

Development of an orbital-free approach for simulation of multi-atomic nanosystems with covalent bonds

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PACS 03.65.-w

DOI 10.17586/2220-8054-2016-7-3-427-432

On the example of the three-atomic clusters Al₃, Si₃, and C₃, it is shown that an orbital-free version of the density functional theory may be used for finding equilibrium configurations of multi-atomic systems with both metallic and covalent bonding. The equilibrium interatomic distances, interbonding angles and binding energies are found to be in good agreement with known data.

Keywords: Orbital-free, density functional, covalent bonding, angle dependence.

Received: 9 November 2015

Revised: 17 December 2015

1. Introduction

A number of works (for instance [1–8]) have been devoted to the development of the orbital-free (OF) version of the density functional theory (DFT) [9–13] over the last few years. This approach, in contrast to the Kohn–Sham (KS) method, does not use the wave functions (orbitals) and operates with the only electron density. The OF approach is the result of further development of the ideas of Hohenberg–Kohn [10]; i.e., that the basic state of a quantum system can be completely described by means of electronic density. There has been significant progress in the description of diatomic systems [8, 14, 15] and simple crystals [16]. However, an essential hindrance to further development of the OF method 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 [17], atoms of carbon build a linear chain [18], and atoms of aluminum really behave like balls – they form a correct equilateral triangle [19]. The present work is an attempt to develop a technique which would allow us to adequately describe the geometry of interatomic bonds in polyatomic systems within the OF approach.

2. A general description of the OF approach

As is well-known the DFT claims that the energy E_{el} of the ground state of any quantum system can be found by minimization of some function which depends only on the electronic density of this system ρ :

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

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:

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

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

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

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

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

where μ is the Lagrange parameter gives one a sense of the electron chemical potential.

Introducing $F[\rho] = \frac{\delta E_{el}[\rho]}{\delta \rho} - \mu$, we obtain the equation:

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

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

There are some realistic approximations for exchange $\mu_{ex}(\rho)$ and correlation $\mu_c(\rho)$ potentials; the potential of the electron-electron repulsion $\varphi(\mathbf{r})$ may be calculated using Fourier transformations or Poisson equations; the external potential $V_{ext}(\mathbf{r})$ usually consists of atomic potentials or of pseudopotentials. The key problem is to find the potential of kinetic energy $-\mu_{kin}(\rho)$. In the Kohn–Sham approach, this problem is absent because the kinetic energy is calculated using electron orbitals (wave functions).

Quantum mechanical pseudopotentials are usually constructed for different angular states. Thus, we have to present the total density as a sum of partial densities:

$$\rho = \rho_s + \rho_p + \rho_d + \dots \quad (5)$$

For the s - p case, we may write the equations:

$$\begin{aligned} F_s[\rho_s, \rho] &\equiv -V_s(\mathbf{r}) + \varphi(\mathbf{r}) + \mu_{kin}^s(\rho_s) + \mu_{ex}(\rho) + \mu_c(\rho) - \mu_s = 0, \\ F_p[\rho_p, \rho] &\equiv -V_p(\mathbf{r}) + \varphi(\mathbf{r}) + \mu_{kin}^p(\rho_p) + \mu_{ex}(\rho) + \mu_c(\rho) - \mu_p = 0, \end{aligned} \quad (6)$$

where $V_s(\mathbf{r})$ and $V_p(\mathbf{r})$ are the s , p components of atomic pseudopotential. The electrostatic potential $\varphi(\mathbf{r})$, 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 .

As designing of pseudopotentials is followed by the finding of equilibrium pseudo-wave functions, it is always possible to calculate partial densities of the isolated atom $\rho_s(\mathbf{r})$ and $\rho_p(\mathbf{r})$, as well as its full equilibrium electronic density $\rho(\mathbf{r}) = \rho_s(\mathbf{r}) + \rho_p(\mathbf{r})$. If we know the type of these functions we could calculate energy E_{kin} and find the total energy of a single atom using Eq. (2). However, there is no basis to believe that there are some functions for kinetic functional and energy, which could be used for atoms of any type and any quantity. Moreover, as it was recently shown [20], the Hohenberg–Kohn idea about the existence of a universal density functional leading to the energy minimum was not strictly proved, and it is possible to say only about approximate solutions for the problem. However, in our case, the problem consists not in finding of the energy of a single atom (this can be done in more traditional ways), but in calculation of the energy of the interatomic interaction, and in finding the geometry of the polyatomic system corresponding to this interaction.

