A Practical Way to Develop the Orbital-free Density Functional Calculations

Victor G. Zavodinsky[1*] and Olga A. Gorkusha[2]

[1]*Institute of Materials, Tikhookeanskaya Street. 153, 680042, Khabarovsk, Russia.*
[2]*Institute of Applied Mathematics, Dzerzhinskogo Street. 54, 680000, Khabarovsk, Russia.*

Authors' contributions

This work was carried out in collaboration between both authors. Author VGZ managed the analytic and physical parts of the study. Author OAG managed the algorithms, programming and calculations. Both authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Aims: For modeling of large polyatomic systems one may use the variation principle for energy density functional. The key point to make this is to find the functional of kinetic energy in the orbital-free approach.

Study Design: We describe a way to find functionals of kinetic energy for single atoms and to use them for modeling of polyatomic systems. On examples of diatomic systems Si_2, Al_2, and P_2 the equilibrium interatomic distances and binding energies were calculated in good comparison with published data. Results for Si-Al, Si-P and Al-P dimers are also close to results of Kohn-Sham calculations.

Place and Duration of Study: Institute of Materials, Khabarovsk, Russia; Institute of Applied Mathematics, Khabarovsk, Russia; 2011-2013.

Methodology: We worked in the frameworks of pseudo potentials and the local density approximation of the density functional theory. We used the Kohn-Sham calculations as start steps to find the kinetic energy functionals for single atoms (Al, Si, P). Then we constructed the total energy functionals for dimers and calculated equilibrium interatomic distances and the binding energies.

Results: We constructed the total energy functional for a dimer Si_2 and minimized it with some parameters in order to obtain the equilibrium interatomic distance and the binding energy in good comparison with published data. Then we modeled Al_2, P_2, Si-Al, Si-P, and Al-P dimers with the same parameters and also obtained good results.

Conclusion: We have demonstrated a principal possibility to find equilibrium densities,

---

*Corresponding author: Email: vzavod@mail.ru;

interatomic distances and binding energies in the orbital-free approach using the kinetic energy functionals for single atoms calculated by the Kohn-Sham method.

1. INTRODUCTION

The modern materials science combining nano and macro scales represents special inquiries to modeling of atomic interactions. When the system reaches a length scale of microns it contains millions or billions of electrons, the task to find its quantum-mechanical state using wave functions (orbitals) becomes almost insoluble. Intensive attempts to develop an orbital-free (OF) approach for modeling of polyatomic systems on the basis of the density functional theory (DFT) [1] were made by a number of groups in last two decades [2-8]. In some special cases these attempts are very successful and even led to constructing of the computing programs, allowing to model systems of many thousands of atoms [9]. In general, all of them stand on idea of using some universal functionals for kinetic energy – in approaches of Tomas-Fermi [10,11], Weizsacker [12] and their modifications and combinations. However, in recent years there appeared a number of works [13,14] in which it was shown that the hypothesis of existence of universal density functional is incorrect, and first of all it concerns functional of kinetic energy. Nevertheless, the problem of creation of the general approach for the OF-modeling of polyatomic systems remains tempting and actual. In this paper we show how it is possible, using single-atoms calculations by the Kohn-Sham DFT method (KS-DFT) [15], to find numerically the kinetic energy functionals for atoms and then to use them for orbital-free modeling of atomic interactions.

2. METHODOLOGY

Let us remember that DFT claims [1] that electronic energy E_{el} of the ground state of any quantum system can be found by minimization of the some functional depending only on full electronic density of this system ρ (equations 1 – 4):

$$E_{el}[\rho] = E_{kin}[\rho] + E_{ex}[\rho] + E_c[\rho] + E_H[\rho] - \int V_{ext}(\boldsymbol{r})\rho(\boldsymbol{r})\mathrm{d}^3\boldsymbol{r}, \qquad (1)$$

where V_{ext} is an external potential, E_{kin} *is* kinetic energy, E_{ex} is exchange energy, E_c is correlation energy, and E_H is Hartree energy:

$$E_H[\rho] = \frac{1}{2}\int \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}|} d^3\boldsymbol{r}\,d^3\boldsymbol{r}.$$

