

Geometry and Energetics of Nano Gears

Ya-Lin Li¹, Yin-Li Liu², Qian Wang³, and Qiang Sun^{4,5,*}

¹Gannan Medical University, Ganzhou, JiangXi 341000, China

²School of Applied Mathematics, University of Electronic Science and Technology of China, Chengdu, Sichuan 610054, China

³Physics Department, Virginia Commonwealth University, Richmond, VA 23284-2000

⁴Department of Advanced Materials and Nanotechnology, Peking University, Beijing 100871, China

⁵Center for Applied Physics and Technology, Peking University, Beijing 100871, China

Benzene is one of the most interesting molecules in chemistry, when binding with carbon nanotubes, nano-gears can be formed, providing an excellent example of nano engineering by molecular assembly. Using first-principles theory, we investigate the geometry, binding, and electronic structure of such nano-gears. We show that although the formation heat of benzyne from benzene is positive due to the high stability of benzene molecule itself, once benzyne is formed, it can strongly interact with carbon nanotube forming a tooth, and the binding causes some local geometric deformations, especially the two linking C atoms on the nanotube are pulled outward apparently. The distance between the benzyne and the (5, 5) carbon nanotube is about 1.49 Å with the binding energy of 3.55 eV. When two gears are coupled, the equilibrium distance is 2.32 Å, and the gearing energy is found to be 0.71 eV, this is stronger than van der Waals interaction but weaker than covalent bonding, which can guarantee the stability of geometry and the flexibility of the gearing. Furthermore, the gearing energy can be tuned by changing the size and/or the component of teeth.

Keywords: Nano Engineering, Molecular Assembly, Nano Gear.

1. INTRODUCTION

It is well-known that the macroscopic mechanical gears are widely used to generate and control rotational movement and produce useful work in numerous mechanical devices such as in clocks, watches, transmissions, car, trains and robots. At the microscopic level, there are two kinds of gears, molecular gears and nano-gears. The rotation around single bonds in molecule is the norm, such bonds can serve as the axles. The design and synthesis of molecular systems that work as gears have attracted a lot of interest.¹ The finding of the reaction of benzyne with C₆₀ stimulates the idea of nano-gears,^{2,3} which consists of carbon nanotubes and benzynes. The high stability and rich properties of carbon nanotubes and benzene make such kind of nano-gears very attractive and interesting. Benzene is one of the most fascinating molecules, and benzyne is its derivative. Since the first isolation in 1825 by Michael Faraday from an oily film that deposited from the gas used for lighting, benzene (benzyne) has been comprehensively studied and widely used in the production of plastics, paints, rubber, resins, detergents, lubricants, drugs, pesticides, synthetic fabrics, and in molecular electronics. From the viewpoint of binding, the p-orbitals in

each neighboring C overlap to form a delocalized molecular orbital which extends around the ring, giving additional stability, which makes benzyne molecule a good choice for the tooth part of a nano-gear. The combinations of benzene and carbon nanotubes provide a promising clue for nano engineering. However, there are some fundamental questions need to be answered: (1) Carbon nanotubes and benzene are quite stable themselves. To synthesize a nano gear, how much is the formation energy? (2) After benzyne is absorbed on carbon nanotubes, how are the geometry and electronic structure changed? (3) When two gears are geared, how strong is the interaction and how is the structure changed? In this paper, we present the theoretical investigation that addresses above issues.