3. From dimers to trimers: a role of quantum rules and restrictions

3.1. Dimers

For simplicity, we will consider dimers consisting of atoms of one type. The elementary approach for the electronic density of such dimer ρ_{dim} is the sum of densities of the atoms:

$$\rho_{dim}(\mathbf{r}) = \rho_{at}(\mathbf{r} - \mathbf{R}_A) + \rho_{at}(\mathbf{r} - \mathbf{R}_B), \quad (7)$$

where \mathbf{R}_A and \mathbf{R}_B are coordinates of points in which the A and B atoms with densities ρ_{at} are situated.

Then, the binding energy (per one atom) would be calculated as follows:

$$E_b = \frac{1}{2} (E_{dim} - 2E_{at}), \quad (8)$$

where $E_{at} = E_{at}^{tot} = \int E^{el}[\rho_{at}(\mathbf{r})] d^3\mathbf{r}$,

$$E_{dim} = \int E^{el}[\rho_{dim}(\mathbf{r})] d^3\mathbf{r} + \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}, \quad (9)$$

Z_A and Z_B are the positive charges of atomic cores equal to absolute values of charges of valence electrons.

We took Al, Si, and C as test elements (for the reasons stated above: trimers of these elements have essentially different geometric configurations). For all three elements we accepted the following function $\mu_{kin}(\rho)$ as the universal function for s - and p -states and:

$$\mu_{kin}(\rho) = 0.9\rho^{1/3} - 15\rho^2. \quad (10)$$

We used the FHI98pp [21] package as a generator of pseudo-potentials. We calculated exchange and correlation potentials in the local density approach [19, 20]. The studied atoms were located in a cubic cell of the L size

TABLE 1. Equilibrium distances d and binding energies E_b (absolute values, per atom) for Si_2 , Al_2 and C_2 in comparison to known calculated data

| Dimer | Source of data | d , Å | E_b , eV |
|---------------|--------------------|----------------------------|--------------------|
| Si_2 | Our method | 2.1 | 2.0 |
| | Other calculations | 2.23 ^a | 1.97 ^a |
| | | 2.21 ^b | 1.599 ^b |
| Al_2 | Our method | 2.4 | 1.2 |
| | Other calculations | 2.46 ^c | 1.0 ^d |
| | | 2.95 ^e | 1.23 ^e |
| C_2 | Our method | 1.3 | 4.8 |
| | Other calculations | 1.247 – 1.367 ^f | 4.7 ^f |
| | | 1.316 ^g | 3.5 ^g |

Notations: ^a [17], ^b [25], ^c [23], ^d [19], ^e [27], ^f [28], ^g [29]

($L = 52$ a.u.; 1 a.u. = 0.529 Å). The cell was divided into $128 \times 18 \times 128$ elementary sub-cells for the integration with the integration step ΔL of 0.406 a.u. Results of calculations were compared to the published data.

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.

3.2. Trimers

To describe the angle dependence of interatomic bonding, we must analyze the reasons for this dependence in the standard quantum-mechanical approach, which uses wave functions and electronic states. For example, it is specified in the work [24] that the angle peculiarities of a cluster Si_3 are defined by the Yang–Teller effect, which is caused by the existence of an energy gap between the occupied and empty states. In other words, the differences in semiconductor and metal small cluster structures are connected with the difference of their bond wave functions: namely, covalent atoms have localized functions oriented between nearest atoms, while metallic atoms have dispersed functions without spatial orientation.

In our case, both wave functions and electronic states are absent, and therefore, we cannot speak about any energy gap. In the OF approach, we deal only with the electronic density which defines all energies and structures of the polyatomic system. However, the main quantum-mechanical rules still remain fair in this case. Besides the Schrödinger's (or Kohn–Sham) equations, out of which wave functions and electron states arise, we must not forget Pauli's principle which specifies that in one quantum state there can be only two electrons (without taking into account spin). In our case, this principle may be paraphrased in 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 completely reconstructed). In the case of metals, the conduction states are close each other and electrons can easily "flow" from one state to another during the changing of atomic geometry.

