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Orbital-Free Pseudo potential Approach for Simulation of Multi-Atomic Systems with Covalent Bonds

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ABSTRACT

We showed that the use of the restriction principle for the interatomic density (following from the Paulie's principle) allows us to describe correctly angular dependences of the interatomic bonding in polyatomic systems in the framework of the orbital-free version of the density functional theory. On the example of the three- and four-atomic clusters of aluminum, silicon, and carbon we show that an orbital-free version of the density functional theory may be used for finding equilibrium configurations of multi-atomic systems with both the metallic and covalent bonding. In particular, the equilateral triangle is favorable for the Al_3 cluster; 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 compared with known data.

Keywords: Orbital-Free, Density Functional, Covalent Bonding, Angular Bond Dependence

I. INTRODUCTION

A number of works (for instance [1-9]) devoted to development of the orbital-free (OF) version of the density functional theory (DFT) [10-11] was appeared last years. This approach, in contrary to the Kohn-Sham (KS) method, does not use the wave functions (orbitals) and operates with the only electron density. The OF approach is a consecutive development of the idea of Hohenberg-Kohn [11] that the basic state of a quantum system can be completely described by means of electronic density.

One of the key problems of the OF approach is presentation of the kinetic part of the energy functional. Most of known OF works stand on using of some universal functional for kinetic energy – in approaches of Tomas-Fermi [12, 13], Weizsacker [14], and their modifications and combinations. However, in recent years some works appeared [15, 16] in which it was shown that the hypothesis of existence of universal density functional is incorrect, and first of all it concerns the functional of kinetic energy (FKE).

In our recent papers [17, 18] we have showed how it is possible, using single-atoms calculations by the Kohn-Sham DFT method (KS-DFT), to find the kinetic functional for single atoms and to use them for orbital-free modelling of atomic dimers. Certainly, we know that there was a significant progress in modelling of two-atomic systems [3, 8] and even simple crystals [19] before our works. However, even now there is a big unsolved problem interfering further development of the OF approach. This problem concerns description of the angular dependence of the interatomic bonding in multi-atomic systems with covalent bonds. Us we know till now there are no works where this problem is solved awfully.

An essential trouble is the fact that the electronic density of a single (isolated) atom is spherical, i.e. the “orbital-free” atom has a shape of a ball, but balls form the close packed structures. For example, three identical atoms are obliged to form an equilateral triangle with corners of 60 degrees. At the same time, it is known that three atoms of silicon form an isosceles triangle with the main corner of about 80 degrees [20], atoms of carbon build a linear chain [21], and atoms of aluminum really behave like balls – they form a correct equilateral triangle [22]. Obviously, if an approach can describe the angular properties of trimers it will can do it for more complicated atomic systems. Thus, the present work is an attempt to develop (on example of Al, Si, and C trimers) a technique which would allow to describe an adequate geometry of interatomic bonds in polyatomic systems in the framework of the OF approach.

II. METHODS AND MATERIAL

A General Description Of The Orbital-Free Approach

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 ρ(***r***):

$$E[\rho]=\int\varepsilon(\rho)d\boldsymbol{r}=\int V(\boldsymbol{r})\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}+\frac{1}{2}\int\varphi(\rho)\rho(\boldsymbol{r})d\boldsymbol{r}+\int\varepsilon_{ex-c}(\rho)d\boldsymbol{r}+\int\varepsilon_{kin}(\rho)d\boldsymbol{r} ,$$

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 potential Hartree, $\varepsilon_{ex\text{-}c}$ and ε_{kin} are exchange-correlation and kinetic energies (per electron).

Minimization of $E[\rho]$ with the condition $\int\rho(\boldsymbol{r})d\boldsymbol{r}=N$ means solution the following equation:

$$F[p]\equiv\frac{\delta\varepsilon[\rho]}{\delta\rho}=V(\boldsymbol{r})+\varphi(\boldsymbol{r})+\mu_{ex-c}(\rho)+\mu_{kin}(\rho)=0 \quad ,$$

where μ is the electron chemical potential;d N is the number of electrons in the system; $\mu_{ex-c}(\rho)=\frac{\delta\varepsilon_{ex-c}(\rho)}{\delta\rho}$, $\mu_{kin}(\rho)=\frac{\delta\varepsilon_{kin}(\rho)}{\delta\rho}$.