The total energy E_{tot} is given by integral:

$$E_{tot} = \int E_{el}[\rho(\boldsymbol{r})]d^3\boldsymbol{r}. \qquad (2)$$

Minimization of (1) with a condition $\int \rho(\boldsymbol{r})d^3\boldsymbol{r} = N$ means solving the following equation:

$$\frac{\delta E_{el}[\rho]}{\delta\rho} - \mu = 0, \tag{3}$$

where μ is the Lagrange parameter having a sense of the electron chemical potential. Introducing $F[\rho] = \dfrac{\delta E_{el}[\rho]}{\delta\rho} - \mu$, we obtain the equation

$$F[\rho] \equiv -V_{ext}(\boldsymbol{r}) + \varphi(\boldsymbol{r}) + \mu_{kin}(\rho) + \mu_{ex}(\rho) + \mu_c(\rho) - \mu = 0, \tag{4}$$

where $\varphi(\boldsymbol{r}) = \int\dfrac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}d^3\boldsymbol{r}'$, $\mu_{kin}(\rho) = \dfrac{\delta E_{kin}[\rho]}{\delta\rho}$, $\mu_{ex}(\rho) = \dfrac{\delta E_{ex}[\rho]}{\delta\rho}$, $\mu_c(\rho) = \dfrac{\delta E_c[\rho]}{\delta\rho}$.

There are some realistic approximations for exchange $\mu_{ex}(\rho)$ and correlation $\mu_c(\rho)$ potentials, the potential of electron-electron repulsion $\varphi(\boldsymbol{r})$ may be calculated using Fourier transformations, the external potential $V_{ext}(\boldsymbol{r})$ usually consists of atomic potentials or of pseudo potentials. The key problem is to find the potential of kinetic energy $\mu_{kin}(\rho)$. In the Kohn-Sham approach this problem is absent because kinetic energy is calculated using electron orbitals (wave functions). We may use this approach to find $\mu_{kin}(\rho)$ for single atoms and then to apply them for polyatomic systems. Below we will demonstrate our method in the pseudo potential case as a more simple one.

Realistic quantum mechanical pseudo potentials are usually constructed for different angular states. Thus we have to present the total density as a sum of partial densities:

$$\rho = \rho_s + \rho_p + \rho_d + \dots$$

Being limited for simplicity to a *s-p* case, we may write the equations

$$F_s[\rho_s, \rho] \equiv -V_s(\boldsymbol{r}) + \varphi(\boldsymbol{r}) + \mu_{kin}^s(\rho_s) + \mu_{ex}(\rho) + \mu_c(\rho) - \mu = 0,$$

$$\tag{5}$$

$$F_p[\rho_p, \rho] \equiv -V_p(\boldsymbol{r}) + \varphi(\boldsymbol{r}) + \mu_{kin}^p(\rho_p) + \mu_{ex}(\rho) + \mu_c(\rho) - \mu = 0,$$

where $V_s(\boldsymbol{r})$ and $V_p(\boldsymbol{r})$ are *s* and *p* components of atomic pseudo potential. The electrostatic potential $\varphi(\boldsymbol{r})$, exchange and correlation potentials $\mu_{ex}(\rho)$ and $\mu_c(\rho)$ are calculated through the total density ρ while partial kinetic potentials $\mu_{kin}^s(\rho_s)$ and $\mu_{kin}^p(\rho_p)$ depend on corresponding partial densities ρ_s and ρ_p.

3. RESULTS AND DISCUSSION

3.1 Single Atoms

If we calculate the ground state of an atom in the KS-DFT pseudo potential approach we may declare that its partial electron densities minimize its energy functional or in other words

the equations (5) are satisfied. Thus we can find $\mu_{kin}^{s}(\rho_{s})$ and $\mu_{kin}^{p}(\rho_{p})$ for this atom as functions of space coordinates:

$$\mu_{kin}^{s}(\boldsymbol{r}) = V_{s}(\boldsymbol{r}) - \varphi(\boldsymbol{r}) - \mu_{ex}(\boldsymbol{r}) - \mu_{c}(\boldsymbol{r}) + \mu \ ,$$

$$\mu_{kin}^{p}(\boldsymbol{r}) = V_{p}(\boldsymbol{r}) - \varphi(\boldsymbol{r}) - \mu_{ex}(\boldsymbol{r}) - \mu_{c}(\boldsymbol{r}) + \mu \ .$$

(6)

However in order to calculate kinetic energy we have to make integration firstly on ρ and then on *r*:

$$E_{kin} = \int\int \mu_{kin}^{s}(\rho_{s})d\rho_{s}d^{3}\boldsymbol{r} + \int\int \mu_{kin}^{p}(\rho_{p})d\rho_{p}d^{3}\boldsymbol{r} \ .$$

(7)

Therefore, we have to pass from the coordinate determination of $\mu_{kin}^{s}(\boldsymbol{r})$ и and $\mu_{kin}^{p}(\boldsymbol{r})$ to their determination through ρ_{s} и and ρ_{p}, and then coming back to the coordinate determination to make integration over the space.

