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Fast Calculation of Cohesive Energy for Large Diamond Nanoparticles: The Orbital-Free Simulation

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Abstract

A full-electron orbital-free modeling method, developed in the framework of the density functional theory (DFT), was used for calculation of the cohesive energy of cubic diamond nanoparticles. Numbers of included atoms were changed from 64 up to 1000. The kinetic energy functional was constructed using Kohn-Sham (KS) calculations for a single carbon atom and a C_8 cubic particle. Interatomic distances were changed to find the total energy minima. The calculation speed was found much higher than that of the KS method; the calculation time grows linearly with increasing of the system.

Keywords: Density functional theory; Orbital-free; Full-electron; Diamond nanoparticles; Cohesive energy

Introduction

In the last 20 years many research groups see for example [1-6]. Made great efforts to develop on the basis of the density functional theory. A method for modeling large polyatomic systems, namely, an orbital-free (OF) method, dispensing with wave functions, working only with electron density, however they did not achieve serious success yet. In our opinion the reason of difficulties is that those works rely on the authority of Hohenberg and Kohn [7]. Who declared that there is a universal functional of kinetic energy and the task consists only in that to find it. However, as shown recently [8,9]. The idea of Hohenberg and Kohn about existence of a universal density functional leading to the energy minimum is not strictly proved. Thus, there are bases to believe that attempts to construct an OF method based on use of any universal functional are obviously doomed to failure. Our alternative OF approach is based on the kinetic energy functionals specified for the each type of atoms. In previous works [10-14]. We demonstrated ability of our method to describe in the pseudopotential approximtion the structure and energy of atomic systems consisted of two, three, and four atoms of various types. Recently we have developed a full-electron version of the orbital free modeling method [15]. Which allows us to study large systems. Now we demonstrate how this full-electron method can simulate large nanoparticles of diamond.

Simulation Technique

In short, our approach is as follows. The total energy of the polyatomic system E is found by minimizing the functional

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

at the condition $\int \rho(r)dr = N$, where V(r) is a potential of atomic nuclei, φ is the Hartree potential, $\varepsilon^{ex\text{-}c}$ and ε^{kin} are exchange-correlation and kinetic energy functionals, N is the total number of electrons in the systems.

Minimization of (1) with the $\int \rho(r)dr = N$ leads to an equation

$$F[\rho] = \frac{\partial \varepsilon(\rho)}{\partial \rho} - \mu = V(r) + \varphi(r) + \mu_{\text{ex-c}}(\rho) + \mu_{\text{kin}}(\rho) - \mu = 0, \quad (2)$$

Where μ is the electron chemical potential, $\mu_{\textbf{ex-c}}(\rho) = \frac{\partial \varepsilon_{\textbf{ex-c}}(\rho)}{\partial \rho}$ and $\mu_{\textbf{kin}}(\rho) = \frac{\partial \varepsilon_{\textbf{kin}}(\rho)}{\partial \rho}$ are exchange-correlation and kinetic potentials. In this work we used the both Local Density Approximation (LDA) [16]. Generalized Gradient Approximation (GGA) [17]. For calculation of the exchange-correlation potential. For the kinetic potential we used a technique described in our recent work this technique allows us to find the kinetic potential for a multi-atomic system if we know the kinetic potentials of single atoms. The single atom kinetic potential $\mu_{\text{kin}}^{\text{at}}$ may be calculated easily using the Kohn-Sham (KS) approach [18]. An analysis of the C_8 cubic system in the frame of the KS method (using the full-electron ELK code [19]. Had allowed us to find for the carbon multiatomic systems the following dependence of μ_{kin} on the average distance d between atoms:

$$\mu_{kin} = \mu_{kin}^{at} \cdot \left[1.21 - \frac{2.12}{\mathrm{d}} + \frac{342}{d^2}\right] \text{ For LDA, } (3)$$

$$\text{And } \mu_{kin} = \mu_{kin}^{at} \cdot \left[0.95 - \frac{1.64}{\mathrm{d}} + \frac{4.10}{d^2}\right] \text{ for GGA, } (4)$$

Results and Discussion

We studied cubic diamond particles with numbers of atoms from 64 to 2744. Calculations were fulfilled in the cubic space of the 3.2 nm side with a 100×100×100 3D-greed. The interatomic distances were changed and the energy minima were found. Calculated equilibrium average distances d are collected in the Table 1;

Table 1: *The average interatomic distances d of studied diamond particles.*

Number of atoms	64	216	512	1000	1728	2744	Diamond (bulk)
d, Å (LDA)	1.465	1.501	1.521	1.526	1.527	1.530	1.546
d, Å (GGA)	1.502	1.517	1.523	1.528	1.529	1.532	

the values of corresponded cohesive energies are shown in the (Figure 1).

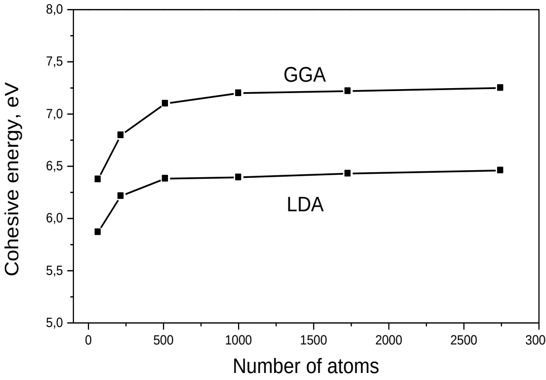
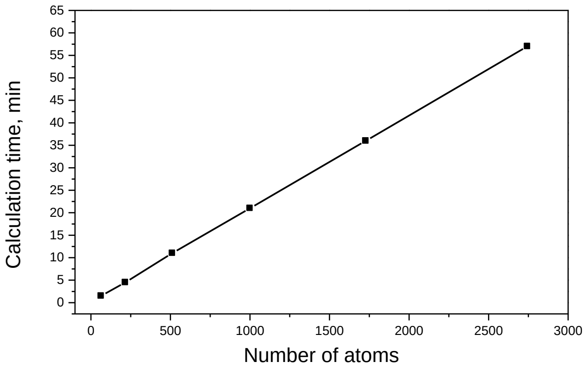


