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New Orbital Free Simulation Method Based on the Density Functional Theory

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Abstract: A practical way to simulate multi-atomic systems without using of wave functions (orbitals) is proposed. Kinetic functionals for each type of atoms are constructed and then are used for complex systems. On examples of clusters containing Al, Si, C, and O it is shown that this method can describe structures and energies of multi-atomic systems not worse than the Kohn-Sham method but faster. Besides, it is demonstrated that the orbital-free version of the density functional theory may be used for finding equilibrium configurations of multi-atomic systems with covalent bonding. The equilibrium interatomic distances, interbonding angles and binding energies for Si_3 and C_3 clusters are found in good accordance with known data.

Keywords: Orbital-free, Density Functional, Hetero-Atomic Systems, Interatomic Distances, Interbonding Angles

1. Introduction

The orbital-free (OF) approach is an alternative to the Kohn-Sham (KS) [1] method to simulate multi-atomic systems in the framework of the density functional theory (DFT) [2]. The OF approach operates with the electron density only (without wave functions) and being developed enough can be applied for simulation of very large systems: up to millions atoms [3]. Several groups [3-11] are working in this area with different success, and the calculation of the kinetic energy is noted as a main problem. In the previous papers [12, 13] it was suggested that there is no universal way to describe the kinetic energy of different atoms and compounds. In the present work it is described how it is possible to extend this approach to systems with more large systems.

2. A General Description of the of Approach

As it is known the DFT claims that the energy E 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 $\rho(\mathbf{r})$:

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

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

Minimization of (1) means solution the following equation:

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

with the condition $\int \rho(\mathbf{r})d\mathbf{r} = N$ where N is the number of electrons in the system, and $\mu_{kin}(\rho) = \frac{\delta\varepsilon_{kin}(\rho)}{\delta\rho}$,

$$\mu_{ex-c}(\rho) = \frac{\delta\varepsilon_{ex-c}(\rho)}{\delta\rho} \ .$$

There are some realistic approximations for exchange-correlation potential $\mu_{ex-c}(\rho)$ there; the potential Hartree $\phi(r)$ may be calculated using Fourier transformations or Poisson equations; the external potential $V(r)$ usually consists of atomic potentials. The only real problem is the kinetic potential μ_{kin}.

Pseudopotential Approach for Dimers

In practice, the DFT calculations are simpler if one uses pseudopotentials instead of full electron potentials. Therefore let us rewrite the above equations in the pseudopotential approach, and, for simplicity, let us limit yourself by two-atomic systems and s- and p-components of pseudopotentials.

We present the total density ρ_{12} as a sum of partial densities: $\rho_{12} = \rho_{12-s} + \rho_{12-p}$.

The electron energy of this system $E_{12} = \int \varepsilon_{12}(\rho_{12-s}, \rho_{12-p}) dr$ must be minimal with the condition $\int (\rho_{12-s} + \rho_{12-p}) dr = N_{12}$, where ε_{12} is the electron energy per electron for the two-atomic system with the total number of electrons N_{12}. In the other words we have to find the density ρ_{12} that satisfies the system of two equations:

$$\frac{\delta\varepsilon_{12}}{\delta\rho_{12-s}} = 0 \tag{3}$$

$$\frac{\delta\varepsilon_{12}}{\delta\rho_{12-p}} = 0 \tag{4}$$

Thus we may write:

$$V_{1-s}(r) + V_{2-s}(r) + \varphi_{12}(r) + \mu_{12-s}^{kin}(\rho_s) + \mu_{12}^{ex-c}(\rho_{12}) = 0 \tag{5}$$

$$V_{1-p}(r) + V_{2-p}(r) + \varphi_{12}(r) + \mu_{12-p}^{kin}(\rho_p) + \mu_{12}^{ex-c}(\rho_{12}) = 0 \tag{6}$$

where где $V_{1-s}(r)$, $V_{2-s}(r)$, $V_{1-p}(r)$, and $V_{2-p}(r)$ are s and p components of pseudopotentials of the first and second atoms, $\varphi_{12}(r)$ and $\mu_{12}^{ex-c}(\rho_{12})$ are the electrostatic and exchange-correlation potentials calculated for the total electron density ρ_{12} of a dimer, $\mu_{12-s}^{kin}(\rho_{12-s})$ and $\mu_{12-p}^{kin}(\rho_{12-p})$ are partial kinetic potentials depending on corresponding partial densities ρ_{12-s} and ρ_{12-p}.