The above-mentioned concepts may be reformulated in the language of the electronic density: the density integral (n_{int}) between atoms with covalent bonding, has to remain its value with a change of distance between atoms; in the case of metal bonding, the integral n_{int} can have any possible value.

Certainly, there is a question: on what space do we have to provide integration, and what do we have to do with intermediate cases, with atoms of different types? We will leave these questions for the future, and now we will try to explain the differences in the structures of covalent and metal systems using the following homogeneous clusters Al_3 , Si_3 and C_3 as examples.

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 slab situated between two nearest atoms (Fig. 1) and oriented perpendicularly to the plane in which the trimer triangle is placed. The thickness of a slab was taken as $2\Delta L$. As the number of the integration points can be changed with a change in the trimer configuration, the value of n_{int} was normalized to one point.

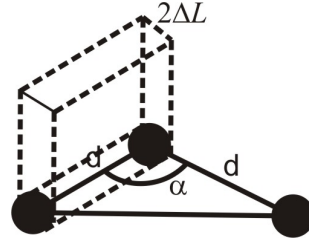


FIG. 1. The scheme for the arrangement of atoms in a trimer. Dashed lines show the space on which the electronic density is integrated for definition the number of the electrons involved in the covalent bond; α is a corner between bonds with identical lengths of d

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

$$\rho_{trim}(\mathbf{r}) = \rho_{at}(\mathbf{r} - \mathbf{R}_A) + \rho_{at}(\mathbf{r} - \mathbf{R}_B) + \rho_{at}(\mathbf{r} - \mathbf{R}_C), \quad (11)$$

where \mathbf{R}_A , \mathbf{R}_B , and \mathbf{R}_C are coordinates of points in which the A , B , and C atoms with densities ρ_{at} are situated. The binding energy is:

$$E_b = \frac{1}{3} (E_{trim} - 3E_{at}), \quad (12)$$

where

$$E_{trim} = \int E^{el}[\rho_{trim}(\mathbf{r})]d^3\mathbf{r} + \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} + \frac{Z_A Z_C}{|\mathbf{R}_A - \mathbf{R}_C|} + \frac{Z_B Z_C}{|\mathbf{R}_B - \mathbf{R}_C|}, \quad (13)$$

Z_A and Z_B are the positive charges of atomic cores equal to absolute values to charges of valence electrons.

Let us take the interatomic bond in a dimer as a standard. Let us call the value $P = \frac{n_{int}^{trimer}}{n_{int}^{dimer}}$ (the relation of n_{int} of trimer to n_{int} of dimer) as “the bonding strength” and accept that for covalent bonds, the value of P shouldn’t exceed 1.0 with a change of distance between atoms. For metallic bonds, P can have any possible value.

Calculated values P for clusters Al_3 , Si_3 , and C_3 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 cluster. One can see that P is approximately 1.0 at $\alpha = 180^\circ$ and increases when α approaches 60° . The maximum value ($P = 1.40$) is observed for carbon, which has the smallest interatomic distances. Interatomic distances in aluminum and silicon are approximately the same, therefore it should come as no surprise that the “bonding strengths” for the Al_3 and Si_3 trimers are approximately equal.

We repeated the calculations using thicker slabs ($4\Delta L$ and $8\Delta L$) for integration of $n_{int}(\text{dimer})$ and $n_{int}(\text{trimer})$ values between atoms in dimers and trimers and we found that results changed by no more than by 2 per cent.

In Figure 3 (curve A), we present the results for calculations of binding energies 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 maxima of the binding energy (on the absolute value) correspond to triangular clusters, “bonding strengths” in which significantly exceed the corresponding values, characteristic for linear chains. This result looks natural for aluminum as its states have the metallic, not localized character; but for the clusters of Si_3 and C_3 having covalent bonds it is necessary to introduce 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 clusters (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 energetically favorable; atoms of silicon prefer to form an isosceles triangle with the angle α of 80 degrees.

Equilibrium values for interatomic distances d , angles α , and binding energies E_b 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 good. Thus, we showed that an orbital-free approach is capable of correctly describing the orientations of interatomic bonds in atomic clusters, as well as values of interatomic distances and binding energies.

