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***Ab initio* calculations of the structural and electronic properties of Hg_mTe_n clusters**X. Q. Wang,^{1,*} S. J. Clark,² and R. A. Abram²¹*Department of Physics, College of Science, Chongqing University, Chongqing 400044, People's Republic of China*²*Department of Physics, University of Durham, South Road, Durham DH1 3LE, United Kingdom*

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The structural and electronic properties of Hg_mTe_n ($m \neq n = 13, 16, 19, \text{ and } 28$) clusters are calculated using density functional formalism and the pseudopotential method within the generalized gradient approximation. The initial structures of all the clusters are chosen to be fragments of bulk phase HgTe with T_d symmetry. It is found that the relaxed structures of $\text{Hg}_{13}\text{Te}_{16}$ and $\text{Hg}_{16}\text{Te}_{19}$ retain their initial symmetry, whereas those of $\text{Hg}_{16}\text{Te}_{13}$, $\text{Hg}_{19}\text{Te}_{16}$, $\text{Hg}_{19}\text{Te}_{28}(=\text{Hg}_{16}\text{Te}_{19}+12\text{Te})$, and $\text{Hg}_{28}\text{Te}_{19}(=\text{Hg}_{16}\text{Te}_{19}+12\text{Hg})$, due to the Jahn-Teller distortions except for the last one, change to lower symmetries. However, it is apparent that the 12 additional Te atoms in the $\text{Hg}_{19}\text{Te}_{28}$ cluster act to stabilize the $\text{Hg}_{19}\text{Te}_{16}$ core, while the 12 additional Hg atoms in the $\text{Hg}_{28}\text{Te}_{19}$ cluster do not do so. It is also found that all the clusters studied here are initially semimetals with zero or very small highest occupied molecular orbital (HOMO) - lowest unoccupied molecular orbital (LUMO) gaps. However, after structural relaxation, $\text{Hg}_{16}\text{Te}_{13}$, $\text{Hg}_{19}\text{Te}_{16}$, $\text{Hg}_{19}\text{Te}_{28}$, and $\text{Hg}_{28}\text{Te}_{19}$ are semiconductors, while the other two clusters with unchanged symmetry are still semimetallic in nature. Therefore, as well as the size quantization, the symmetry of a cluster would seem to be another significant factor to determine its HOMO-LUMO gaps.

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I. INTRODUCTION

Semiconductor nanoparticles or quantum dots (QDs) have attracted much attention over the last decade due to their unique physical properties and potential use in a wide range of applications.^{1,2} For example, high-quality II-VI semiconductor (CdS, CdSe, CdTe, and HgTe) quantum dots, which are promising candidates for use in light emitting devices (LEDs) with tuneable emission, have recently been synthesized by colloidal chemistry.³⁻⁹ Meanwhile, there have been a number of theoretical studies devoted to the structural, electronic, and optical properties of these QDs and the smaller bare clusters.¹⁰⁻²⁴

In much previous theoretical work, the effective mass method has been applied to investigate the size-dependent electronic properties of the larger QDs, in which the underlying structure is less important.²⁵⁻²⁹ Alternatively, semi-empirical tight-binding methods have been used to get more detailed structural and electronic information of QDs up to 31 Å diameter.^{15,18-22} Also the atomistic pseudopotential approach has been applied to study the quasiparticle gap²³ and the excitonic transitions²⁴ of QDs. However, there have been much fewer first principles studies due to the computational demands. Gurin^{13,16,30} used a Hartree-Fock based method to investigate the electronic and atomic structures of CdS and ZnS clusters of about 10 atoms, and found that the microscopic structure and bonding have more of an influence on the electronic properties than the quantum confinement of electrons. Eichkorn and Ahlrichs¹⁴ have computed the structural and electronic characteristics of small ligand-stabilized CdSe clusters using a density functional theory (DFT) approach, and proposed some structural principles for clusters of this kind. Applying a simplified linear combination of atomic orbitals scheme based on the local density approximation (LDA), Joswig *et al.*¹² have studied the properties of CdS clusters with up to 200 atoms and found that the relative

stability of zincblende and wurzite structures is strongly dependent on the size of the system, and also that there is a close connection between the stability of the dot and the size of the band gap. In a more recent *ab initio* study, Troparevsky and Chelikowsky¹⁰ calculated the ground state structural and electronic properties of CdS and CdSe clusters with up to 16 atoms using the finite-difference pseudopotential method within the LDA and found a strong correlation between the binding energy and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap.