Let us consider typical atoms with s and p electrons, Al, Si and P. For constructing of pseudo potentials and calculation of equilibrium densities and energies we will use the FHI98pp [16] package widely used for KS-DFT calculations. Exchange and correlation potentials we will consider in the local density approximation [17,18]. Then the partial densities $\rho_{s}(\boldsymbol{r})$ and $\rho_{p}(\boldsymbol{r})$ for example for Si atom look as follows (Fig. 1).

The partial kinetic energy potentials $\mu_{kin}^{s}(\boldsymbol{r})$ and $\mu_{kin}^{p}(\boldsymbol{r})$ are plotted in Fig. 2.

As it was said above we can use dependencies $\rho_{s}(\boldsymbol{r})$ and $\rho_{p}(\boldsymbol{r})$ pass from the coordinate determination $\mu_{kin}^{s}(\boldsymbol{r})$ and $\mu_{kin}^{p}(\boldsymbol{r})$ to their determination through ρ_{s} and ρ_{p}. The calculated dependencies $\mu_{kin}^{s}(\rho_{s})$ and $\mu_{kin}^{p}(\rho_{p})$ for Al, Si, and P atoms are shown in Fig. 3. Analyzing these curves we can see that universal dependence doesn't exist, at least for these three types of atoms. There are essential differences between *s* and *p* components; and the curves received for various atoms, considerably differ from each other. However we see also important common features of these curves. All of them have regions with reverse motion (i.e. two-branches) and besides, each curve has the limited range of definition corresponding to the maximum value of density for this atom. Reverse motions of curves are geometrically connected with the volumes inside core spheres. To avoid ambiguity, we will separately determine density inside the sphere and outside, setting radiuses of spheres by the positions of maxima of the corresponding density.
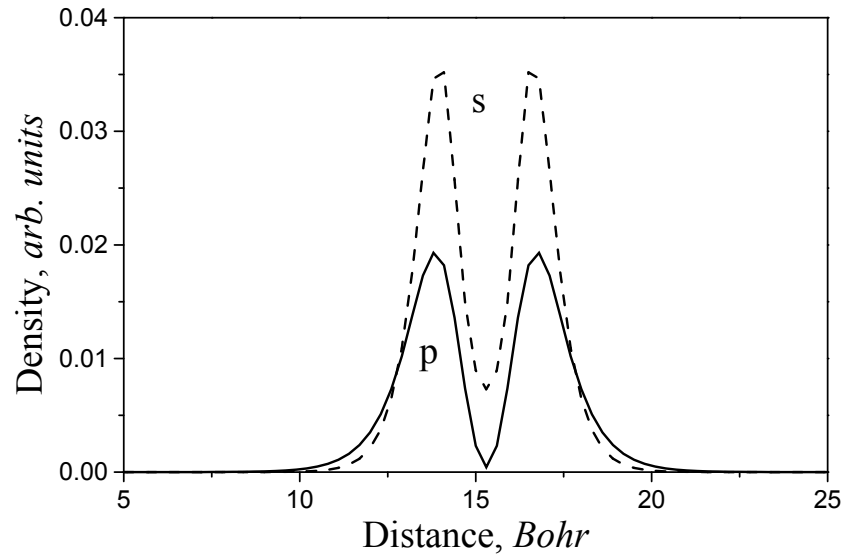
Fig. 1. Partial densities ρ$_s$(*r*) and ρ$_p$(*r*) for Si atom. The point of minima corresponds to the atomic centre. The dashed line shows s-states; the solid curve demonstrates p-states
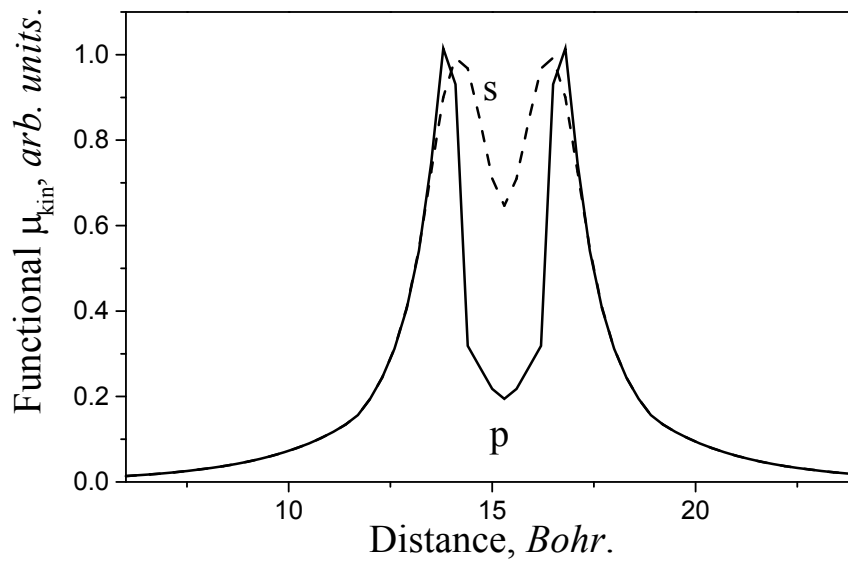