Certainly, it is interesting to compare our results for interatomic densities with results of standart DFT-KS calculations. For this purpose, we calculated “bonding strenghts” P for Si_3 and Al_3 using the popular DFT-KS code FHI96md [31] for the same triangles as were studied above. We have found that P were equal 1 (± 0.02) for all cases for Si_3 , but it increased up to 1.3 for the Al_3 equilateral triangle. These results are in excellent agreement with ours.

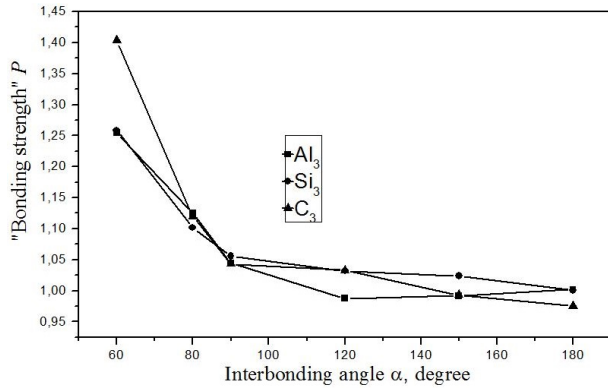


FIG. 2. “The bonding strengths” in the Al_3 , Si_3 and C_3 trimers as functions of the corner between interatomic bonds in the case when there are no restrictions on the interatomic electron density

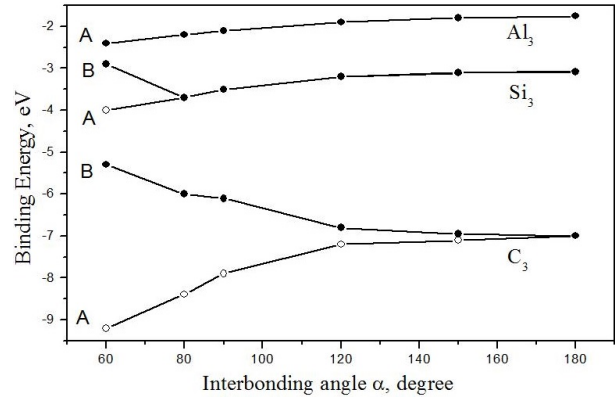


FIG. 3. Calculated dependence of binding energy (on atom) on the angle between interatomic bonds for the Al_3 , Si_3 and C_3 trimers. A) Values are obtained without restrictions on electronic density in interatomic bonds; B) values calculated with the condition $P = 1.0$

TABLE 2. 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 | Our method | ≈ 80 | 2.1 | 3.7 |
| | Other calculations | 77.8 ^a | 2.26 ^b | 2.51 ^b |
| | | 78.10 ^c | 2.177 ^c | 2.93 ^d |
| | | 79.6 ^e | | |
| Al_3 | Our method | 60 | 2.3 | 2.4 |
| | Other calculations | 60 ^f | 2.50 ^f | 1.74 ^g |
| | | 60 ^h | 2.55 ^h | 1.96 ^f |
| C_3 | Our method | 180 | 1.2 | 7.0 |
| | Other calculations | 180 ⁱ | 1.29 ^j | 6.8 ⁱ |
| | | 180 ^k | 1.3 ^k | 5.0 ^l |
| | | 1.316 ^l | | |

Notations: ^a [17], ^b [25], ^c [30], ^d [31], ^e [32], ^f [27], ^g [19], ^h [33], ⁱ [18], ^j [30], ^k [28], ^l [29]

4. Conclusion

We showed that the use of the restriction principle for the interatomic density (following from Pauli’s principle) allows us to correctly describe the angular dependences of the interatomic bonding in polyatomic clusters within 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 an isosceles triangle with angles of 80 and 50 degrees, and the three atoms of carbon are present as a linear chain. Calculated equilibrium interatomic distances and binding energy values are in fair agreement with known data. As the problem of correctly describing the angles between interatomic bonds is a key point in the modeling of polyatomic systems, it is possible to consider that our work opens a direct way to design an effective method for modeling of big nanosystems and supermolecules.

We have to note that the consideration which is carried out above 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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