Among the II-VI QDs mentioned above, HgTe dots are of particular interest. This is because bulk HgTe is a semimetal with a small negative band gap of around -0.14 eV at 300 K,³¹ and a semimetal-to-semiconductor transition can thus be produced by size quantization. As a result, HgTe QDs of an appropriate size have been proposed as the active component of optical amplifiers operating at 1.3 and 1.5 μm wavelengths for use in telecommunication systems.^{8,32,33} Obviously, HgTe dots are of significant interest both from the fundamental point of view and for their potential applications, and it is important to get a better understanding of their properties. Unfortunately, there are only a few experimental investigations of HgTe dots,^{8,32} and almost all previous theoretical studies of II-VI semiconductor QDs have been devoted to CdSe and (or) CdS QDs. To our knowledge, no first-principles study of HgTe QDs or clusters have been reported so far.

As a first stage in working towards the study of the HgTe QDs containing more than 100 atoms, which can be readily produced experimentally, we shall focus on some smaller bare clusters in this paper. In fact, the theoretical study of small clusters is also challenging due to their many degrees of freedom, the possibility of low symmetry structures, and the lack of good structural information from experiment. In *ab initio* calculations, the predicted structure of a cluster may

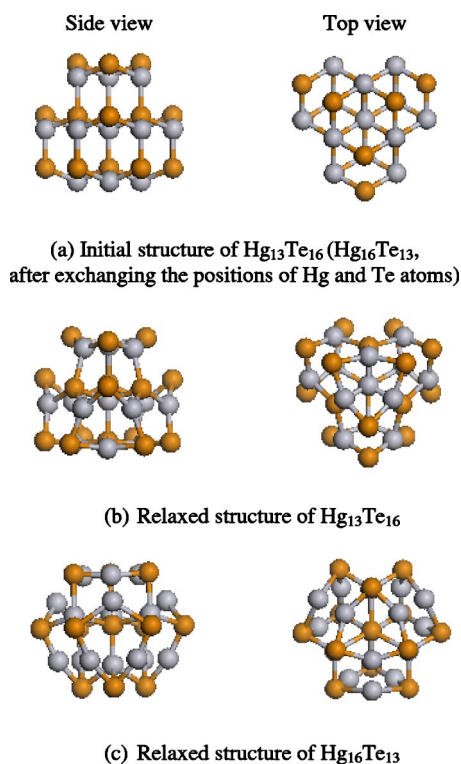


FIG. 1. (Color online) The initial and the relaxed structures of $\text{Hg}_{13}\text{Te}_{16}$ and $\text{Hg}_{16}\text{Te}_{13}$ clusters. Hg: dark ball; and Te: light ball.

depend sensitively on the initial structure used since to optimize the structure completely to seek its ground state is extremely computationally expensive. Such geometrical optimization has only been carried out for very small CdS and CdSe clusters using Langevin molecular dynamics (LMD) coupled with the simulated annealing procedure.¹⁰ However, once the cluster size exceeds about 15 atoms, this method may not be reliable owing to the long simulation times required. Therefore, in the present work, we concentrate on the structural relaxations of a group of nonstoichiometric Hg_mTe_n ($m \neq n$) clusters starting from initial states with high symmetry. By analyzing the relaxed clusters, we not only can get some information about the size effects on the binding energy and an estimate of the HOMO-LUMO gap, but also we aim to investigate the relation between the initial and the relaxed structures and the influence of the relative ratio of the numbers of component atoms within the nonstoichiometric clusters on their physical properties.

Finally, the DFT calculations carried out so far for II-VI semiconductor clusters^{10–12,14} are within the framework of LDA, which is believed to substantially overestimate the binding energies of small systems such as molecules and clusters. In this paper, we shall instead use the generalized gradient approximation (GGA), which can be expected to produce more reliable predictions of the structures and slightly better band gaps. Before carrying out the calculations reported here, we applied the same method (both within LDA and GGA) to small $(\text{CdSe})_n$ clusters as a test. The LDA binding energies and energy gaps obtained were in good agreement with those of Troparevsky *et al.*¹¹ and the GGA binding energies were a little lower as expected.