Figure 1: *Dependence of the cohesive energy of cubic diamond particles on numbers of atoms.*

One can see in the Table 1 that the average interatomic distance increases with increasing of nanoparticles and tends to the value corresponded to bulk diamond [20,21]. The demonstrates that the calculated cohesive energy also grows with increasing of particles and its value tends to the cohesive energy of bulk diamond (7.5 eV) (Table 1). It should be noted that the calculated values of cohesive energy and interatomic distances in the GGA are larger than in the LDA, as is usually the case in DFT calculations. The main advantage of the OF approach is its high speed resulting from the rejection of wave functions. This is what makes it attractive for modeling of large nano systems (Figure 2).



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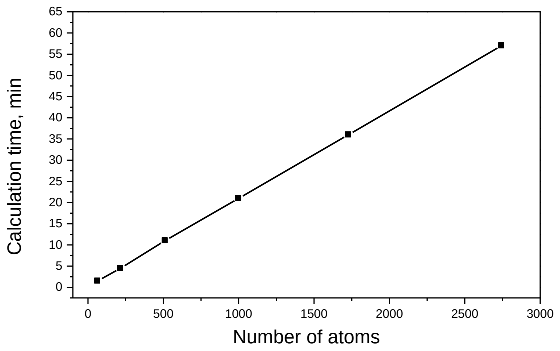

Figure 2: *Dependence of the OF calculation time on numbers of atoms in the studied diamond particles.*

Shows the dependence of the time spent on finding the equilibrium energy for particles of different sizes. For comparison, the time of the corresponding calculation that we carried out for the C_{64} particle by the KS method.

Conclusions

Thus, we have shown that our full-electron orbital-free method allows us to describe the energetics of large carbon diamond nanoparticle. Namely, we have found that the cohesive energy grows with increasing of particles and its value tends to the the cohesive energy of bulk diamond. Interatomic distances also tends to the bulk diamond ones with increasing of particles. The calculation speed is much more than that of the Kohn-Sham method; the calculation time grows linearly with increasing of the system.

References

1. Wang YA, Carter EA. Theoretical methods in condensed phase chemistry in a new book series of progress in theoretical chemistry and physics. Schwartz. 2000; 13: 117-184.
2. Huajie Chen and Aihui Zhou. Orbital-free density functional theory for molecular structure calculations, numerical mathematics: theory methods and applications. 2008; 1: 1-28.
3. Karasiev V, Jones S, Trickey S, Harris F. Recent advances in developing orbital-free kinetic energy functionals. New Develop Quantum Chem. 2009; 81: 25-54.
4. Chakraborty D. Computing the kinetic energy from electron distribution functions. Chem Thesis McMaster Uni Hamilton Ontario Canada. 2012.
5. Huang C, Carter EA. Nonlocal orbital-free kinetic energy density functional for semiconductors. Phys. Rev. B. 2010; 81: 45206-452015.
6. Ho GS, Ligneres VL, Carter EA, Introducing PROFESS: A new program for orbital-free density functional theory calculations. Comp Phys Commun. 2008; 179: 839-854.
7. Hohenberg H, Kohn W. Inhomogeneous electron gas. Phys Rev. 1964: 136: 864-871.
8. Sarry AM, Sarry MF. On the density functional theory. Fizika Tverdogo Tela. 2012; 54: 1237-1243.
9. Bobrov VB,Trigger SA. The problem of the universal density functional and the density matrix functional theory. J Exper Theor Phys. 2013; 116: 635-640.
10. Zavodinsky VG, Gorkusha OA. A simple quantum-mechanics way to simulate nanoparticles and nanosystems without calculation of wave functions. Inter Schol Res Net Nano materials. 2012.
11. Zavodinsky VG, Gorkusha OA. Quantum-Mechanical modeling without wave functions. Phys Solid States. 2014; 56:2329-2335.
12. Zavodinsky VG, Gorkusha OA. Development of an orbital free approach for simulation of multiatomic nanosystems with covalent bonds. Nanosystems: Phys Chem Mathem. 2016; 7: 427-432.
13. Zavodinsky VG, Gorkusha OA. Development of the orbital free approach for heteroatomic systems. Nanosys Phys Chem , Mathem. 2016; 7: 1010-1016.
14. Zavodinsky VG, Gorkusha OA, Kuz'menko AP. Energetics of carbon nanotubes with open edges: Modeling and experiment. Nanosys: phys chem mathem. 2017; 8: 635-640.
15. Zavodinsky VG, Gorkusha OA. On a possibility to develop a full-potential orbital-free modeling approach. nanosys: phys chem mathem. 2019, 10: 402-409.
16. Perdew JP, Zunger AS. Self-interaction correction to density functional approximation for many-electron systems. Phys Review, 1981; 23: 5048-5079.
17. Ceperley DM, Alder BJ. Ground state of the electron gas by a stochastic method. Phys Review. 1980; 45: 566-569.
18. Perdew JP, Wang Y. Accurate snd simple density functional for the electronic exchange energy. Phys Rev. 1986; 33: 3399-4008.
19. Kohn W, Sham JL. Self-consistent equations including exchange and correlation effects. Phys Rev. 1965; 140: 1133-1138.
20. http://elk.sourceforge.net.
21. 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 dynamic. Comput Phys Commun. 1997; 107: 187-205.

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