Fig. 2. Partial kinetic energy potentials $\mu_{kin}^{s}(r)$ and $\mu_{kin}^{p}(r)$ plotted along the line going through the centre of Si atom

Carrying out integration of functions on density, and then on coordinates, we find for silicon E_{kin} = 1.4484 Hartree и and E_{tot} = -3.5338 Hartree (1 Hartree = 27.2 eV.) Calculation by the KS-DFT method gives 1.2840 and -3.7472, respectively. Thus we have distinction about 0.2 Hartree caused by overestimation of kinetic energy. However exact calculation of single atoms is not our task. Our task is to show efficiency of the OF approach for the description of polyatomic interactions. Now we will try to calculate interaction of two atoms. If we find such important values as equilibrium distance and energy of bonding close to results of KS-calculations, our approach at this stage can be considered successful.
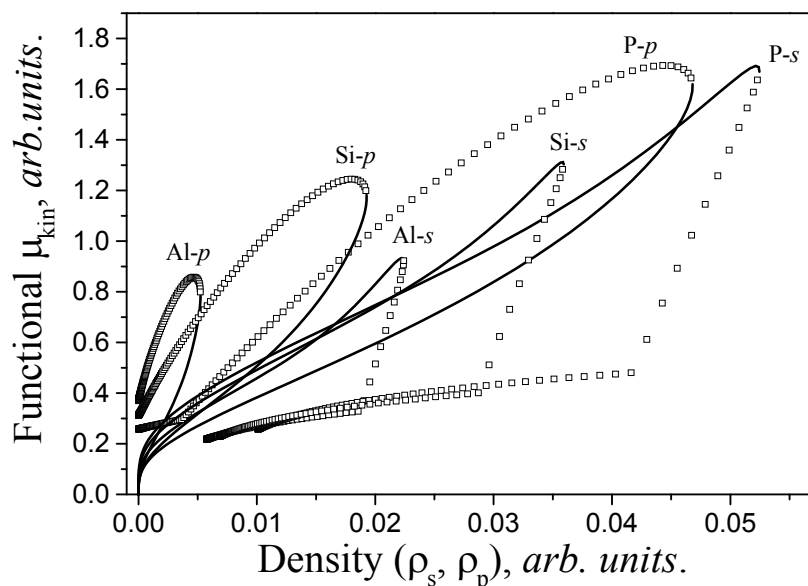

Fig. 3. Dependencies $\mu_{kin}^{s}(\rho_{s})$ и and $\mu_{kin}^{p}(\rho_{p})$ for Al, Si, and P single atoms. Solid curves describe functionals in outside valence regions, the hole quadrates demonstrate behavior of functionals inside core spheres

3.2 Atomic Dimers

An attempt to consider atomic interactions immediately leads to the problem: atomic densities are summarized and under certain conditions (a close arrangement of atoms) the total electronic density can significantly exceed the maximum value, for which the function $\mu_{kin}(\rho)$ is determined. How to construct $\mu_{kin}^{s}(r)$ and $\mu_{kin}^{p}(r)$ in this case? How to extend dependences $\mu_{kin}^{in}(\rho)$ and $\mu_{kin}^{out}(\rho)$ to higher densities? Probably, the exact answer to these questions will be found in some future, but now we offer other, an approximate way for finding of equilibrium density and energy of interacting atoms.