It is useful to present $\mu_{12-s}^{kin}(\rho_{12-s})$ and $\mu_{12-p}^{kin}(\rho_{12-p})$ in the form of $\mu_{12-s}^{kin}(\rho_{12-s}) = \mu_{12} + \Delta\mu_{12-s}^{kin}(\rho_{12-s})$ and $\mu_{12-p}^{kin}(\rho_{12-p}) = \mu_{12} + \Delta\mu_{12-p}^{kin}(\rho_{12-p})$ and rewrite Eqs. (4-s), (4-p) for a two-atomic system as it follows below:

$$V_{1-s}(r) + V_{2-s}(r) + \phi_{12}(r) + \mu_{12}^{ex-c}(\rho_{12}) + \Delta\mu_{12-s}^{kin}(\rho_{12-s}) \tag{7}$$

$$V_{1-p}(r) + V_{2-p}(r) + \phi_{12}(r) + \mu_{12}^{ex-c}(\rho_{12}) + \Delta\mu_{12-p}^{kin}(\rho_{12-p}) \tag{8}$$

The electron energy $\varepsilon_{12}(\rho_{12})$ contains terms of electrostatic energy $\varepsilon_{estat} = V_{1-s}(r)\rho_{12-s} + V_{2-s}(r)\rho_{12-s} + V_{1-p}(r)\rho_{12-p} + V_{2-p}(r)\rho_{12-p} + \frac{1}{2}\phi_{12}(r)\rho_{12}\sqrt{b^2-4ac}$, exchange-correlation $\varepsilon_{12}^{ex-c}(\rho_{12})$ and kinetic energies $\varepsilon_{12}^{kin}(\rho_{12}) = \varepsilon_{12-s}^{kin}(\rho_{12-s}) + \varepsilon_{12-p}^{kin}(\rho_{12-p})$.

Namely:

$$\varepsilon_{12}(\rho_{12}) = \varepsilon_{estat} + \varepsilon_{12}^{ex-c}(\rho_{12}) + \varepsilon_{12-s}^{kin}(\rho_{12-s}) + \varepsilon_{12-p}^{kin}(\rho_{12-p}) \tag{9}$$

Obviously, for two isolated atoms it possible to write equations similar to (7) and (8):

$$V_{1-s}(r) + \varphi_1^a(r) + \mu_1^{ex-c}(\rho_1^a) + \mu_{1-s}^{kin}(\rho_{1-s}^a) = 0 \tag{10}$$

$$V_{1-p}(r) + \varphi_1^a(r) + \mu_1^{ex-c}(\rho_1^a) + \mu_{1-p}^{kin}(\rho_{1-p}^a) = 0 \tag{11}$$

$$V_{2-s}(r) + \varphi_2^a(r) + \mu_2^{ex-c}(\rho_2^a) + \mu_{2-s}^{kin}(\rho_{2-s}^a) = 0 \tag{12}$$

$$V_{2-p}(r) + \varphi_2^a(r) + \mu_2^{ex-c}(\rho_2^a) + \mu_{2-p}^{kin}(\rho_{2-p}^a) = 0 \tag{13}$$

From which it is followed:

$$V_{1-s}(r) = -\varphi_1^a(r) - \mu_1^{ex-c}(\rho_1^a) - \mu_{1-s}^{kin}(\rho_{1-s}^a) \tag{14}$$

$$V_{1-p}(r) = -\varphi_1^a(r) - \mu_1^{ex-c}(\rho_1^a) - \mu_{1-p}^{kin}(\rho_{1-p}^a) \tag{15}$$

$$V_{2-s}(r) = -\varphi_2^a(r) - \mu_2^{ex-c}(\rho_2^a) - \mu_{2-s}^{kin}(\rho_{2-s}^a) \tag{16}$$

$$V_{2-p}(r) = -\varphi_2^a(r) - \mu_2^{ex-c}(\rho_2^a) - \mu_{2-p}^{kin}(\rho_{2-p}^a) \tag{17}$$