2. COMPUTATIONAL METHOD

The theoretical calculations are carried out by using an iterative solution of the Kohn–Sham equations of density-functional theory, based on the minimization of the norm of the residual vector to each eigenstate and an efficient charge density mixing.^{4,5} For the exchange-correlation functional, a gradient-corrected functional in the form of the generalized gradient approximation (GGA)⁶ has been chosen. In order to optimize geometry effectively,

*Author to whom correspondence should be addressed.

a plane-wave basis set is adopted with the projector-augmented wave (PAW) method originally developed by Blöchl⁷ and adapted by Kresse and Joubert.⁸ The advantage of the PAW method over the ultrasoft pseudopotentials is that the pseudization of the augmentation charge can be avoided. In all the calculations, the structures have been fully relaxed and the structure optimization was carried out with symmetry unrestricted by using conjugate-gradient algorithm. We have used supercells with 12 Å vacuum spaces along the *x*, *y*, and *z* directions for all the calculated systems. The Γ point is used to represent the Brillouin zone due to the large supercell. The cutoff energy was set to 400 eV, whereas the convergence criterion in energy and force were set to 10^{-4} eV and 0.003 eV/Å, respectively.

3. RESULTS AND DISCUSSION

We first do some test calculations. For H₂ molecule, the calculated binding energy is 4.535 eV with the bond length of 0.749 Å, in good agreement with the experimental values of 4.750 eV and 0.74 Å.⁹ For benzene molecule, the C–C and C–H bond lengths are found to be 1.394 and 1.089 Å, respectively. The average binding energy per atom is calculated to be 5.163 eV, which is comparable to the experimental value of 4.973 eV.¹⁰

To synthesize a gear, the first step is to generate benzyne from benzene: $C_6H_6 \rightarrow C_6H_4 + H_2$. In experiment, benzyne can be produced in situ by adding anthranilic acid to benzene solution.² The formation energy of this reaction is found to be +4.259 eV. Figure 1 shows the geometry of C₆H₆ and C₆H₄. When two neighboring H atoms are removed, the bond length between these two C atoms is reduced to 1.262 Å from 1.394 Å, and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) becomes 3.324 eV from 5.070 eV of C₆H₆, suggesting C₆H₄ is more active than C₆H₆.

As armchair carbon nanotubes are normally more stable energetically as compared to others with different chiralities,¹¹ in the present study, we chose a (5, 5) carbon nanotube as an example to study the formation, geometry, electronic properties, and energetics of nano-gears. The

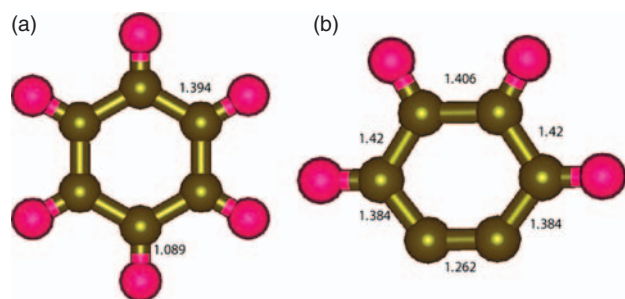


Fig. 1. Geometry of C₆H₆ (a) and C₆H₄ (b) molecules.

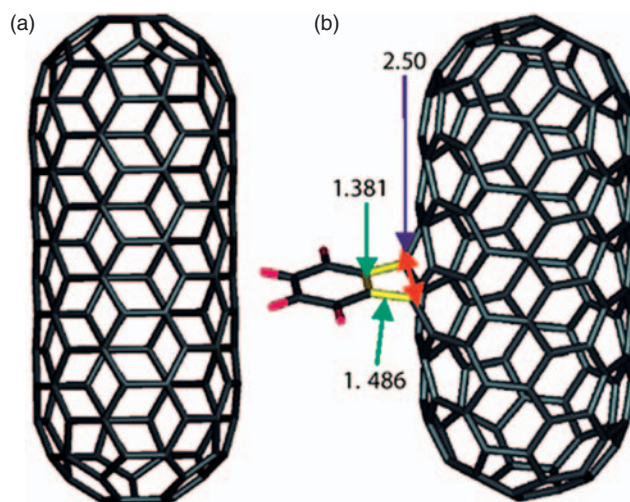


Fig. 2. Geometries of the capped (5, 5) C nanotube (a) and nanogear with one tooth (b).