Let us consider two atoms of silicon. Each of them, being in the ground free state, possesses equilibrium partial densities $\rho_{s}(r)$ and $\rho_{p}(r)$, which correspond to pseudo potentials $V_{s}(r)$ and $V_{p}(r)$. Equilibrium densities $\rho_{s}(r)$ and $\rho_{p}(r)$ correspond to functionals

F_s and F_p, equal to zero. If we place these atoms close enough their densities are intersected and the new superimposed density is formed, for which the conditions $F_s=0$, $F_p=0$ are invalid. The density starts to change, its changing leads to changing of F_s and F_p, and finally to changing of the total energy, which aspires to some minimum if F_s and F_p aspire to zero.

As we say about rather little changes (and calculations confirm this), it is possible to consider that change of density is proportional to the value of density, and the coefficient of proportionality is proportional to the value of functional $F_{s(p)}$, while the change of functional $F_{s(p)}$ is proportional to change of density. Then we can write down (postulate) the following iterative equations:

$$\frac{\Delta\rho_n(r)}{\Delta t} = K_1 F_n(r)\rho(r), \quad \frac{\Delta F_n(r)}{\Delta t} = -K_2\frac{\Delta\rho_n(r)}{\Delta t}, \quad n=s,p, \tag{8}$$

where $\Delta\rho_n$ and $\Delta F_n(r)$ are changes of densities and functionals in the space point r during the time of one iteration Δt, K_1 and K_2 are some coefficients probably the same for various types of atoms.

Calculations were performed using a cubic cell of 30 *Bohr* size (1 *Bohr* = 0.0529 nm) divided by the 100×100×100 grid for integration. To find the binding energies E_b and equilibrium distances d_0 between atoms in dimers we consider the total energy E_{tot} as a sum of the electron energy E_{el} and the energy of "ion-ion" repulsion

$$E_{rep} = \frac{Z_1 Z_2}{|\mathbf{R}_1 - \mathbf{R}_2|},$$

where Z_1 and Z_2, are positive charges of ions with numbers 1 and 2 situated at $\mathbf{R}_1$ and $\mathbf{R}_2$ points. The binding energy per atom E_b was determined as follows:

$$E_b = \frac{E_{tot} - E_1 - E_2}{2},$$

where E_{tot} is the energy of two interacted atoms, E_1 and E_2 are energies of free atoms.

Results of calculations were compared with results obtained in the framework of the KS-DFT approach using the FHI96md package [19] and other published data. We fitted coefficients $K_1=0.2$ and $K_2=500$ for the Si dimer and used the same values for other dimers. The preference was given to comparison of our results with the results obtained by the FHI96md package and the reasons were two. First, the FHI96md package applies the same pseudo potentials and exchange-correlation approximations as we used. Second, we could not find published data for all studied dimers and were compelled to be content with comparison of our OF results with ourselves KS-DFT calculations.

The Fig. 4 demonstrates the dependence of the binding energy (per atom) for Si_2 on the distance between atoms; and the Fig. 5 shows changes of the total electron density during the iteration process for various interatomic distances. We can see that our results correlate

with results obtained by the KS-DFT method: the both methods lead to similar changes of density in the process of calculation.