Let us introduce notations:

$$\Delta\mu_{12-s}^{kin}(\rho_{12-s}) = \mu_{12-s}^{kin}(\rho_{12-s}) - \mu_{1-s}^{kin}(\rho_{1-s}^a) - \mu_{2-s}^{kin}(\rho_{2-s}^a) \tag{18}$$

$$\Delta\mu_{12-p}^{kin}(\rho_{12-p}) = \mu_{12-p}^{kin}(\rho_{12-p}) - \mu_{1-p}^{kin}(\rho_{1-p}^a) - \mu_{2-p}^{kin}(\rho_{2-p}^a) \tag{19}$$

$$\Delta\mu_{12}^{ex-c}(\rho_{12}) = \mu_{12}^{ex-c}(\rho_{12}) - \mu_1^{ex-c}(\rho_1^a) - \mu_2^{ex-c}(\rho_2^a) \tag{20}$$

$$\Delta\varphi_{12}(\rho_{12}) = \varphi_{12}(\rho_{12}) - \varphi_1(\rho_1^a) - \varphi_2(\rho_2^a) \qquad (21)$$

Now equations (5-s) and (5-p) can be transformed to simple forms:

$$\Delta\varphi_{12}(\mathbf{r}) + \Delta\mu_{12}^{ex-c}(\rho_{12}) + \Delta\mu_{12\text{-s}}^{kin}(\rho_{12-s}) = 0 \quad (22)$$

$$\Delta\varphi_{12}(\mathbf{r}) + \Delta\mu_{12}^{ex-c}(\rho_{12}) + \Delta\mu_{12\text{-p}}^{kin}(\rho_{12-p}) = 0 \quad (23)$$

It is possible to solve these equations using some probe functions for $\Delta\mu_{12\text{-s}}^{kin}(\rho_{12-s})$, $\Delta\mu_{12\text{-p}}^{kin}(\rho_{12-p})$, $\Delta\mu_{1\text{-s}}^{kin}(\rho_{1-s}^a)$, $\Delta\mu_{1\text{p}}^{kin}(\rho_{1-p}^a)$, $\Delta\mu_{2\text{-s}}^{kin}(\rho_{2-s}^a)$, $\Delta\mu_{2\text{-p}}^{kin}(\rho_{2-p}^a)$ and then to calculate the total energy with $\mu_{12\text{-s}}^{kin} = \mu_{12} + \Delta\mu_{12\text{-s}}^{kin}$ and $\mu_{12-p}^{kin} = \mu_{12} + \Delta\mu_{12-p}^{kin}$. The probe functions must lead to the equilibrium interatomic distances and binding energy for dimers.

The binding energy for a dimer (per one atom) would be calculated as follows:

$$E_b = \frac{1}{2}\left(E_{\dim} - 2E_a\right),$$ where E_a is the atomic energy,

$$E_{\dim} = \int \varepsilon_{12}[\rho_{12}(\mathbf{r})]d\mathbf{r} + \frac{Z_1 Z_2}{|\mathbf{R}_1 - \mathbf{R}_2|}.$$

Dimers with identical atoms

Al, Si, and C were taken as test elements. The FHI98pp [14] package was used as a generator of pseudo-potentials and equilibrium partial electron densities. Exchange and correlation potentials were calculated in the local density approach [15, 16]. Studied atoms were located in a cubic cell *of the* L size ($L=30$ a.u.; 1 a.u. = 0.529 Å). The cell was divided on $150 \times 150 \times 150$ elementary sub-cells for the integration with the step ΔL of 0.406 a.u. Results of calculations were compared with published data.

The same types of kinetic functions $\Delta\mu_s^{kin}$ and $\Delta\mu_p^{kin}$ for isolated atoms and dimers and trimers were used, however they were found different for different types of atoms.