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

If we have results of any self-consistent calculation of equilibrium density ρ_a^0 for a single atom, the kinetic potential may be directly found:

$$\mu_{kin}^{a}(\rho_a^0)=V_a(\boldsymbol{r})-\varphi_a(\boldsymbol{r})-\mu_{ex-c}(\rho_a^0) .$$

The total energy of any polyatomic system contains not only the electronic energy but the energy of the ionic repulsion E_{rep} too. For example for a dimer we can write: $E_{\dim}^{tot}=E_{\dim}^{el}+E_{rep}$; where $E_{rep}=\frac{Z_1Z_2}{|\boldsymbol{R}_1-\boldsymbol{R}_2|}$, Z_1 and Z_2 are positive charges of atomic ions having coordinates $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$.

Pseudopotentials are usually generated in partial terms (s, p, and so on). Let us present the total density of a dimer ρ_{12} as a sum of partial densities: $\rho_{12}=\rho_{12-s}+\rho_{12-p}+\ldots$ For the *s*-*p* case, the electron energy of this system $E_{12}=\int\varepsilon_{12}(\rho_{12-s},\rho_{12-p})d\boldsymbol{r}$ must be minimal with the condition $\int(\rho_{12-s}+\rho_{12-p})d\boldsymbol{r}=N_{12}$, where ε_{12} is the electron energy per electron for the two-atomic system with the total number of electrons N_{12}. As the energy functional depends now on two densities ρ_{12-s} and ρ_{12-p} we need to write two equations:

$$F_{12-s}\equiv\frac{\delta\varepsilon_{12}}{\delta\rho_{12-s}}=V_{1-s}(\boldsymbol{r})+V_{2-s}(\boldsymbol{r})+\varphi_{12}(\boldsymbol{r})+\mu_{12}^{ex-c}(\rho_{12})+\mu_{12-s}^{kin}(\rho_{12-s})=0 ,$$

$$F_{12-p}\equiv\frac{\delta\varepsilon_{12}}{\delta\rho_{12-p}}=V_{1-p}(\boldsymbol{r})+V_{2-p}(\boldsymbol{r})+\varphi_{12}(r)+\mu_{12}^{ex-c}(\rho_{12})+\mu_{12-p}^{kin}(\rho_{12-p})=0$$

where $V_{1-s}(\boldsymbol{r})$, $V_{2-s}(\boldsymbol{r})$, $V_{1-p}(\boldsymbol{r})$ and $V_{2-p}(\boldsymbol{r})$ are s and p components of pseudopotentials of the first and second atoms; $\varphi_{12}(\boldsymbol{r})$ 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 $\rho_{12\text{-s}}$ and $\rho_{12\text{-p}}$.

Then we may write equations for finding $\rho_{12\text{-s}}$ and $\rho_{12\text{-p}}$:

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

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

Using the similar equations for two isolated atoms we can obtain:

$$V_{1-s}(\boldsymbol{r})=-\varphi_1^0(\boldsymbol{r})-\mu_1^{ex-c}(\rho_1^0)-\mu_{1-s}^{kin}(\rho_{1-s}^0) ,$$

$$V_{1-p}(\boldsymbol{r}) = -\varphi_1^0(\boldsymbol{r}) - \mu_1^{ex-c}(\rho_1^0) - \mu_{1-p}^{kin}(\rho_{1-p}^0),$$
$$V_{2-s}(\boldsymbol{r}) = -\varphi_2^0(\boldsymbol{r}) - \mu_2^{ex-c}(\rho_2^0) - \mu_{2-s}^{kin}(\rho_{2-s}^0),$$
$$V_{2-p}(\boldsymbol{r}) = -\varphi_2^0(\boldsymbol{r}) - \mu_2^{ex-c}(\rho_2^0) - \mu_{2-p}^{kin}(\rho_{2-p}^0).$$