Results (equilibrium distances d_0 and binding energies E_b) for Al_2, Si_2, and P_2 dimers are collected in Table 1 in comparison with results obtained by us using the FHI96md package and with other published data. One can seen that our OF results are close to others; differences are not larger than known dispersion. Analogous calculations, with the same K_1 and K_2, were performed for Al-Si, Si-P, and Al-P dimers. Results are also presented in Table 1. In this case our OF method also demonstrates satisfactory accordance with the KS-DFT approach.
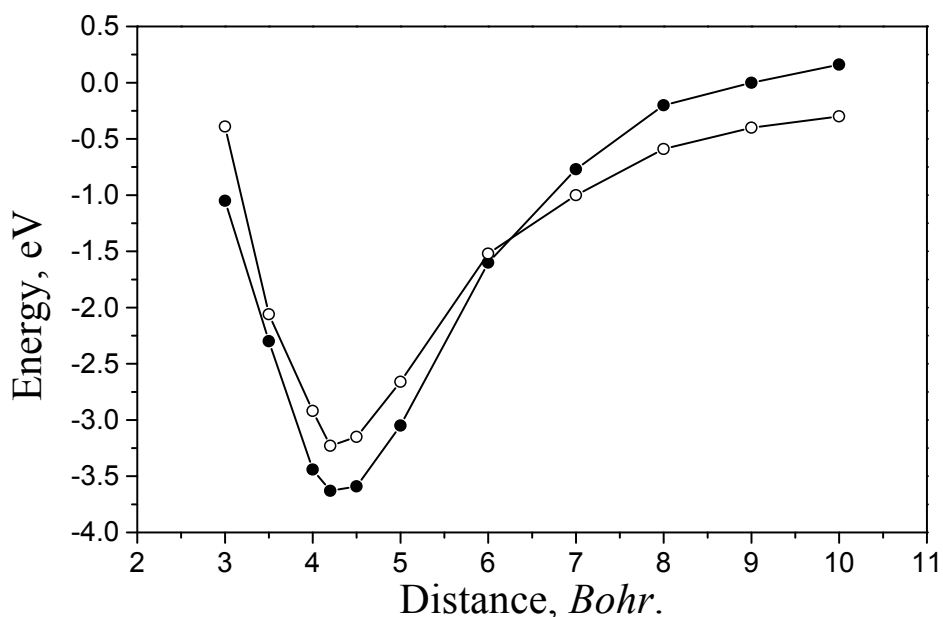

Fig. 4. Binding energy (per atom) in the Si_2 dimer versus the interatomic distance. Solid circles represent our OF results; hole circles illustrate calculations by the Kohn-Sham method (the FHI96md package). Experimental values of equilibrium distance and binding energy are 4.46 *Bohr* [26] and 3.21 eV [20], correspondingly

Above we have showed a basic suitability of our approach to calculate equilibrium interatomic distances and energies for some types of atomic dimers: namely, for s and p atoms. It is possible to expect that in a further development we will be able to expand our approach for atoms containing d-shells. However, if we assume to use it further for modeling of very big systems, it is important to show the speed of convergence of working procedures.

The energy convergence and the decreasing of functionals F_s и and F_p for Si_2 dimer during the iteration process are shown in Fig. 6. It is clear that convergence is very good, thus the calculation procedure may be efficiently used for polyatomic systems.

Table 1. Equilibrium distances d_0 and binding energies E_b (per atom) for Si_2, Al_2, P_2, Al-Si, Si-P and Al-P

Dimers	Methods	d_0, nm	E_b, eV
Si_2	Our method	0.222	3.63
	FHI96md	0.220	3.25
	Other data	0.223[a], 0.211[b]	3.7[a], 3.07[c]
Al_2	Our method	0.259	1.66
	FHI96md	0.261	1.61
	Other data	0.251[d]	1.55[d], 1.96[e]
P_2	Our method	0.190	5.19
	FHI96md	0.190	5.04
	Other data	-	-
Al-Si	Our method	0.242	2.30
	FHI96md	0.231	1.97
Si-P	Our method	0.206	4.31
	FHI96md	0.203	3.42
Al-P	Our method	0.222	3.70
	FHI96md	0.215	3.33