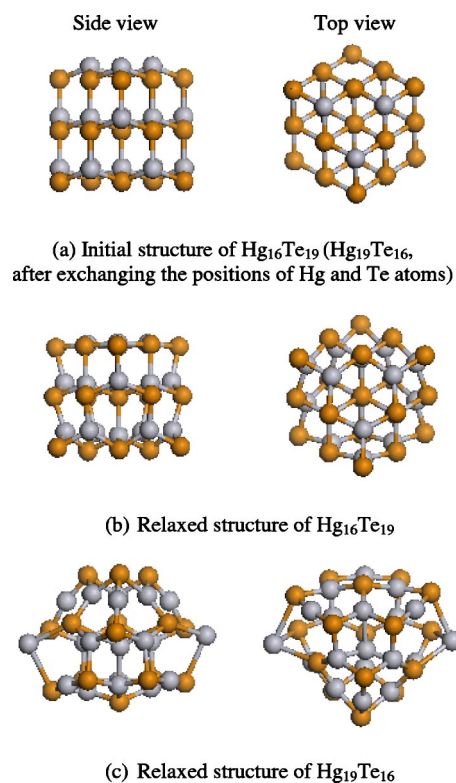


FIG. 2. (Color online) The initial and the relaxed structures of $\text{Hg}_{16}\text{Te}_{19}$ and $\text{Hg}_{19}\text{Te}_{16}$ clusters. Hg: dark ball; and Te: light ball.

II. DETAILS OF THE CALCULATIONS

Because there is no direct experimental information about the structure of HgTe clusters, we chose the initial clusters as parts of the bulk phase HgTe. Although the structures, symmetries, and coordination numbers of small clusters could be very different from those of the bulk material, we believe that the clusters of medium size ($N=30\text{--}50$) chosen in this way are a reasonably representative sample. In this paper, we focused on six nonstoichiometric Hg_mTe_n ($m \neq n=13, 16, 19,$ and 28) clusters, which were initially constructed as the fragments of bulk HgTe in the zincblende structure and have the same T_d symmetry as a unit cell of the crystal [shown in Figs. 1(a), 2(a), and 3(a)]. Note that we can easily get the initial $\text{Hg}_{19}\text{Te}_{16}$ and $\text{Hg}_{19}\text{Te}_{28}$ structures from the initial $\text{Hg}_{13}\text{Te}_{16}$ structure by adding the Hg and Te atoms to it symmetrically. Also the initial $\text{Hg}_{16}\text{Te}_{13}$, $\text{Hg}_{16}\text{Te}_{19}$, and $\text{Hg}_{28}\text{Te}_{19}$ clusters with the same symmetry can be obtained by just simply exchanging the positions of Hg and Te atoms in the above three clusters. These choices are convenient for us to compare the roles of the two types of atoms within the clusters.

The CASTEP code³⁴ has been used for our *ab initio* density-functional calculations based on the pseudopotential method in the GGA. For the Hg atoms, the d electrons were not frozen in the ionic core, but were instead treated as valence electrons, which is necessary to obtain reliable prediction of the structural and electronic properties of the clusters. The electron-ion interaction was described using Vanderbilt's ultrasoft pseudopotentials³⁵ and the exchange and correlation

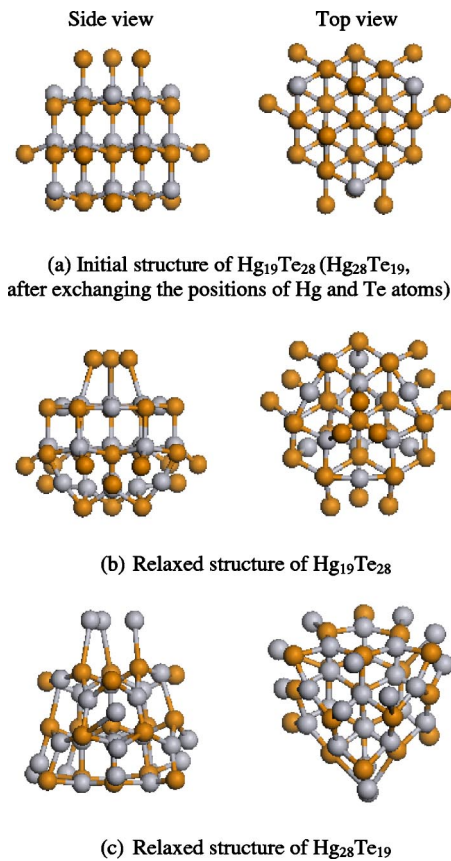


FIG. 3. (Color online) The initial and the relaxed structures of $\text{Hg}_{19}\text{Te}_{28}$ and $\text{Hg}_{16}\text{Te}_{13}$ clusters. Hg: dark ball; and Te: light ball.

functional for the GGA was taken to have the form developed by Perdew, Burke, and Ernzerhof (PBE).³⁶ The relativistic effects, which are important for the electronic properties of a heavy element such as Hg, are also taken into account in CASTEP code.