Finally we obtain equations for finding ρ_{12-s} and ρ_{12-p}:

$$\varphi_{12}(\boldsymbol{r}) - \varphi_1^a(\boldsymbol{r}) - \varphi_2^a(\boldsymbol{r}) + \mu_{12}^{ex-c}(\rho_{12}) - \mu_1^{ex-c}(\rho_1^0) - \mu_2^{ex-c}(\rho_2^0) + \mu_{12-s}^{kin}(\rho_{12-s}) - \mu_{1-s}^{kin}(\rho_{1-s}^0) - \mu_{2-s}^{kin}(\rho_{2-s}^0) = 0,$$

$$\varphi_{12}(\boldsymbol{r}) - \varphi_1^a(\boldsymbol{r}) - \varphi_2^a(\boldsymbol{r}) + \mu_{12}^{ex-c}(\rho_{12}) - \mu_1^{ex-c}(\rho_1^0) - \mu_2^{ex-c}(\rho_2^0) + \mu_{12-p}^{kin}(\rho_{12-p}) - \mu_{1-p}^{kin}(\rho_{1-p}^0) - \mu_{2-p}^{kin}(\rho_{2-p}^0) = 0$$

The dimer kinetic functionals $\mu_{12-s}^{kin}(\rho_{12-s})$ and $\mu_{12-p}^{kin}(\rho_{12-p})$ may be presented as follows

$$\mu_{12-s}^{kin}(\rho_{12-s}) = \mu_{1-s}^{kin}(\rho_{1-s}^0) + \mu_{2-s}^{kin}(\rho_{2-s}^0) + \Delta\mu_{12-s}^{kin}(\rho_{12-s}),$$
$$\mu_{12-p}^{kin}(\rho_{12-p}) = \mu_{1-p}^{kin}(\rho_{1-p}^0) + \mu_{2-p}^{kin}(\rho_{2-p}^0) + \Delta\mu_{12-p}^{kin}(\rho_{12-p}),$$

where $\Delta\mu_{12-s}^{kin}(\rho_{12-s})$ and $\Delta\mu_{12-p}^{kin}(\rho_{12-p})$ are unknown functions of partial densities for the two-atomic system. These functions must aspire to zero if the interatomic distance aspires to infinity. We used the following simple approximation for them:

$$\Delta\mu_{12-s}^{kin}(\rho_{12-s}) \approx \nu_{\mathrm{A}-s}^{kin}(\rho_{12-s}) - \nu_{\mathrm{A}-s}^{kin}(\rho_{1-s}^0) - \nu_{\mathrm{A}-s}^{kin}(\rho_{2-s}^0),$$
$$\Delta\mu_{12-p}^{kin}(\rho_{12-p}) \approx \nu_{\mathrm{A}-p}^{kin}(\rho_{12-p}) - \nu_{\mathrm{A}-p}^{kin}(\rho_{1-p}^0) - \nu_{\mathrm{A}-p}^{kin}(\rho_{2-p}^0),$$

where $\nu_{\mathrm{A}-s}^{kin}(\rho_s)$ and $\nu_{\mathrm{A}-p}^{kin}(\rho_p)$ are some functions having the same kind for single atoms and for dimers formed from atoms of the same type A.

We can solve these equations with some fitting functions $\nu_{\mathrm{A}-s}^{kin}$ and $\nu_{\mathrm{A}-p}^{kin}$ and then calculate the total energy. We found the test functions from the simple request: they must lead to the equilibrium interatomic distances and binding energy for dimers. We hope that these functions will be suitable for more complicated systems in future.

