer from the s-states to the d-shell. Copper with its valence configuration of 3d104s1 represents an opposite case. Namely, Cu electrons can move from d-states to s-states. In the both types of atoms p-electrons are absent.

We started our investigation from modeling of Ti2 and Cu2 dimers. We used pseudopotentials and atomic densities generated by the FHI98PP package [19] as start points for the OF calculations. Studied dimers and clusters were placed in a cubic cell with a side of 30 a.u. (1 a.u. = 0.529 Å); the cell was divided to 250x250x250 subcells for the Fast Fourier calculations of potentials.

It was found, in contrast with the s-p case, that kinetic functionals for d systems cannot be presented as simple functions of densities. To describe the interatomic interactions correctly we are obliged to use more complicated expressions which are connected to the s-d transfer. We observed that the level of this transfer near some atom is correlated with some value SVor which reflects the influence of the nearest neighbours:

$$S_{Vor} = \int_{Vor} [V_s(\boldsymbol{r}) + \varphi(\boldsymbol{r})]\rho_s(\boldsymbol{r})d\boldsymbol{r} \quad . \qquad (6)$$

Integral in equation (40) is taken over the Voronoy cell (Vor) [20] that represents a generalization of the Wigner-Seitz cell used in the crystal lattice theory.

We have found for Ti the following kinetic functions:

$$\mu^{kin}_{\mathrm{Ti}-s}(\rho_s) = K_{\mathrm{Ti}}(\rho_s^{1/4} + 4.0\rho_s); \qquad (7)$$

$$\mu^{kin}_{\mathrm{Ti}-d}(\rho_d) = 1.1\rho_d^{1/5} + 12\rho_d \exp(-1.2\rho_{\mathrm{d}})(1.0 - 0.6\rho_d);(8)$$

$$K_{\mathrm{Ti}} = 0.62\exp\left[-70\cdot\left(\frac{S_{\mathrm{Vor}} - S_{\mathrm{Vor-single}}}{S_{\mathrm{Vor-single}}}\right)^2\right] + \\ + 0.80\left[1 - \exp\left(-70\cdot\left(\frac{S_{\mathrm{Vor}} - S_{\mathrm{Vor-single}}}{S_{\mathrm{Vor-single}}}\right)^2\right)\right], \qquad (9)$$

where $S_{\mathrm{Vor\text{-}single}}$ is the value of S_{Vor} for a single atom. We have found that the d-density in the Ti dimer increases due to interatomic interactions while the s-density decreases. This density transfer corresponds to bonding of atoms. The binding energy for the Ti dimer is presented in Table 1. The above described functions $\mu^{kin}_{Ti-s}(\rho_s)$ and $\mu^{kin}_{\mathrm{Ti}-d}(\rho_d)$ were applied for modeling of Ti_3 and Ti_4 clusters. Results are also presented in Table 1.

TABLE 1. Equilibrium bond lengths *d*, binding energies E_b, and deviations of number of s-electrons □□$_s$ (per atom) for Ti_n clusters in comparison with reported values: experimental (Exp) and KS-calculations (KS).

	n=		**2**	**3**	**4**
Our results	E_b, eV		0.6	2.1	2.7
	d, Å		2.0	2.2	2.4
Exp	E_b, eV	[20]	0.615		
	d, Å	[20]	1.97		
KS	E_b, eV	[21]	1.929	2.229	2.643
		[22]	2.34	2.93	3.23
		[23]	1.9165	2.3726	2.9463

	d, Å	[21]	1.969	2.418	2.418
		[22]	1.93	2.28	2.51
		[23]	2.9463	2.35	2.52

For Ti_3 the equidistant rectangle was found more favorable than the line chain in accordance with data of other authors. This result for the OF calculation is expected because of a spherical shape of OF atoms. ForTi_4 cluster the T_d-symmetry pyramid was found more preferable than a rhombus one in accordance with [21, 22]. This is also naturally for spherical atoms. However there is another opinion. Authors of [23] claim that the most stable structure for Ti_4 can be considered as an atom capped on an equilateral triangle with the C_{3v} symmetry.