two ends of the tube are capped with a half of C₆₀ to terminate the dangling bonds, as shown in Figure 2(a). As a matter of fact, such carbon nanotubes with two closed ends have been successfully synthesized in experiment.¹² The total number of carbon atoms in this tube is 140. The average binding energy is found to be 7.725 eV/C atom with the HOMO-LUMO gap of 0.420 eV. When a C₆H₄ molecule binds with this nanotube, a nano-gear with one tooth is formed (see Fig. 2(b)), labeled as Gear1. The tooth binding energy, ΔE_1 , is defined as: $\Delta E_1 = E(\text{Gear1}) - [E(\text{Tube}) + E(C_6H_4)]$, where $E(\text{Gear1})$, $E(\text{Tube})$ and $E(C_6H_4)$ are the total energies of Gear1, the carbon

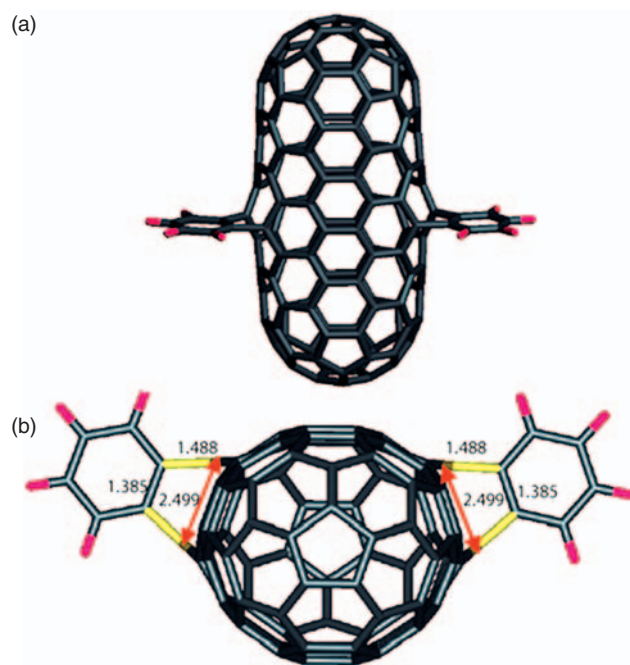


Fig. 3. Side view (a) and top view (b) of Gear2 with two teeth in stick display style.

nanotube and C_6H_4 molecule, respectively. The tooth binding energy is calculated to be -3.551 eV, suggesting that the tooth C_6H_4 is strongly bonded to the nanotube.

From a benzene molecule and a nanotube to a nano-gear, the whole formation process can be described by the reaction: $\text{Tube} + C_6H_6 \rightarrow \text{Gear1} + H_2$. The corresponding gear formation energy is found to be $+0.708$ eV, indicating that external energy should be supplied to the system in order to form a nano-gear. The nearest distance between the tooth and the tube is found to be 1.486 Å. The bond length for the two linking C atoms in C_6H_4 increases to 1.381 Å from 1.262 Å, and distance of the two linking C atoms in the nanotube increases to 2.501 Å from 2.421 Å, they are pulled outward, as shown in Figure 2(b). The HOMO-LUMO gap for this nano-gear is found to be 0.412 eV, which is smaller than that of the C nanotube. This implies that the introduction of C_6H_4 into the tube makes the system more reactive, this is favorable for the tooth growth in the next step.

We next attach one more C_6H_4 to Gear1 where the second C_6H_4 binds with two C atoms being the second neighboring pair with respect to the previous tooth in the same circumference. In this way a nano-gear with two teeth is formed, as shown in Figures 3(a and b). We label it as

