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Ab initio large unit cell calculations of the electronic structure of diamond nanocrystals

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ABSTRACT

In order to reduce computational efforts, and separate surface and core properties, diamond nanocrystals in the present model is represented by a heterojunction between the surface and the core in which the surface represents the outer most four layers and the core by the rest of the internal region of nanocrystal. Ab initio restricted Hartree-Fock (RHF) method coupled with the large unit cell method (LUC) is used to determine the electronic structure and physical properties of diamond nanocrystals core part with different sizes. The use of STO-3G basis choice is made to be able to compare to semiempirical methods using the complete neglect of differential overlap (CNDO) that uses Slater type orbitals (STO). The oxygenated (001)-(1 × 1) facet that expands with larger sizes of nanocrystals is also investigated to determine the rule of the surface in nanocrystals electronic structure. The results show that the present method agrees with semiempirical method contraction of lattice constant with increasing nanocrystal size but disagrees with energy gap variation with nanocrystal size in some regions. After nearly 1.4 nm the energy gap which is controlled by surface states begins to rise. The lowest unoccupied molecular orbital (LUMO) is attributed to surface states that largely reduce the value of energy gap. The sources of disagreement between semiempirical and ab initio results are discussed. The present method shows a maximum increment of the lattice constant by 3.3% over the calculated bulk for the smallest diamond nanocrystals. The surface states are found mostly non-degenerated because of the effect of surface discontinuity and oxygen atoms. Valance and conduction bands are wider on the surface due to splitting and oxygen atoms. The method also shows fluctuations in the converged energy gap, valence band width and cohesive energy of the core part of nanocrystal. These fluctuations might partially explain the controversial experimental results for diamond nanocrystals greater than 1.4 nm in size. The method of the present model has threefold results; it can be used to obtain the electronic structure of bulk, surface, and nanocrystals.

1. Introduction

Diamond has unique properties that differentiate it from most of other materials. It is known to be the hardest material on earth with a high thermal conductivity that is several times greater than copper. On the other hand, diamond can be considered as a semiconductor with a wide band gap. Nanocrystaline diamond particles, wires, and films are expected to carry many of diamonds physical properties. These structures are found in detonation residues and meteorites or can be synthesized in many different ways [1]. The investigation of diamond nanocrystals properties is a current research activity, in particular, the energy gap is of controversial results both experimentally and theoretically [2–11].

The large unit cell (LUC), which is some kind of supercell methods, was suggested and first applied for the investigation of electronic band structure of bulk materials and in particularly elemental semiconductors [12–17] in the 70s of the last century. After its success in describing the electronic structure of bulk semiconductors, the method was also applied to a variety of systems [18–21]. The method was usually coupled with semiempirical methods to overcome ab initio computational difficulties of large scale and deformed systems. The method was also recently applied to diamond nanocrystals in conjunction with the complete neglect of differential overlap (CNDO) [22]. In the present work we introduce the ab initio version of large unit cell method and apply the method to diamond nanocrystals. We shall discuss the various benefits over molecular dynamic methods that can be gained in this application such as reaching higher number of carbon atoms, reducing computational efforts, investigating nanocrystals physical properties that were not investigated before, obtaining more

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accurate results than that obtained from approximate semi-empirical CNDO theory.

Cluster calculations of nanoparticles require the use of molecular dynamics for geometry optimization that include all the atoms of the nanoparticle. In LUC method only the lattice constant is optimized for the core part. However, the surface part bond lengths and angles still need to be optimized because of surface reconstruction. In the present method we divide the problem into two parts namely; core and surface parts which is the traditional method used in solid state calculations. We shall perform the core part using the LUC method and the oxygenated (001)–(1 × 1) surface case that can be added to obtain a complete electronic structure view. The periodic boundary condition (PBC) method available in GUSSIAN 03 program [23] is used to perform the present tasks.

Table 1
Diamond LUCs translational vectors, number of atoms in each LUC, total number of atoms in nanocrystal, and the length of the corresponding diamond nanocrystal.