Obviously functions $\Delta\mu_{12\text{-s}}^{kin}(\rho_{12-s})$ must go to zero when the interatomic distance increases. Let our dimmer consists from atoms of an A type. Let us find $\Delta\mu_{12\text{-s}}^{kin}(\rho_{12-s})$ and $\Delta\mu_{12\text{-p}}^{kin}(\rho_{12-p})$ in the following form:

$$\Delta\mu_{A12\text{-s}}^{kin}(\rho_{12-s}) = v_{A\text{-s}}^{kin}(\rho_{12-s}) - v_{A\text{-s}}^{kin}(\rho_{1-s}^a) - v_{A\text{-s}}^{kin}(\rho_{2-s}^a) \quad (24)$$

$$\Delta\mu_{A12\text{-p}}^{kin}(\rho_{12-p}) = v_{A\text{-s}}^{kin}(\rho_{12-p}) - v_{A\text{-p}}^{kin}(\rho_{1-p}^a) - v_{A\text{-p}}^{kin}(\rho_{2-p}^a) \quad (25),$$

where $v_{A\text{-s}}^{kin}(\rho)$ and $v_{A\text{-p}}^{kin}(\rho)$ are unknown functions of density, which must make the dimer binding energy and the equilibrium distance close to results of Kohn-Sham calculations.

Namely, for Al they are:

$$v_s^{kin} = 1.2\rho_s^{1/4} - 0.3\rho_s, \; v_p^{kin} = 1.2\rho_p^{1/4} - 0.3\rho_p \,;$$

for Si:

$$v_s^{kin} = 1.4\rho_s^{1/4} + 4.4\rho_s, \; v_p^{kin} = 1.62\rho_p^{1/4} + 4.4\rho_p \,;$$

and for C:

$$v_s^{kin} = 1.9\rho_s^{1/4} + 0.6\rho_s, \; v_p^{kin} = 2.0\rho_p^{1/4} + 0.6\rho_p \,.$$

Calculated values of interatomic distances and binding energies for the Al$_2$, Si$_2$, and C$_2$ dimers are collected in Table 1 in comparison with known published data. It is clear that agreement is rather good.

Table 1. *Equilibrium distances d and binding energies E_b (absolute values, per atom) for Si$_2$, Al$_2$ and C$_2$ in comparison with known calculated data.*

Dimer	Source of data	d, Å	E_b, eV
Si$_2$	OF method	2.22	2.6
	Other calculations	2.23 [18]	1.97 [18]
		2.21 [19]	1.599 [19]
	KS	2.23	2,4
	Experiment	2.24 [32]	1.6 [32]
Al$_2$	OF method	2.35	1.1
	Other calculations	2.46 [20]	1.0 [21]
		2.95 [22]	1.23 [22]
	KS	2.51	0.92
	Experiment	2.56 [31]	0.78 [31]
C$_2$	OF method	1.32	5.0
	Other calculations	1.247-1.367 [23]	4.7 [23]
		1.316 [24]	3.5 [24]
	KS	1.23	4.8
	Experiment	1.24 [33]	3.1 [33]

Notation: "KS" means the calculations used the FHI96md package [17] based on the Kohn-Sham method.

Dimers with different atoms

As different atoms have different functions for kinetic energy, some procedure to calculate the total kinetic functions $\Delta\mu_{12}^{kin}$ in the space of the atomic system has to be developed. Near each atom it has to be approximately equal to its atomic function, but it has to be equal to mixture of the specific atomic functions between atoms. It seems that the simple way to construct this total function $\Delta\mu_{12}^{kin}$ is to summarize the specific atomic functions with some weights:

$$\Delta\mu_{12\text{-s}}^{kin}(\mathbf{r}) = W_{s1}\Delta\mu_{1\text{-s}}^{kin}(\mathbf{r}) + W_{s2}\Delta\mu_{2\text{-s}}^{kin}(\mathbf{r}) \,; \qquad (26)$$

$$\Delta\mu_{12\text{-p}}^{kin}(\mathbf{r}) = W_{p1}\Delta\mu_{1\text{-p}}^{kin}(\mathbf{r}) + W_{p2}\Delta\mu_{2\text{-p}}^{kin}(\mathbf{r}) \,. \qquad (27)$$