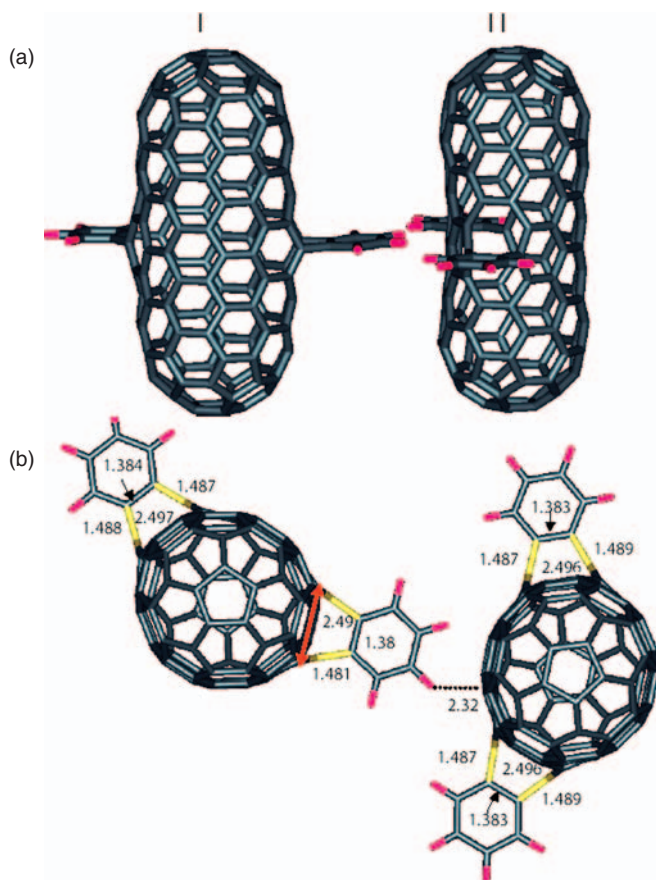


Fig. 4. Side view (a) and top view (b) of coupled two nano-gears.

Gear2. The tooth binding energy of the second tooth to Gear1, ΔE_2 , is calculated by using the equation:

$$\Delta E_2 = E(\text{Gear2}) - [E(\text{Gear1}) + E(C_6H_4)]$$

where $E(\text{Gear2})$, $E(\text{Gear1})$ and $E(C_6H_4)$ are the total energies of Gear2, Gear1 and C_6H_4 , respectively. ΔE_2 is found to be -3.682 eV, indicating the interaction between the second tooth C_6H_4 and the tube becomes slightly stronger as compared to that of the first tooth. The HOMO-LUMO gap of Gear2 is 0.405 eV. From a tube to Gear1 and to Gear2, our calculated results suggest that the nano-gears would become more dentrite-like when more tooth (C_6H_4) are introduced, and the gear will become more reactive as the HOMO-LUMO gap gradually decreases.

We next study the coupling between two nano-gears to see how strong the interaction is when they are geared and how far away they can stay. We brought the two gears (gear-I and gear-II) together, as shown in Figure 4, where one tooth in gear-I is in between the two teeth in gear-II, and the nearest distance between the two gears is initially

