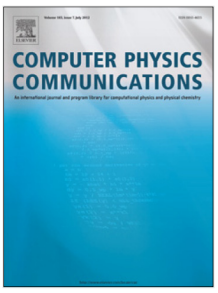
Accepted Manuscript



Studying the varied shapes of gold clusters by an elegant optimization algorithm that hybridizes the density functional tight-binding theory and the density functional theory

Tsung-Wen Yen, Thong-Leng Lim, Tiem-Leong Yoon, S.K. Lai

PII: S0010-4655(17)30209-6
DOI: http://dx.doi.org/10.1016/j.cpc.2017.07.002
Reference: COMPHY 6261

To appear in: *Computer Physics Communications*

Received date : 3 February 2017
Revised date : 30 June 2017
Accepted date : 1 July 2017

Please cite this article as: T. Yen, T. Lim, T. Yoon, S.K. Lai, Studying the varied shapes of gold clusters by an elegant optimization algorithm that hybridizes the density functional tight-binding theory and the density functional theory, *Computer Physics Communications* (2017), http://dx.doi.org/10.1016/j.cpc.2017.07.002

Studying the varied shapes of gold clusters by an elegant optimization algorithm that hybridizes the density functional tight-binding theory and the density functional theory

Tsung-Wen Yen[a], Thong-Leng Lim[b], Tiem-Leong Yoon[c], S.K. Lai[a,*]

[a]*Complex Liquids Laboratory, Department of Physics, National Central University, Chungli 32001 Taiwan*

[b]*Faculty of Engineering and Technology, Multimedia University, Melaka Campus, Jalan Air Keroh Lama, Bukit Beruang 75450 Melaka, Malaysia*

[c]*School of Physics, Universiti Sains Malaysia, 11800 USM, Pulau Penang, Malaysia*

(Revised manuscript, June 28, 2017)

We combined a new parametrized density functional tight-binding (DFTB) theory [Fihey et al., J. Comput. Chem. 36 (2015) 2075] with an unbiased modified basin hopping (MBH) optimization algorithm [T. W. Yen and S. K. Lai, J. Chem. Phys. 142 (2015) 084313] and applied it to calculate the lowest energy structures of Au clusters. From the calculated topologies and their conformational changes, we find that this DFTB/MBH method is a necessary procedure for a systematic study of the structural development of Au clusters but is somewhat insufficient for a quantitative study. As a result, we propose an extended hybrized algorithm. This improved algorithm proceeds in two steps. In the first step, the DFTB theory is employed to calculate the total energy of the cluster and this step (through running DFTB/MBH for given Monte-Carlo steps) is meant to efficiently bring the Au cluster near to the region of the lowest energy minimum since the cluster as a whole has explicitly considered the interactions of valence electrons with ions, albeit semi-quantitatively. Then, in the second succeeding step, the energy-minimum searching process will continue with a skilledly replacement of the energy calculated by the DFTB in the first step by one that is carried out in a full density functional theory (DFT). In these subsequent DFT calculations, we couple it also with the MBH strategy and proceed the DFT/MBH optimization until the lowest energy value is found. We checked that this extended algorithm successfully predicts the twisted pyramidal structure for the Au_{40} cluster and correctly predicts also the linear shape of C_8 which our previous DFTB/MBH method failed to do so. Perhaps more remarkable is the topological growth of Au_n: it changes from a planar (n=3-11) → an oblate-like cage (n=12-15) → a hollow-like cage (n=16-18) and finally a pyramidal-like cage (n=19,20). These varied forms of the cluster's shapes are consistent with those reported in the literature.

Keywords: metallic cluster; density functional theory; optimization algorithm; topological transition

* Corresponding author: *sklai@coll.phy.ncu.edu.tw*