The weights have to be determined through gauss functions those are fitted to atomic densities:

$$W_{s1} = \frac{A_{s1}\exp\left(-\frac{(\mathbf{r}-\mathbf{R}_1)^2}{B_{s1}}\right)}{A_{s1}\exp\left(-\frac{(\mathbf{r}-\mathbf{R}_1)^2}{B_{s1}}\right) + A_{s2}\exp\left(-\frac{(\mathbf{r}-\mathbf{R}_2)^2}{B_{s2}}\right)} \,; \quad (28)$$

$$W_{s2} = \frac{A_{s2} \exp\left(-\frac{(r - R_2)^2}{B_{s2}}\right)}{A_{s1} \exp\left(-\frac{(r - R_1)^2}{B_{s1}}\right) + A_{s2} \exp\left(-\frac{(r - R_2)^2}{B_{s2}}\right)} ; \quad (29)$$

$$W_{p1} = \frac{A_{p1} \exp\left(-\frac{(r - R_1)^2}{B_{p1}}\right)}{A_{p1} \exp\left(-\frac{(r - R_1)^2}{B_{p1}}\right) + A_{p2} \exp\left(-\frac{(r - R_2)^2}{B_{p2}}\right)} ; \quad (30)$$

$$W_{p2} = \frac{A_{p2} \exp\left(-\frac{(r - R_2)^2}{B_{p2}}\right)}{A_{p1} \exp\left(-\frac{(r - R_1)^2}{B_{p1}}\right) + A_{p2} \exp\left(-\frac{(r - R_2)^2}{B_{p2}}\right)} . \quad (31)$$

An example of fitting of densities is demonstrated, Figure 1 the fitting of atomic densities for silicon and oxygen. Value A and B for Si, Al, C and O are collected in Table 2.
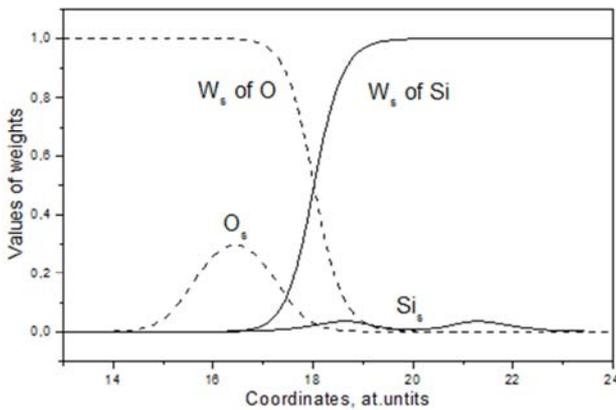
Figure 1. *The s-densities and the weights W_s for oxygen (dash) and silicon (solid) atoms.*

Table 2. *Value A and B for Si, Al, C and O.*

Specie	A_s	A_p	B_s	B_p
Si	0.065	0.040	3.5	4.5
Al	0.045	0.009	4.0	7.5
C	0.200	0.160	1.5	1.5
O	0.300	0.450	1.0	1.5

Calculations for the SiC, SiAl, AlC, SiO, CO, and AlO dimers were fulfilled with parameters shown in Table 2. The kinetic functions for oxygen ($v_s^{kin} = 0.5\rho_s^{1/4}$; $v_p^{kin} = 0.6\rho_p^{1/4}$) were constructed through simulation of the SiO dimer. Because of the high values of the electron density, the $200 \times 200 \times 200$ grid was used for the cell integration for dimers contained oxygen. Results of calculations are presented in Table 3.

Table 3. *Equilibrium distances d and energies of dissociation E_d (absolute values) for SiC, SiAl, AlC, SiO, CO, and AlO in comparison with other data.*

Dimer	Source of data	d, Å	E_d, eV
SiC	OF method	1.75	6.2
	KS	1.69	6.66
SiAl	OF method	2.35	3.3
	KS	2.30	3.10
AlC	OF method	1.93	4.0
	KS	1.83	4.32
SiO	OF method	1.55	15.4
	KS	1.48	13.2
CO	OF method	1.0	17.5
	KS	1.15	18.6
AlO	Our method	1.7	8.5
	KS	1.55	9.0

Notation: "KS" means the calculations used the FHI96md package [17 based on the Kohn-Sham method.

It is clear from Table 3 that our calculated values for Si-C, Si-Al, Al-C, Si-O, C-O and Al-O are very close to KS-DFT results.