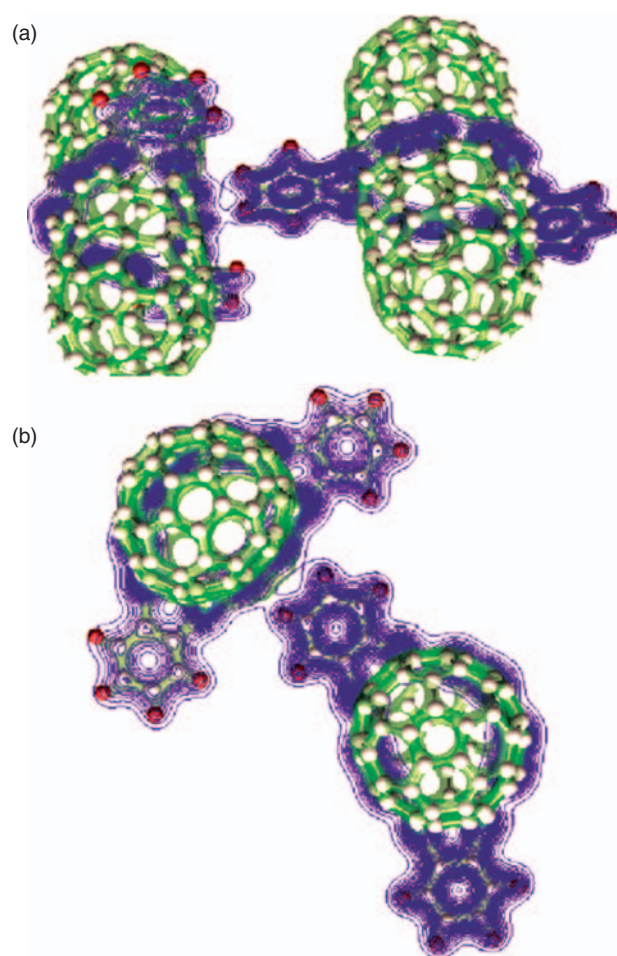


Fig. 5. Side view (a) and top view (b) of charge distributions in the coupled gears. The white and red balls represent C and H atoms, respectively. The green color is for the iso-surface, and the blue lines are the contour plot in the plane through the teeth.

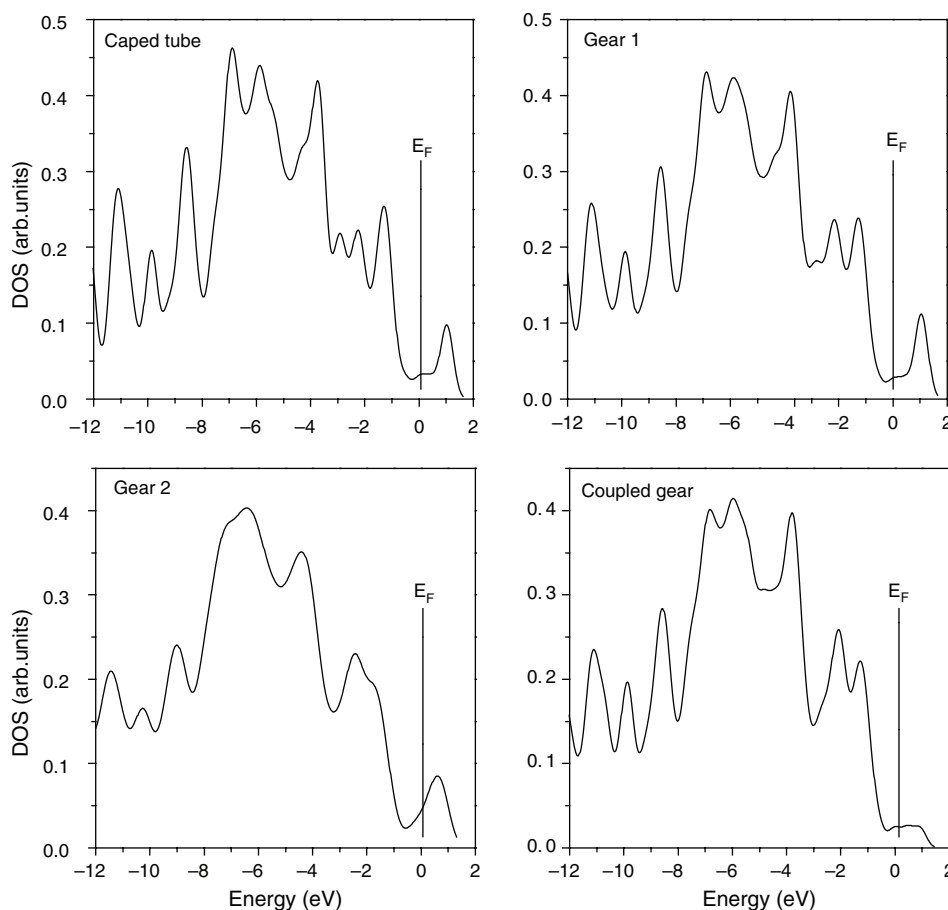


Fig. 6. Density of states (DOS). The dotted lines are for the Fermi levels.

set to be 1.1 Å, which corresponds to the bond length of CH molecule.