Since the valence electronic wave functions are expanded in a plane wave basis set in CASTEP, periodic boundary conditions must be used. To apply these conditions, we have to construct a periodic array of clusters and then consider a supercell of the system. In our calculations, the cutoff energy of the plane wave basis set was 400 eV, which converges the total energy of the supercell to about 0.005 eV/atom. Meanwhile, the size of the supercell is set to be 19.9 Å, which is sufficiently large that the interactions between the clusters are negligible even for the largest cluster in the present study. A preconditioned conjugate gradients routine³⁷ was used to minimize the total energy of the electronic system, and for geometry optimization, we utilized the Broyden-Fletcher-Goldfarb-Shanno (BFGS)³⁸⁻⁴¹ algorithm, which is more efficient for a complex system than the commonly used conjugate gradients approach.

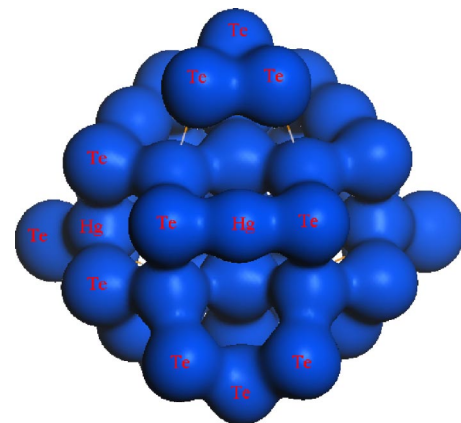
III. RESULTS AND DISCUSSIONS

The initial and the relaxed structures of Hg_mTe_n clusters ($m \neq n = 13, 16, 19, \text{ and } 28$) are shown and compared in Figs. 1-3. First, we examine the changes of the symmetry of each

TABLE I. The symmetries, average Hg-Te bond lengths, binding energies, and HOMO-LUMO gaps of the relaxed Hg_mTe_n ($m \neq n = 13, 16, 19, \text{ and } 28$) clusters.

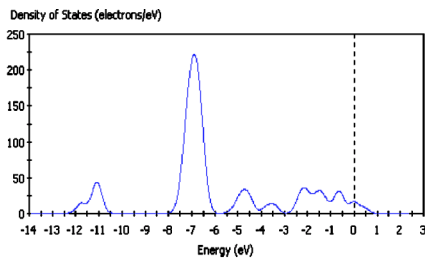
| Cluster | Symmetry | Average bond length (Å) | Binding energy (eV/atom) | Gap (eV) |
|--------------------------------|----------|-------------------------|--------------------------|----------|
| $\text{Hg}_{13}\text{Te}_{16}$ | T_d | 2.79 | 1.70 | 0.01 |
| $\text{Hg}_{16}\text{Te}_{13}$ | C_{3v} | 2.86 | 1.49 | 1.16 |
| $\text{Hg}_{16}\text{Te}_{19}$ | T_d | 2.80 | 1.70 | 0.00 |
| $\text{Hg}_{19}\text{Te}_{16}$ | C_s | 3.01 | 1.56 | 1.63 |
| $\text{Hg}_{19}\text{Te}_{28}$ | C_{3v} | 2.90 | 1.94 | 0.34 |
| $\text{Hg}_{28}\text{Te}_{19}$ | C_1 | 2.99 | 1.36 | 0.77 |

cluster after structural relaxation. Although the initial symmetries of all the clusters are T_d , the relaxed clusters do have different symmetries (as listed in Table I). We noticed that, for the Te-rich clusters $\text{Hg}_{13}\text{Te}_{16}$ and $\text{Hg}_{16}\text{Te}_{19}$, with the larger binding energies, the structural relaxations were not large enough to break their initial T_d symmetry, and thus their structures more closely resemble those of the HgTe bulk phase fragments, but for the Hg-rich clusters with the weaker binding, the structural relaxations broke their initial symmetry and the lower C_{3v} and C_s symmetries become favorable for $\text{Hg}_{16}\text{Te}_{13}$ and $\text{Hg}_{19}\text{Te}_{16}$, respectively. Among these clusters, the relaxed structure of $\text{Hg}_{19}\text{Te}_{16}$ is especially noticeable since it has almost lost all its initial symmetric properties. During its relaxation, the Hg atom at the center of the cluster has pushed the nearest four Te atoms away from it, so that the average length of the corresponding four bonds (4.37 Å) is much greater than the average taken over the whole cluster (3.01 Å). Meanwhile, there are two Hg atoms on the surface that have moved outwards [see Fig. 2(c)]. The overall result is that the symmetry of the cluster is changed from T_d to C_s . Indeed, the symmetry breakings of $\text{Hg}_{16}\text{Te}_{13}$ and $\text{Hg}_{19}\text{Te}_{16}$ (also $\text{Hg}_{28}\text{Te}_{19}$ below) can be attributed to the Jahn-Teller distortion, and this will be discussed later.