Interbonding angles

To describe the angle depending of interatomic bonding it is useful to analyze the reasons of this depending in the standard quantum-mechanical approach, which uses wave functions and electronic states. As it is specified in the work [25] the angle peculiarities of the cluster Si3 are defined by the Yang-Teller effect caused by existence of the energy gap between occupied and empty states. In other words, the difference of structures of semiconductor and metal small clusters is connected with the difference of their bond wave functions: namely, covalent atoms have localized functions orientated between nearest atoms, while metallic atoms have dispersed functions without orientation in the space.

In the orbital-free case wave functions are absent, electronic states are absent too, and, therefore, one cannot speak about any energy gap. In the OF approach there is only the electronic density which defines all energy and structure of the polyatomic system. However the main quantum-mechanical rules remain fair and in this case. Besides the Schrödinger's (or Kohn-Sham) equations out of which wave functions and electron states are brought, there is the Paulie's principle specifying that in one quantum state there can be only two electrons (without taking into account a spin). In the OF case this principle may be paraphrased by the following way: a covalent bond is formed by two electrons, the common wave function of which is localized in the space between two nearest atoms. It is obvious that the quantity of the electrons which are responsible for this bond doesn't change as the distance between atoms changes (if, of course, the bond isn't broken at all and the electronic structure isn't reconstructed completely). In case of metals the conduction states are close each other and electrons can easily "flow" from one state to another during the changing of the atomic geometry.

Talking about covalent bonding in the language of the electronic density one obliges to base on the results of wave functions calculations. The main result of such calculations is that an atomic system with saturated covalent bonds (having

two electrons in each bond) has extremely clear energy gap between occupied and empty states.

Let us consider some multi-atomic system which density has local maximums ρ_{ij} between the nearest neighbors i,j. Let a part of these maximums overcome the value of ρ^0 in some etalon system (for example, in dimer or trimer). Then the excess of energy appears: $\Delta E = \frac{1}{2}C\sum_{i\neq j}(\rho_{i,j}/\rho^0 - 1)^2$, where C is an unknown coefficient.

The density between the nearest atoms may be changed by two ways: 1) changing the interatomic distance; 2) changing the interbonding angle. The first way is caused by quantum forces calculated from interatomic interactions described above. The second way may be characterized by some additional, so called Paulie forces.

The electronic density of the trimer ρ_{trim} may be found as follows:

$$\rho_{trim}(\mathbf{r}) = \rho_{at}(\mathbf{r}-\mathbf{R}_A) + \rho_{at}(\mathbf{r}-\mathbf{R}_B) + \rho_{at}(\mathbf{r}-\mathbf{R}_C), \quad (32)$$

where R_A, R_B, and R_C are coordinates of points in which the A, B, and C atoms with densities ρ_{at} are situated. The binding energy is $E_b = \frac{1}{3}(E_{trim} - 3E_{at})$, where

$$E_{trim} = \int E^{el}[\rho_{trim}(\mathbf{r})]d^3\mathbf{r} + \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} + \frac{Z_A Z_C}{|\mathbf{R}_A - \mathbf{R}_C|} + \frac{Z_B Z_C}{|\mathbf{R}_B - \mathbf{R}_C|} + \Delta E,$$

Z_A and Z_B are the positive charges of atomic cores equal to absolute values to charges of valence electrons.
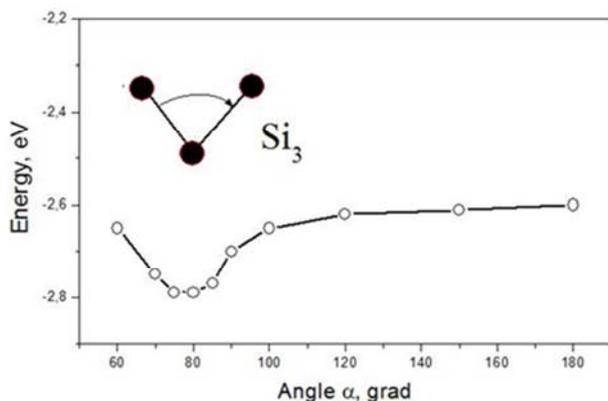
Figure 2. *Dependence of the energy of the Si$_3$ cluster on the angle between bonds.*

Figure 2 presents dependence of the energy of the Si$_3$ cluster on the angle between bonds. It demonstrates a minimum at the angle of 78°. For C$_3$ a minimum was found at 180° (a linear chain), and for Al$_3$ (where covalent bonds absent) all angles were found of 60° (an equilateral triangle).