The calculated results are given in Figure 4(b). It was found that the nearest distance between the two gears increases to 2.32 Å after fully geometry optimization. Gearing makes the C–C bond lengths either in the teeth or in the nanotubes slightly shorter thus resulting in a more compact geometry. The interaction energy between these two gears, namely gearing energy, is found to be 0.71 eV, the bonding is stronger than van der Waals interaction but weaker than covalent bonding. The interaction causes some local distortions in the two gears, especially the atoms in the gearing side on gear-II are slightly squeezed inward.

To further understand the gearing interaction and the electronic structure of the nano-gears, we plot the charge distributions of the coupled gears in Figure 5 and the density of states (DOS) in Figure 6. The charge distributions clearly show that: (1) Gearing takes place between the teeth as well as the tooth and the body atoms on the tube; (2) Due to the π bonding of C-ring in tooth, charges accumulate there. While from Figure 6 we can see some details of the electronic structures for the four different geometries. The (5, 5) carbon nanotube itself has metallic feature, the capping in the two ends makes it less metallic-like. The

introduction of a tooth gradually changes the feature, especially when two teeth grow on the capped tube, the shape and the details of DOS are changed a lot, and the number of states at the Fermi level increases obviously, making the system more metallic-like, while when two gears are coupled, the number of states at the Fermi level is reduced, the system becomes less metallic-like. Therefore, gearing not only causes some local geometric distortions but also changes the electronic structure.

To further understand the changes in geometry when going from a C nanotube to Gear1, Gear2 and to coupled gears, we investigate the pair distribution function, which describes the distribution of interatomic distances in a system, as shown in Figure 7. The first three peaks in Figure 7(a) correspond to the nearest-, 2nd-, and 3rd-neighbouring distance in the carbon nanotube, respectively. While the first peak in Figures 7(b–d) is for C–H bond length in the tooth (or teeth). We can see that the bond length change due to gearing is minor, showing the intrinsic stability of the gear.

In summary, the formation energy, binding energy, the changes in geometry and electronic structure of the nano-gears are systematically studied. We have found that (1) the teeth (benzynes) can strongly bind with the carbon