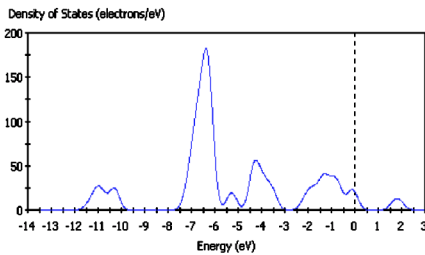


$\text{Hg}_{19}\text{Te}_{28}$ ($\text{Hg}_{19}\text{Te}_{16} + 12\text{Te}$)

FIG. 4. (Color online) Isosurfaces of total electron density of the relaxed $\text{Hg}_{19}\text{Te}_{28}$ clusters (view along the c axis of the supercell). The value of the electron density on the surfaces shown is 0.15 electrons/Å³.



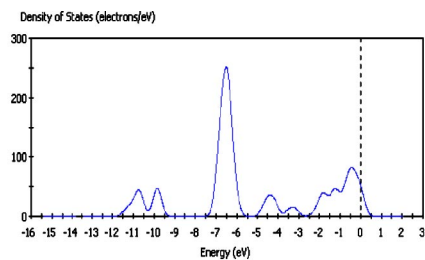
(a) Density of states (arbitrary units) of the initial $\text{Hg}_{19}\text{Te}_{16}$ cluster. The peaks have been Gaussian broadened.



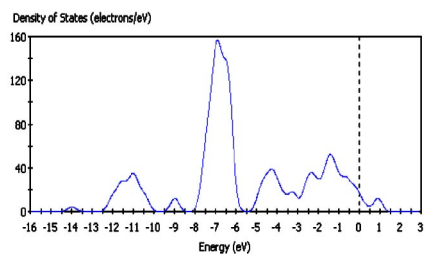
(b) Density of states (arbitrary units) of the relaxed $\text{Hg}_{19}\text{Te}_{16}$ cluster. The peaks have been Gaussian broadened.

The situation for the $\text{Hg}_{19}\text{Te}_{28}$ and $\text{Hg}_{28}\text{Te}_{19}$ is a little different from that for the other four clusters. Their initial configurations were constructed by symmetrically adding 12 singly bonded Te atoms to $\text{Hg}_{19}\text{Te}_{16}$ ($\text{Hg}_{19}\text{Te}_{16}+12\text{Te}$) and 12 singly bonded Hg atoms to $\text{Hg}_{16}\text{Te}_{19}$ ($\text{Hg}_{16}\text{Te}_{19}+12\text{Hg}$), respectively. The role of these 12 extra atoms should be somewhat similar to that of ligand molecules, and can be expected to make the original cluster more stable. Therefore it is no surprise that the $\text{Hg}_{19}\text{Te}_{28}$ cluster relaxed to a state with higher symmetry (C_{3v}) and larger binding energy (1.94 eV/atom) than for the $\text{Hg}_{19}\text{Te}_{16}$ (C_s and 1.56 eV/atom). Because of the 12 extra Te atoms, the $\text{Hg}_{19}\text{Te}_{16}$ core did not relax like the bare $\text{Hg}_{19}\text{Te}_{16}$ cluster,

but in the manner similar to $\text{Hg}_{16}\text{Te}_{19}$, keeping the initial T_d symmetry. The overall symmetry of the relaxed $\text{Hg}_{19}\text{Te}_{28}$ was reduced to C_{3v} only because the 12 extra Te atoms formed Te–Te bonds in two different ways. The Te atoms go into four groups of three atoms. In one group, the atoms form three bonds with an equal length of 2.73 Å, and in the other three groups, only two bonds are formed with a length of 2.69 Å. The Te–Te bonds are clearly shown in Fig. 4, where an isosurface of the total electron density of the relaxed $\text{Hg}_{19}\text{Te}_{28}$ cluster is presented. In the case of ligand molecules, there would be no bond formed between them because of the absence of dangling bonds. However, the structure of the $\text{Hg}_{28}\text{Te}_{19}$ cluster relaxed in a less regular way. As



(a) Density of states (arbitrary units) of the initial $\text{Hg}_{19}\text{Te}_{28}$ cluster. The peaks have been Gaussian broadened.