Notations: [a] [21], [b] [22], [c] [23], [d] [24], [e] [25]
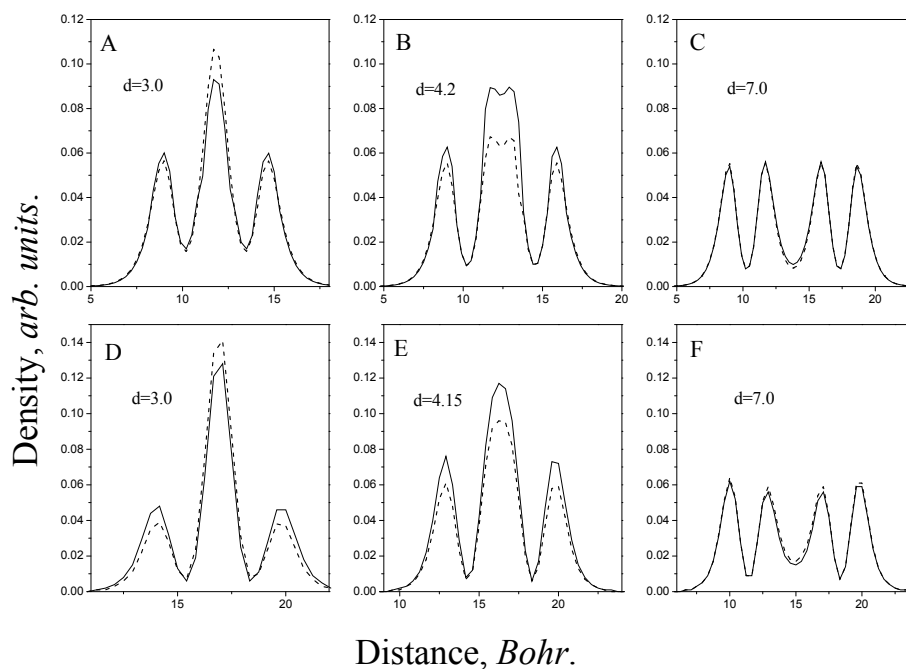

Distance, *Bohr.*

Fig. 5. Changes of the total electron density in the Si_2 dimer during the iteration process for various interatomic distances. The upper row (A, B, C) demonstrates calculations by our method; the low row (D, E, F) shows results of the Kohn-Sham calculations (FHI96md). The B and E panels correspond to equilibrium distances. Dashed curves describe initial densities; solid ones illustrate final functions
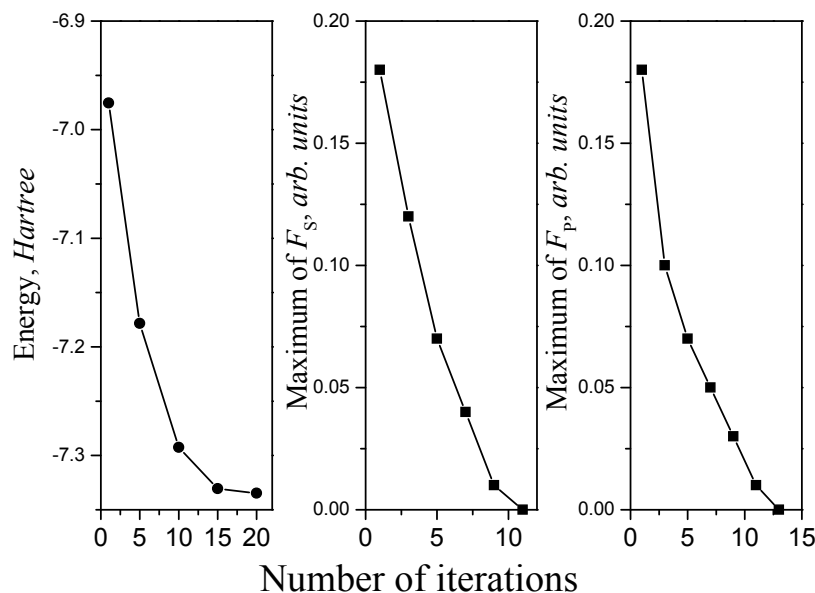
Fig. 6. Left: The total energy of the Si$_2$ dimer as it depends on the number of iterations. Middle and right: changing of maximum values of F_s и and F_p for the Si$_2$ dimer during the iteration process at the equilibrium interatomic distance

4. CONCLUSION

It was shown that the Kohn-Sham results for single atoms may be used as start points for orbital-free calculations for multi-atomic systems. On examples of diatomic systems Si$_2$, Al$_2$, and P$_2$ the equilibrium interatomic distances and binding energies were calculated in good comparison with published data. Results for Si-Al, Si-P and Al-P dimers are also correlate with results of Kohn-Sham calculations, and this is our main result. The convergence of energy and its functionals during the iteration process is very good, thus the calculation procedure may be efficiently used for polyatomic systems.