The electron energy of a dimer E_{dim}^{el} contains the electrostatic energy

$$E_{12}^{e-stat} = \int [V_{1-s}(\boldsymbol{r}) + V_{2-s}(\boldsymbol{r})]\rho_{12-s} d\boldsymbol{r} + \int [V_{1-p}(\boldsymbol{r}) + V_{2-p}(\boldsymbol{r})]\rho_{12-p} d\boldsymbol{r} + \frac{1}{2}\int \varphi_{12}(\boldsymbol{r})\rho_{12} d\boldsymbol{r},$$

the exchange-correlation energy $E_{12}^{ex-c} = \int \varepsilon_{12}^{ex-c}(\rho_{12}) d\boldsymbol{r}$

and the kinetic energy

$$E_{12}^{kin} = E_1^{kin} + E_2^{kin} + \iint \left[\nu_{12-s}^{kin}(\rho_{12-s}) d\rho_{12-s} + \nu_{12-s}^{kin}(\rho_{12-p}) d\rho_{12-s}\right] d\boldsymbol{r}.$$

Thus the total energy E_{dim}^{tot} is equal $E_{\mathrm{dim}}^{tot} = E_{12}^{e-stat} + E_{12}^{ex-c} + E_{12}^{kin} + E_{12}^{rep}$.

The binding energy for a dimer (per one atom) would be calculated as follows: $E_b = \frac{1}{2}\left(E_{\mathrm{dim}}^{tot} - 2E_a\right)$, where E_a is the atomic energy.

III. RESULTS AND DISCUSSION

For simplicity we consider the dimers and trimmers consisting of atoms of the same type. We took Al, Si, and C as test elements (for the reasons stated above: 1) trimmers of these elements have essentially different angular configurations); 2) Al is metal, Si and C are covalent species.

We used the FHI98pp [23] package as a generator of pseudo-potentials and equilibrium partial electron densities. We calculated exchange and correlation potentials in the local density approach [24, 25]. 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 150×150×150 elementary sub-cells for the integration with the step Δ*L* of 0.2 a.u. Results of calculations were compared with published data

A. Dimers

We used the same types of kinetic functions ν_s^{kin} and ν_p^{kin} for isolated atoms and dimers, however they were found different for different species. Namely, we have found

for Al: $\nu_s^{kin} = 1.0\rho_s^{1/4.5}$; $\nu_p^{kin} = 22.0\rho_p^{1/1.5}$;

for Si: $\nu_s^{kin} = 8.0\rho_s^{1/1.5}$; $\nu_p^{kin} = 1.6\rho_p^{1/3}$;

for C: $\nu_s^{kin} = 1.75\rho_s^{1/3}$; $\nu_p^{kin} = 1.8\rho_p^{1/3}$.

Calculated values of interatomic distances and binding energies for the Al_2, Si_2, and C_2 dimers are collected in Table I in comparison with other data. The agreement is quite satisfactory if we take into account that the published calculated data often differ from results of experiment and from each other.

TABLE I

EQUILIBRIUM DISTANCES *D* AND BINDING ENERGIES E_B FOR SI_2, AL_2 AND C_2 IN COMPARISON WITH KNOWN CALCULATED DATA.

Dimer	**Source**	***d*, Å**	***E_b*, eV**
Si_2	Our OF method	2.2	1.8
	Other calculations	2.21 [a] 2.23 [b]	1.599 [a] 1.97 [b]
	Experiment	2.24 [c]	3.0 [c]
Al_2	Our OF method	2.8	1.4
	Other calculations	2.95[d] 2.51[e]	1.23[d] 1.55[e]
	Experiment	2.56[f]	1.56[f]
C_2	Our OF method	1.4	3.0
	Other calculations	1.24[g] 1.36 [h]	2.6 [g] 2.7 [h]
	Experiment	1.24 [i]	3.1[i]

Notations: [a][26], [b][20], [c][27], [d][28], [e][29], [f][30], [g][31], [h][32], [i][33].

B. Trimers

To describe the angular dependence of interatomic bonding we have to analyze the reasons of this dependence in the standard quantum-mechanical approach, which uses wave functions and electronic states. For example, it is specified in the work [20] that the angular peculiarities of a cluster Si_3 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 electronic structures and wave functions. Namely, covalent atoms have full occupied bonding states corresponded to localized functions oriented between the nearest atoms; these states are separated by the energy gap from non-occupied states. Metallic atoms have dispersed functions without orientation in the space and without energy gaps between them.