(b) Density of states (arbitrary units) of the relaxed $\text{Hg}_{19}\text{Te}_{28}$ cluster. The peaks have been Gaussian broadened.

FIG. 5. The density of states of the initial (a) and the relaxed (b) $\text{Hg}_{19}\text{Te}_{16}$ cluster. The curves are plotted by applying Gaussian broadening with a width of 0.2 eV to the CASTEP eigenvalues. The Fermi energy is set to be the zero point of the energy for each case.

FIG. 6. The density of states of the initial (a) and the relaxed (b) $\text{Hg}_{19}\text{Te}_{28}$ cluster. The curves are plotted in the same way as in Fig. 5.

a result, the symmetry of this cluster is changed from T_d to C_1 . This means that the 12 extra Hg atoms in the $\text{Hg}_{28}\text{Te}_{19}$ cluster do not act like the 12 extra Te atoms in the $\text{Hg}_{19}\text{Te}_{28}$ cluster. We note that it may not be a very good approximation to use Hg or Te as surfactants, but in this work we initially wish to study only the “pure” material. Using other surfactants such as small organic molecules is of interest and will be a future study of ours.

By comparing the initial and the relaxed structures of the six clusters discussed above, we also found that the outermost Hg atoms have the tendency to move inwards whereas the Te atoms have the tendency to move outwards in almost all the cases except for $\text{Hg}_{19}\text{Te}_{16}$, in which the motion of the atoms is rather more complicated. This phenomenon is similar to that found in the surface relaxations of CdS and CdSe clusters,^{12,22,42,43} where the outermost Cd atoms move inwards while the S or Se atoms move outwards.

The calculated binding energies and HOMO-LUMO gaps of the relaxed clusters are listed in Table I. The results show that the Hg-rich clusters, with lower symmetries and smaller binding energies, have larger energy gaps (>1 eV), and the Te-rich clusters, with higher symmetries and larger binding energies, possess smaller energy gaps (<0.4 eV). All three Hg-rich clusters become semiconductors, whereas only one of the Te-rich clusters ($\text{Hg}_{19}\text{Te}_{28}$ in C_v symmetry) becomes a semiconductor with a energy gap of 0.34 eV. The other two clusters ($\text{Hg}_{13}\text{Te}_{16}$ and $\text{Hg}_{16}\text{Te}_{19}$, both in T_d symmetry) are still semimetals, as for the bulk phase HgTe. It is interesting to consider why the size-effect does not lead to a semimetal-semiconductor transition in the two Te-rich clusters. To answer this question, we compared the initial and the relaxed energy level structures and HOMO-LUMO gaps of the clusters. It was found that for the initial configurations with T_d symmetry the HOMOs and LUMOs of the clusters are degenerate (for $\text{Hg}_{16}\text{Te}_{13}$, $\text{Hg}_{19}\text{Te}_{16}$, and $\text{Hg}_{19}\text{Te}_{16}+12\text{Te}$) or are very close to each other (for $\text{Hg}_{13}\text{Te}_{16}$, $\text{Hg}_{16}\text{Te}_{19}$, and $\text{Hg}_{16}\text{Te}_{19}+12\text{Hg}$). After relaxation, $\text{Hg}_{16}\text{Te}_{13}$, $\text{Hg}_{19}\text{Te}_{16}$, $\text{Hg}_{19}\text{Te}_{16}+12\text{Te}$, and $\text{Hg}_{16}\text{Te}_{19}+12\text{Hg}$ reached final states with lower symmetries and the degeneracy of their HOMOs and LUMOs is eliminated, resulting in the appearance of energy gaps of more than 0.3 eV. This is just the result of the so-called Jahn-Teller distortions. But for $\text{Hg}_{13}\text{Te}_{16}$ and $\text{Hg}_{16}\text{Te}_{19}$, because their HOMOs and LUMOs are not degenerate (though very close to each other), the Jahn-Teller distortions did not occur. So, the relaxed $\text{Hg}_{13}\text{Te}_{16}$ and $\text{Hg}_{16}\text{Te}_{19}$ clusters keep initial T_d symmetry,