Translation vectors	Number of atoms in LUC	Total number of atoms	Length of nanocrystal
a(½,½,0), a(½,0, ½), a(0, ½,½)	2		–
a(1,0,0), a(0,1,0), a(0,0,1)	8	216	3a
2a(½,½,0), 2a(½,0, ½), 2a(0, ½,½)	16	325	3.44a
3a(½,½,0), 3a(½,0, ½), 3a(0, ½,½)	54	470	3.89a
2a(1,0,0), 2a(0,1,0), 2a(0,0,1)	64	512	4a
4a(½,½,0), 4a(½,0, ½), 4a(0, ½,½)	128	738	4.52a
3a(1,0,0), 3a(0,1,0), 3a(0,0,1)	216	1000	5a
5a(½,½,0), 5a(½,0, ½), 5a(0, ½,½)	250	1092	5.15a
6a(½,½,0), 6a(½,0, ½), 6a(0, ½,½)	432	1544	5.78a

2. Theory

In the present work we introduce LUC-RHF (large unit cell coupled with restricted Hartree-Fock method) as compared to LUC-CNDO method used previously for diamond and other materials band structure calculations [12–18,24,25]. The usual coupling of LUC method with semiempirical theories is performed to reduce computational time and efforts.

Restricted Hartree-Fock (RHF) method uses the linear combination of atomic orbital:

$$\psi_i = \sum_{\mu} C_{\mu i}\, \varphi_{\mu}. \tag{1}$$

The symbols used in the present work have there usual meanings [12–22]. The combination coefficients ($C_{\mu i}$) of the atomic orbitals (φ_{μ}) are varied so that a set of algebraic equations which are called Roothan–Hall equations [22] are obtained:

$$\sum_{\nu} (F_{\mu\nu} - \epsilon_i S_{\mu\nu})\, C_{\nu i} = 0. \tag{2}$$

ϵ_i are the eigenvalues. The overlap integral $S_{\mu\nu}$ in the above equation is defined by

$$S_{\mu\nu} = \int \varphi_{\mu}(1)\varphi_{\nu}(1) d\tau_1. \tag{3}$$

Where dτ is an element of space. In Eq. (2), the Fock matrix is given by:

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}\left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)\right]. \tag{4}$$

The above equation contains the core Hamiltonian, the density matrix and the two-electron integrals that are respectively given by:

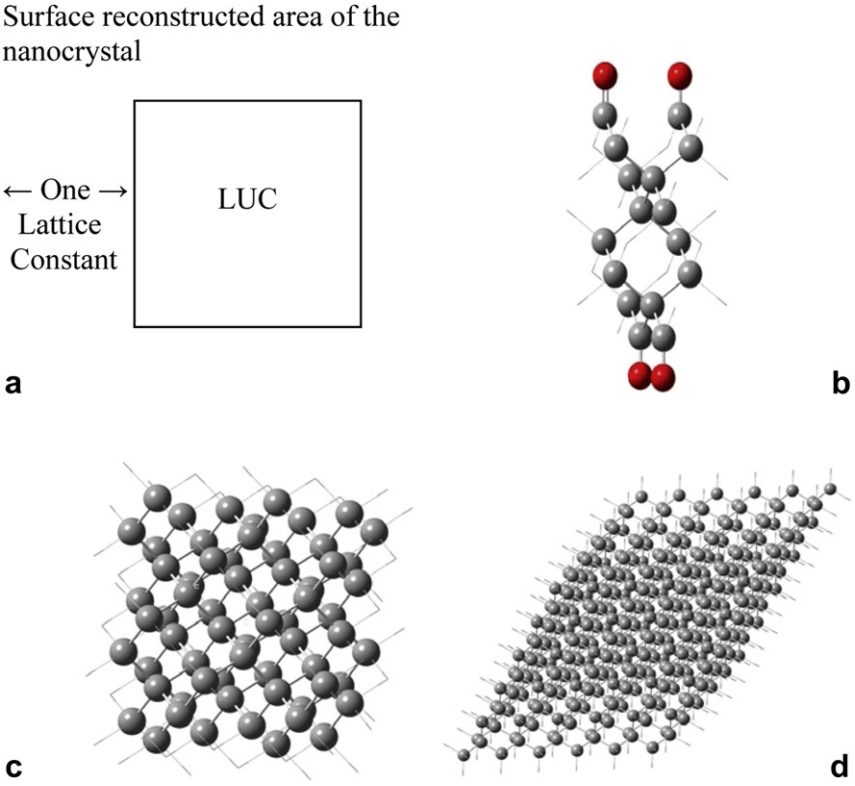

Fig. 1. LUC and surface geometry for nanocrystals (a), slab 2D calculations of oxygenated 8 carbon layers (b), 64 atom LUC (c), and 432 atoms LUC (c) in periodic boundary conditions. Red (dark) circles represent oxygen atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)