In our case wave functions are absent, electronic states are absent too, and, therefore, we cannot speak about any energy gap. In the OF approach we deal only with the electronic density which defines all energy and structure of the polyatomic system. However the quantum rules remain fair in this case too. We have not to forget that quantum mechanics is not only a set of wave functions and electron states. We have not to forget the Paulie's principle specifying that in one quantum state there can be only two electrons (without taking into account a spin). In our case this principle may be paraphrased by a 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 does not change as the distance between atoms changes (if, of course, the bond is not broken at all and the electronic structure is not reconstructed completely). In case of the metals the states are close each to other and electrons can easily "flow" from one state to another during the changing of the atomic geometry.

The above mentions may be reformulated in the language of the electronic density: the density integral (n_{int}) between atoms with covalent bonding has to keep its value at change of distance between atoms; in case of metal bonding the value of the integral n_{int} can be any possible. Certainly, there is a question: on what space we have to provide integration? And what have we to do with intermediate cases, with atoms of different types? We will leave the last question for the future, and now we will try to explain the difference in structure of covalent and metal systems on the example of homogeneous clusters Al_3, Si_3 and C_3.

It is obvious that the space of integration has to be rather local and at the same time it has to give us the information on quantity of the electrons included in a covalent bond. In the present work we used the space having a shape of the cylinder situated between two nearest atoms (Fig. 1). Radius of the cylinder was selected so that the value of the density integral for a dimer, n_{int}^{dim}, corresponded to two electrons ($n_{int}^{dim} = 2.0$).

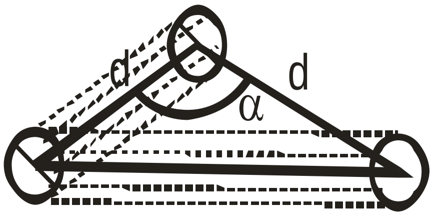

Figure 1: The scheme of an arrangement of atoms in a trimer. Dashed lines show the space on which the electronic density is integrated for definition the number of the electrons involved in the covalent bond; α is an angle between bonds with identical lengths of *d*.

A reader can easily transform the above written dimer equations for the trimer case, therefore we do not write them here directly. As it was said above the integral of electron density between the nearest atoms is the critical parameter for covalent bonding. It cannot be bigger than some value that is a characteristic of a so called saturated bond. Let us take the interatomic bond in a dimer as a standard saturated bond. Let us call the value $P=\frac{n_{\text{int}}^{trimer}}{n_{\text{int}}^{\text{dimer}}}$ (the relation of n_{int} of a trimer to n_{int} of a dimer) as "the bonding strength" and accept that for covalent bonds the value of *P* shouldn't exceed 1.0 at change of the distance between atoms. For metallic bonds the value of *P* can be any possible.

We studied the Al_3, Si_3, and C_3 trimers. We used for them the same kinetic functions ν_s^{kin} and ν_p^{kin} as were used above for dimers. Calculated values *P* are presented in Fig. 2 as functions of the angle between interatomic bonds in the case when restrictions on these values are absent. For each angle we found the values of interatomic distances, which corresponded to the minimum of the total energy of the trimer. One can see that *P* is equal approximately 1.0 at α = 180° and increases when α approaches to 60°. The maximum value (*P* = 1.40) is observed for carbon, that has the smallest interatomic distances. Interatomic distances in aluminum and silicon are approximately equal each to other, therefore no wonder as the "bonding strengths" for the Al_3 and Si_3 trimers are approximately equal.

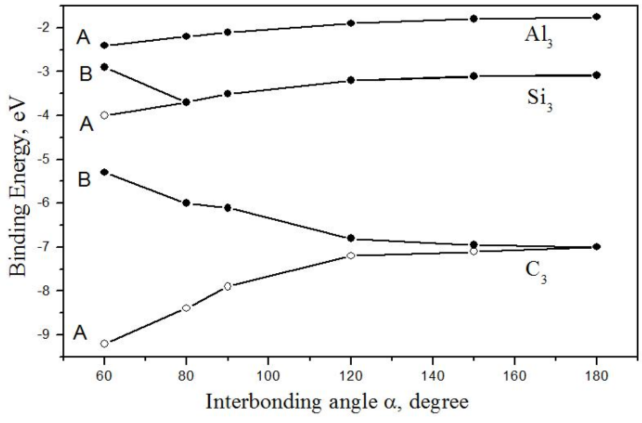

Figure 2. "The bonding strengths" in the Al_3, Si_3 and C_3 trimers as functions of the angle between interatomic bonds in the case when restrictions on the interatomic electron density is absent.