and the basic characteristics of their energy level structure are also unchanged, the HOMO-LUMO gaps being still almost zero. In Figs. 5 and 6, the densities of states of $\text{Hg}_{19}\text{Te}_{16}$ and $\text{Hg}_{19}\text{Te}_{28}$ clusters before and after relaxation are shown. In Fig. 5(b), the formation of the energy gap of the relaxed $\text{Hg}_{19}\text{Te}_{16}$ cluster is very clear. It appears that, at least for the small clusters, the symmetry is another important factor to determine the energy gap besides the size quantization.

In the previous theoretical studies for the stoichiometric CdS and CdSe clusters,^{10–12} it had been found that the calculated HOMO-LUMO gaps correlate strongly with the calculated binding energies. In the present study, if we compare the Te-rich and Hg-rich clusters, or compare each pair of clusters with the same total number of atoms, a similar correlation can be found in both cases although the number of the clusters studied here is not large enough to reach a definite conclusion. However, it is clear that the energy gaps are closely related to the symmetries of the clusters, and some of the studied clusters have larger gaps due to the Jahn-Teller distortions.

IV. CONCLUSION

In summary, the structural and electronic properties of Hg_mTe_n ($m \neq n=13, 16, 19, \text{ and } 28$) clusters have been calculated by density functional techniques. In what we believe is the first *ab initio* study of Hg_mTe_n clusters, our results show that the relaxed structures of $\text{Hg}_{13}\text{Te}_{16}$ and $\text{Hg}_{16}\text{Te}_{19}$ clusters keep the T_d symmetry of the initial state used in the calculations, whereas those of $\text{Hg}_{16}\text{Te}_{13}$, $\text{Hg}_{19}\text{Te}_{16}$, $\text{Hg}_{19}\text{Te}_{28}(=\text{Hg}_{16}\text{Te}_{19}+12\text{Te})$, and $\text{Hg}_{28}\text{Te}_{19}(=\text{Hg}_{16}\text{Te}_{19}+12\text{Hg})$ change to lower symmetries due to the Jahn-Teller distortions except for the last one. The 12 singly bonded Te atoms added to the $\text{Hg}_{19}\text{Te}_{16}$ cluster behave rather like ligand molecules and act to stabilize the initial structures of the core. But the 12 single bonded Hg atoms added to $\text{Hg}_{16}\text{Te}_{19}$ cluster seem not to act in the same way. It is also found that, as well as the size quantization, the symmetry of a cluster is another significant factor in determining the HOMO-LUMO gaps. In the initial state, all the clusters studied here are semimetals with zero or very small HOMO-LUMO gaps. After relaxation, due to the change of the symmetry, $\text{Hg}_{16}\text{Te}_{13}$, $\text{Hg}_{19}\text{Te}_{16}$, $\text{Hg}_{19}\text{Te}_{28}$, and $\text{Hg}_{28}\text{Te}_{19}$ become semiconductors, while the other two clusters with unchanged symmetry are still semimetals.

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¹A. D. Yoffe, *Adv. Phys.* **42**, 173 (1993).

²A. P. Alivisatos, *J. Phys. Chem.* **100**, 13226 (1996).

³T. Vossmeier, L. Katsikas, M. Giersig, I. G. Popovoc, K. Diesner, A. Chemseddine, A. Eychmüller, and H. Weller, *J. Phys. Chem.* **98**, 7665 (1994).

⁴A. L. Rogach, A. Kornowski, M. Gao, A. Eychmüller, and H. Weller, *J. Phys. Chem.* **103**, 3065 (1999).

⁵A. L. Rogach, L. Katsikas, A. Kornowski, D. Su, A. Eychmüller,

and H. Weller, *Ber. Bunsenges. Phys. Chem.* **100**, 1772 (1996).

⁶A. L. Rogach, L. Katsikas, A. Kornowski, D. Su, A. Eychmüller, and H. Weller, *Ber. Bunsenges. Phys. Chem.* **101**, 1668 (1997).

⁷M. Gao, S. Kirstein, H. Möhwald, A. L. Rogach, A. Kornowski, A. Eychmüller, and H. Weller, *J. Phys. Chem. B* **102**, 8360 (1998).

⁸A. L. Rogach, S. V. Kershaw, M. Burt, M. Harrison, A. Kornowski, A. Eychmüller, and H. Weller, *Adv. Mater. (Weinheim, Ger.)* **11**, 552 (1999).