Equilibrium values of interatomic distances, angles α, and binding energies for the trimers Al$_3$, Si$_3$, and C$_3$ are collected in Table 4 in comparison with known data and results of Kohn-Sham calculations. Parameter C of 25000 was used for silicon and carbon clusters; for aluminum C was equal zero.

Table 4. *Equilibrium distances d, angles α and binding energies E$_b$ (absolute values, per atom) for Si$_3$, Al$_3$ and C$_3$ in comparison with known calculated data.*

Trimer	Source of data	α, deg	d, Å	E$_b$, eV
Si$_3$	OF method	78	2.27	2.8
	Other calculations	77.8 [18]	2.26 [19]	2.51 [19]
		78.10 [26]	2.177	2.93 [27]
		79.6[28]	[26]	
	KS	79	2.17	3.48
Al$_3$	OF method	60	2.5	1.6
	Other calculations	60 [22]	2.50 [22]	1.96 [22]
		60[29]	2.55 [29]	1.74 [21]
	KS	60	2.48	1.69
C$_3$	OF method	180	1.27	5.9
	Other calculations	180 [30]	1.29 [30]	6.8 [30]
		180 [23]	1.3 [23]	5.0 [24]
	KS	180	1.25	6.78

Notations: "KS" means the calculations used the FHI96md package [17] based on the Kohn-Sham method.

To experience the OF approach for ability to describe correctly three-dimensional systems we investigated four-atomic clusters Si4, Al4 and C4 with structures of straight lines, rhombuses, and trigonal pyramids. It is known that the Si4 cluster is built in the form of a rhombus [18, 19]; and four carbon atoms form a straight linear chain [23, 24]. As for aluminum, there is no consensus [21, 22, 31]. Some authors claim that the most favorable configuration is rhombus, others favor pyramid. What gives our method?

Our Calculations show that for the four-atomic cluster the most favorable configuration is the linear chain with the interatomic distance of 1.27 Å and the binding energy of 6.3 eV per atom. The Kohn-Sham results are 1.30 Å and 6.76 eV.

It had been found that the rhombus configuration is favorable for the Si4 cluster with the interatomic distance of 2.35 Å and the binding energy of 2.7 eV (the gain is 0.7 eV in comparison with a pyramid). The Kohn-Sham results are 2.32 Å and 4.1 eV (the gain is 0.6 eV).

In the Al case our calculations demonstrate benefit of the pyramid; however the difference with the rhombic configuration is only 0.2 eV per atom. The Kohn-Sham method yields the opposite results: 0.13 eV in favor of a rhombus.

3. Conclusions

The basic principles of modeling of atomic interactions within of an orbital-free version of the density functional theory were formulated; and modeling of some clusters was carried out. The possibility to simulate interactions of atoms of non-identical types in the framework of the orbital-free version of the density functional theory it is shown. A rather simple technique was used for this purpose, namely: first, the atomic kinetic functions were found for homo-atomic dimers Si$_2$, Al$_2$, C$_2$ and for the SiO dimer; second, some atomic weights were proposed using gaussians associated with atomic densities; third, kinetic functions for hetero-atomic dimers were constructed. Equilibrium interatomic distances and dissociation energies for the SiC, SiAl, AlC, SiO and CO

dimers were found in good comparison with other data.

Restriction principle for the interatomic density (following from Paulie's principle) allows us to describe angular dependences of the interatomic bonding in polyatomic clusters. In particular, it had been shown that for the Al_3 cluster the equilateral triangle is favorable; the Si_3 trimer is characterized by the isosceles triangle with angles of 80 and 50 degrees, and three atoms of carbon built the linear chain. Calculated equilibrium interatomic distances and the values of binding energy are well compared with known data.

As calculation of kinetic energy and interbonding angles are key points in modeling of polyatomic systems in the orbital-free approach, it is possible to consider that this work opens a direct way to design an effective method of modeling of complicated nanosystems and supermolecules with a high number of atoms.

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