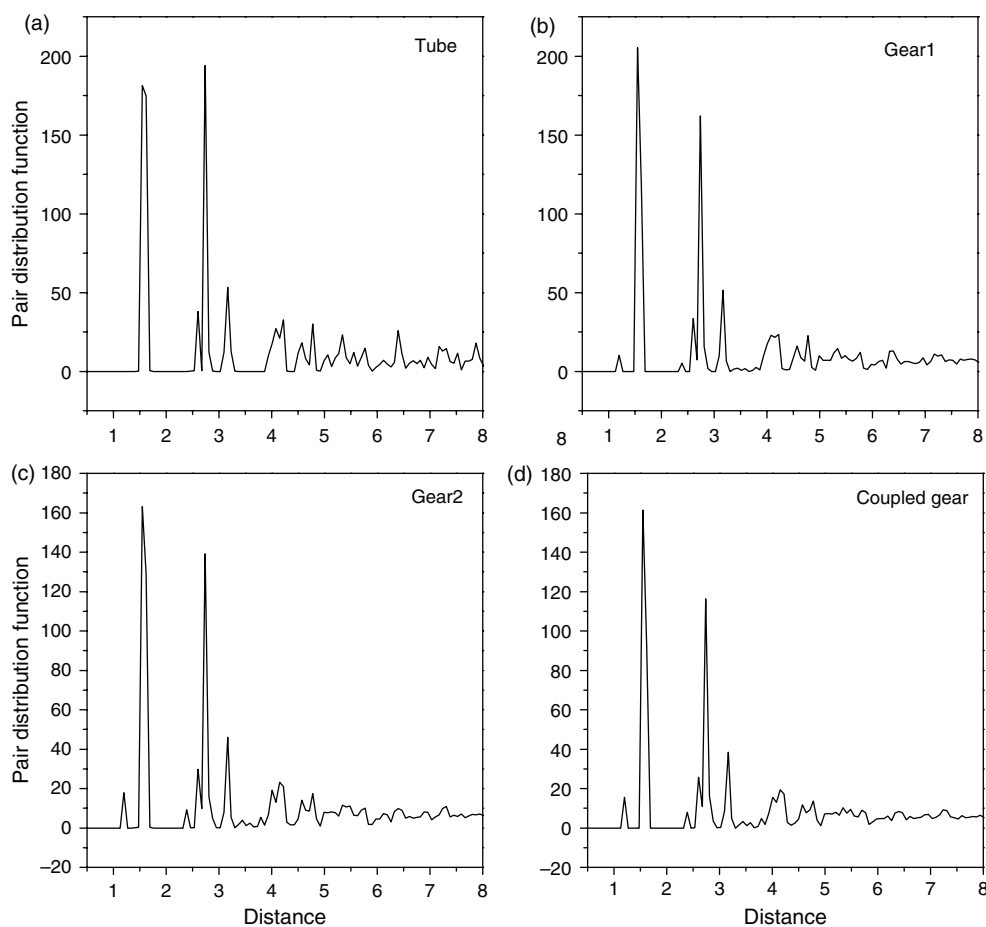


Fig. 7. Pair distribution functions for (a) the carbon nanotube, (b) Gear1, (c) Gear2, and (d) the coupled gears.

nanotube, leading to stable nano-gears and causing some local geometry deformations during the gearing; (2) As the teeth are the frontiers during the gearing, due to the charge accumulation in teeth, the interaction occurs between the teeth and the tube. Thus, one can expect that the gearing interaction can be tuned by changing the component or the size of teeth to form different types of nano-gears for different applications. For instance, one can replace C_6H_4 with C_5H_3 or $C_3N_2H_3$, or $B_3N_3H_4$, each of them has different geometrical and electronic structures, the corresponding gearing energy will be different, which would lead to different functions. The present study provides some new insight for better understanding the energetics of teeth growth and gearing, as well as for a better control of nano engineering process in synthesis.

Acknowledgment: This work is partially supported by grants from the National Natural Science Foundation of China (NSFC-10744006, NSFC-10874007).

References

1. J. P. Sauvage (ed.), *Molecular Machines and Motors*, Springer-Verlag, Berlin Heidelberg (2001).
2. S. H. Hoke, J. Molstad, D. Dilettato, M. J. Jay, D. Carlson, B. Kahr, and R. G. Cooks, *J. Org. Chem.* 57, 5069 (1992).
3. J. Han, A. Globus, R. Jaffe, and G. Deardorff, *Nanotechnology* 8, 95 (1997).
4. G. Kresse and J. Hafner, *Phys. Rev. B* 48, 13115 (1993).
5. G. Kresse and J. Furthmuller, *J. Comput. Mater. Sci.* 6, 15 (1996).
6. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pedersen, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* 46, 6671 (1992).
7. P. Blochl, *Phys. Rev. B* 50, 17953 (1994).
8. G. Kresse and D. Joubert, *Phys. Rev. B* 59, 1758 (1999).
9. D. R. Lide (ed.), *Handbook of Chemistry and Physics*, 74th edn., CRC Press, Boca Raton (1993).
10. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* 46, 6671 (1992), and references therein.
11. S. Han and J. Ihm, *Phys. Rev. B* 61, 9986 (2000).
12. X. Wang, Y. Liu, and D. Zhu, *J. Nanosci. Nanotechnol.* 2, 33 (2002).

Received: 28 August 2009. Accepted: 6 October 2009.