- ⁹S. V. Kershaw, M. Burt, M. Harrison, A. L. Rogach, H. Weller, and A. Eychmüller, *Appl. Phys. Lett.* **75**, 1694 (1999).
- ¹⁰M. C. Tropicovsky and J. R. Chelikowsky, *J. Chem. Phys.* **114**, 943 (2001).
- ¹¹M. C. Tropicovsky, L. Kronik, and J. R. Chelikowsky, *Phys. Rev. B* **65**, 033311 (2001).
- ¹²J.-O. Joswig, M. Springborg, and G. Seifert, *J. Phys. Chem. B* **104**, 2617 (2000).
- ¹³V. S. Gurin, *Int. J. Quantum Chem.* **71**, 337 (1999).
- ¹⁴K. Eichkorn and R. Ahlrichs, *Chem. Phys. Lett.* **288**, 235 (1998).
- ¹⁵K. Leung and K. B. Whaley, *J. Chem. Phys.* **110**, 11012 (1999).
- ¹⁶V. S. Gurin, *Solid State Commun.* **108**, 389 (1998).
- ¹⁷K. Leung, S. Pokrant, and K. B. Whaley, *Phys. Rev. B* **57**, 12 291 (1998).
- ¹⁸N. A. Hill and K. B. Whaley, *J. Chem. Phys.* **100**, 2831 (1994).
- ¹⁹N. A. Hill and K. B. Whaley, *J. Chem. Phys.* **99**, 3707 (1993).
- ²⁰P. E. Lippens and M. Lannoo, *Phys. Rev. B* **41**, 6079 (1990).
- ²¹P. E. Lippens and M. Lannoo, *Phys. Rev. B* **39**, 10 935 (1989).
- ²²Y. R. Wang and C. B. Duke, *Phys. Rev. B* **37**, 6417 (1988).
- ²³A. Franceschetti and A. Zunger, *Appl. Phys. Lett.* **76**, 1731 (2000).
- ²⁴L. W. Wang and A. Zunger, *J. Phys. Chem.* **102**, 6449 (1998).
- ²⁵L. E. Brus, *J. Chem. Phys.* **79**, 5566 (1983).
- ²⁶L. E. Brus, *J. Chem. Phys.* **80**, 4403 (1984).
- ²⁷H. M. Schmidt and H. Weller, *Chem. Phys. Lett.* **129**, 615 (1986).
- ²⁸G. T. Einevoll, *Phys. Rev. B* **45**, 3410 (1992).
- ²⁹Y. Masumoto and K. Sonobe, *Phys. Rev. B* **56**, 9734 (1997).
- ³⁰V. S. Gurin, *Z. Phys. D: At., Mol. Clusters* **42**, 65 (1997).
- ³¹*Semiconductors: Basic Data*, 2nd revised ed., edited by O. Madelung (Springer, Berlin, 1996), p. 187.
- ³²M. T. Harrison, S. V. Kershaw, M. G. Murt, A. L. Rogach, A. Kornowski, A. Eychmüller, and H. Weller, *Pure Appl. Chem.* **72**, 295 (2000).
- ³³A. Eychmüller and A. L. Rogach, *Pure Appl. Chem.* **72**, 179 (2000).
- ³⁴M. D. Segall, P. L. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne, *J. Phys.: Condens. Matter* **14**, 2717 (2002).
- ³⁵D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ³⁶J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ³⁷M. C. Payne, M. P. Teter, and J. D. Joannopolous, *Rev. Mod. Phys.* **64**, 1045 (1992).
- ³⁸C. G. Broyden, *J. Inst. Math. Appl.* **6**, 76 (1970).
- ³⁹R. Fletcher, *Comput. J.* **13**, 317 (1970).
- ⁴⁰D. Goldfarb, *Math. Comput.* **24**, 23 (1970).
- ⁴¹D. F. Shanno, *Math. Comput.* **24**, 674 (1970).
- ⁴²T. N. Horsky, G. R. Brandes, K. F. Canter, C. B. Duke, A. Paton, D. L. Lessor, A. Kahn, S. F. Horng, K. Stevens, K. Stiles, and A. P. Mills, Jr., *Phys. Rev. B* **46**, 7011 (1992).
- ⁴³P. Schröder, P. Krüger, and J. Pollmann, *Phys. Rev. B* **49**, 17 092 (1994).