In Fig. 3 (curve A) we present results of calculations of binding energy for the Al_3, Si_3 and C_3 trimers without restriction of the "bonding strengths". From these curves it is clear that in all three cases the minimums of the binding energy correspond to triangular clusters, "bonding strengths" in which significantly exceed the corresponding values, characteristic for the linear chains. This result looks natural for aluminum as its states have the metallic, non-localized character; but for the trimers of Si_3 and C_3 having covalent bonds it is necessary to introduce the restrictions on values of *P* stipulated above. We have taken into account this condition (*P* = 1) and found dependences of the binding energy on the angle between bonds in the Si_3 and C_3 trimers (Fig.3, curve *B*). One can see that atoms of carbon seek to form linear chains, while for silicon neither a linear chain, nor an equilateral triangle is not energetically favorable: atoms of silicon prefer to form an isosceles triangle with the angle α of 80 degrees.

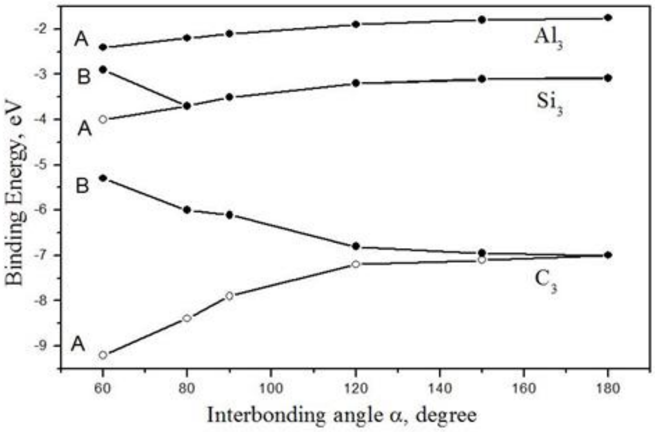

Figure 3. Calculated dependence of binding energy (on atom) for the Al3, Si3 and C3 trimers on the angle between interatomic bonds. A) Values are obtained without restrictions on electronic density in interatomic bonds; B) values calculated with the condition P=1.0.

Equilibrium values of interatomic distances *d*, angles α, and binding energies E_b (absolute values) for the trimers Al_3, Si_3, and C_3 are collected in Table 2 (calculated for the condition *P* = 1) in comparison with known data. One can see that comparison is rather satisfactory, especially taking into account that other results significantly differ each from other and from experimental data. Thus, we have shown that orbital-free approach is capable to describe orientations of interatomic bonds in atomic clusters, as well as values of interatomic distances and binding energies.

TABLE II.
EQUILIBRIUM DISTANCES D, ANGLES α AND BINDING ENERGIES EB FOR SI3, AL3 AND C3 IN COMPARISON WITH KNOWN CALCULATED DATA.

Trimer	Source of data	α, deg	*d*, Å	E_b, eV
Si_3	Our method	≈80	2.1	3.7
	Other calculations	77.8 [a] 79.6 [e]	2.26 [b]	2.51 [b] 2.93 [d]
	Experiment	78.10 [c]	2.177[c]	-
Al_3	Our method	60	2.6	2.4
	Other calculations	60 [f] 60 [h]	2.50 [f] 2.55 [h]	1.74 [g] 1.96 [f]
C_3	Our method	180	1.3	5.0
	Other calculations	180 [i] 180 [j]	1.3[i] 1.3 [j]	4.39 [i] 5.0 [j]
	Experiment	180 [k]	1.3 [k]	4.6 [k]

Notations: [a][20], [b][26], [c][34], [d][35], [e][36], [f][37], [g][38], [h][39], [i][40], [j][41], [k][42].