In the work devoted to atoms with covalent s-p bonds (C and Si) [13] we described the angular dependence of their bonds by some forces, which we named as the "Pauli forces". But we do not know yet how to describe the anisotropy of bonding in d systems. We leave this problem for the future, and now we can calm ourselves by the fact that our method is intended for big systems, but in the big metal systems the closed packing of atoms dominates. We have paid our special attention on the electron transfer between s and d parts of the total density. Taking into account that □N_s = -□N_d we presented in Table 1 values of □N_s for studied Ti_n clusters. One can see that □N_s is negative: n_s decreases with increasing of the size of the cluster.

For Cu we also have found kinetic functionals for Cu_2 dimers. They are presented below:

$$\mu^{kin}_{\text{Cu}-s}(\rho_s) = K_{\text{Cu}}\rho_s^{1/3.1}; \qquad (10)$$

$$\mu^{kin}_{\text{Cu}-d}(\rho_d) = 0.475\rho_d^{1/5}; \qquad (11)$$

$$K_{\text{Cu}} = 1.92\exp\left[-80\cdot\left(\frac{S_{\text{Vor}} - S_{\text{Vor-single}}}{S_{\text{Vor-single}}}\right)^2\right] + \\ +1.4\left[1-\exp\left(-80\cdot\left(\frac{S_{\text{Vor}} - S_{\text{Vor-single}}}{S_{\text{Vor-single}}}\right)^2\right)\right], \qquad (12)$$

The calculated equilibrium bond lengths and binding energies for Cu_2, Cu_3 and Cu_4 clusters are listed in Table 2.

TABLE 2. Equilibrium bond lengths *d*, binding energies E_b, and deviations of number of s-electrons □□$_s$ (per atom) for Cu*n* clusters in comparison with reported values: experimental (Exp) and KS-calculations (KS).

		n=	2	3	4
Our results	E_b, eV		1.0	1.2	1.4
	d, Å		2.2	2.3	2.4
Exp	E_b, eV	[24]	1.02	1.07	1.48
	d, Å	[25]	1.02		
KS	E_b, eV	[26]	1.27	1.40	1.81
		[27]	0.9-1.4	1.0-1.6	1.3-2.0
	d, Å	[26]	1.969	2.418	2.488
		[27]	2.2-2.3	2.3-2.5	2.3-2.5

Naturally, like in the Ti case, we obtained that the compact atomic structures for Cu_3 and Cu_4 are more favorable than non-compact ones. However results of KS calculations [26, 27] claim that the C_{2v} and D_{2h} symmetries are more preferable for them. It once again shows that the OF approach has large difficulties in description of angular dependencies of interatomic interactions in systems with d-electrons and needs in some more complicate development in future. It is appropriate to note that simulation of Cu_n clusters using empirical potentials [28] also leads to the compact structures, however, in contrast with our OF approach it gives very underestimated binding energies (0.29 eV for Cu_2, 0.58 eV for Cu_3, 0.87 eV for Cu_4).

Changes of the s-density (□N_s) in the Cu clusters are positive, the s-density increases with increase of the number of atoms.

To testify our approach for possibility to describe systems with different types of d-atoms we have studied a Ti-Cu dimer. We used the same technique for presentation of the kinetic functional of the heteroatomic system as it was described in our precious works [14]. This way is based on the superposition of functionals of the nearest atoms with some weights depending on geometric parameters of their densities. Results are shown in Table 3.

TABLE 3. Equilibrium bond lengths d_i, binding energies E_b, and deviations of number of s-electrons □□$_s$ (per atom) for Ti-Cu dimer in comparison with reported values.

	E_b, eV	d_i, Å	□N_s(on Ti)	□N_s(on Cu)
Our results	1.7	2.3	-0.05	0.07
KS [29]	1.8	2.45		

We see from Table 3 that our results are in satisfactory agreement with known dara. That means that our OF approach may be used not only for simple d-systems but for complex systems contained d-atoms of different types. Electron s-d transfer in this case is rather small.

IV. CONCLUSION

In summary, we conclude that our version of the orbital-free approach can be applied to *d*-materials rather successfully. On example of Ti_n and Cu_n systems the binding energy and interatomic distances were calculated in good accordance with known Kohn-Sham data and experimental results. Investigation of the Ti-Cu dimer also leads to satisfactory results. We suppose that this OF approach can be used for large systems contained transitional and noble atoms and promises be very useful for purposes of nanotechnology.

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