This work doesn't represent the description of the finished algorithms for modeling of polyatomic systems, we have showed only a basic possibility to create such code. Still it is necessary to include in the GGA options, spin polarization, and certainly d-atoms. Besides, and it is our main future task, it is necessary to add calculations of forces operating on atoms in order to pass from dimers to more complicated test objects. However we consider that we have demonstrated the prospects of our approach and we invite all readers to cooperation.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Hohenberg H, Kohn W. Inhomogeneous Electron Gas. Phys Rev. 1964;136:864-871.
2. Wang YA, Carter EA. Orbital-free kinetic-energy density functional theory. In: Schwartz SD, editor. Progress in Theoretical Chemistry and Physics. Dordrecht: Kluwer; 2000.
3. Huajie Chen, Aihui Zhou. Orbital-Free Density Functional Theory for Molecular Structure Calculations. Numer Math Theor Meth Appl. 2008;1:1-28.
4. Baojing Zhou, Ligneres VL, Carter EA. Improving the orbital-free density functional theory description of covalent materials. J Chem Phys. 2005;122:044103-044113.
5. Hung L, Carter EA. Accurate simulations of metals at the mesoscale: Explicit treatment of 1 million atoms with quantum mechanics. Chem Phys Lett. 2009;475:163-170.
6. Karasiev VV, Trickey SB. Issues and challenges in orbital-free density functional calculations. Comp Phys Commun. 2012;183:2519-2527.
7. Karasiev VV, Chakraborty D, Shukruto OA, Trickey SB. Nonempirical generalized gradient approximation free-energy functional for orbital-free simulations. Phys Rev B. 2013;88:161108-161113(R).
8. Wesolowski TA. Approximating the kinetic energy functional $T_s[\rho]$: lessons from four-electron systems. Mol Phys. 2005;103:1165-1167.
9. Watson SC, Carter EA. Linear-scaling parallel algorithms for the first principles treatment of metals. Comp Phys Commun. 2000;128:67–92.
10. Thomas LH. The calculation of atomic field, Proc. Cambr Phil Soc. 1926;23:542-548.
11. Fermi E. A statistical method for the determination of some atom prioprietà. Rend Accad Lincei. 1927;6:602-607.
12. Von Weizsacker CF. On the theory de nuclear masses. Z Physik. 1935;96:431-458.
13. Bobrov VB, Trigger SA. The problem of the universal density functional and the density matrix functional theory. J Exper Theor Phys. 2013;116(4):635–640.
14. Sarry AM, Sarry MF. To the density functional theory. Physics of the Solid State. 2012;54(6):1315–1322.
15. Kohn W, Sham JL. Self-Consistent Equations including Exchange and Correlation Effects. Phys Rev. 1965;140:1133-1138.
16. Fuchs M, Scheffler M. *Ab initio* pseudo potentials for electronic structure calculations of poly-atomic systems using density-functional theory. Comp Phys Comm. 1999;119:67-98.
17. Perdew JP, Zunger A. Self-interaction correction to density functional approximation for many-electron systems. Phys Rev B. 1981;23:5048-5079.
18. Ceperley DM, Alder BJ. Ground state of the electron gas by a stochastic method. Phys Rev Lett. 1980;45:566-569.
19. Beckstedte M, Kley A, Neugebauer J, Scheffler M. Density-functional theory calculations for poly-atomic systems: Electronic structure, static and elastic properties and ab initio molecular dynamics. Comp Phys Commun. 1997;107:187-205.
20. Huber KP, Herzberg G. Constants of Diatomic Molecules. New York, Van Nostrand Reinhold; 1979.
21. Raghavachari K, Logovinsky V. Structure and bonding in small silicon clusters. Phys Rev Lett. 1985;55:2853-2856.

22. Siqing Wei, Bamett RN, Landman U. Energetics and structures of neutral and charged Si_n($n\leq10$) and sodium-doped Si_nNa clusters. Physical Review B. 1997;55:7935-7944.
23. Tomanek D, Schluter MA. Structure and bonding of small semiconductor clusters. Phys Rev B. 1987;36:1208-1217.
24. Kumar V, Sundararajan V. *Ab initio* molecular-dynamics studies of doped magic clusters and their interaction with atoms. Phys Rev B. 1998;57:4939-4942.
25. Nayak SK, Khanna SN, Jena PJ. Evolution of bonding in AlnN clusters: A transition from nonmetallic to metallic character. Phys Rev B. 1998;57:3787-3790.
26. Wielgus P, Poszak S, Majumdar D, Saloni J, Leszczynski J. Theoretical studies on the bonding and thermodynamic properties of Ge_nSi_m (m+n=5) clusters: The precursors of germanium/silicon nanomaterials. J Chem Phys. 2008;128(6):144-305.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=476&id=33&aid=4611