C. Four-atomic clusters

Four-atomic clusters are interesting as systems, which can have not only one- and two-dimensional structures but the three-dimensional too. We studied the Al_4, Si_4, and C_4 systems with structures of a linear chain, a rhomb, and a trigonal pyramid (Fig. 4).

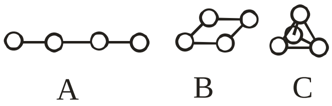

Figure 4. Schemes of four-atomic clusters: A) line chain; B) rhombic structure; C) trigonal pyramid.

We used the same methodic as was described above. Namely, for Si_4 and C_4 we found the total energy of the cluster and compared the density integral $n_{\text{int}}^{tetramer}$ calculated between two atoms of the tetramer with the $n_{\text{int}}^{\text{dimer}}$ of the dimer. If the value $P = \frac{n_{\text{int}}^{tetramer}}{n_{\text{int}}^{\text{dimer}}}$ was bigger than 1.0 we increased the interatomic distances until *P* did not become equal 1.0. For Al_4 we ignored the value of *P*. Results are presented in Table 3 in comparison with known published data and with results obtained by us using the popular KS-DFT code FHI96md [31].

TABLE III.
SIMULATION RESULTS FOR FOUR-ATOMIC SYSTEMS: INTERATOMIC DISTANCES (*d*) AND BINDING ENERGIES (e_b).

Configuration	**Source**	**System**	***d*, Å**	**E_b, eV**
Line chain	Our OF calculation	Si_4	2.2	2.0
		Al_4	2.8	1.15
		C_4	1.3	6.3
	Our KS calculation (FHI96md code)	Si_4	2.2	3.3
		Al_4	2.8	1.62
		C_4	1.3	6.76
	Other calculations	C_4	-	4.58[f]
	Experiment	C_4	-	4.75[g]
Rhomb	Our OF calculation	Si_4	2.4	2.5
		Al_4	2.6	1.18
		C_4	1.9	6.0
	Our KS calculation (FHI96md code)	Si_4	2.3	4.1
		Al_4	2.7	2.00
		C_4	1.3	6.13
	Other calculations	Si_4	2.3[a]; 2.3[b]; 2.3[c]	2.8[a]; 3.2[c]; E_b(rhomb)= E_b(pyramid) +0.4[b]
		Al_4	2.54[d]	2.28[d]
		C_4	1.45-1.49[h]	≈6.2[h]
Pyramid	Our OF calculation	Si_4	2.7	2.1
		Al_4	2.6	1.24
		C_4	2.3	5.2
	Our KS calculation (FHI96md code)	Si_4	2.4	3.5
		Al_4	2.7	1.87
		C_4	1.3	4.76
	Other calculations	Si_4	2.4[b]	E_b(pyramid) =E_b(rhomb)-0.4[b]
		Al_4	2.8[d]; 2.8[e]	2.19[d]; 1.43[e]

Notation: [a][27]; [b][43]; [c][20]; [d][37]; [e][28]; [f][40]; [g][42]; [h][44].

We can see from Table 5 that our OF calculations for Si_4 and C_4 agree with other calculated results and experiment. Namely, we have found that the rhombic Si_4 configuration is more preferable than linear and pyramidal ones, and the linear chain is the most stable for C_4. As for Al_4, it has been found that the studied configurations have very close values of energy. Similar results are obtained by other authors.

IV. CONCLUSION

We showed that the use of the restriction principle for the interatomic density (following from the Paulie's principle) allows us to describe angular dependences of the interatomic bonding in polyatomic clusters in the framework of the orbital-free version of the density functional theory. In particular, it is possible to show 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 the problem of the correct description of angles between interatomic bonds is a key point in modeling of polyatomic systems, it is possible to consider that our work opens a direct way to design an effective method of modeling of big nanosystems and supermolecules.

We have to note that the consideration which is carried out in our work is directly applicable only to the systems consisting of identical atoms and requires a special development for application to more complicated systems.

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