

Scalar relativistic effect on lattice dimerization in metastable gold nanowire of finite length

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Abstract

Recent observation by Xiao et al. [L. Xiao, B. Tollberg, X. Hu, L. Wang, J. Chem. Phys. 124 (2006) 114309.] suggested substantial lattice distortion in linear gold nanowires of finite chain length up to 2 nm and remarkably they have predicted the disappearance of Peierls distortion in the infinite limit. In the present study we adopt the method of constrained relaxation search to find out the existence of true dimerization in these systems. The role of scalar relativistic effect on lattice dimerization in these nanowires has been investigated using first-principle density functional calculations at zero-order regular approximation level. It is well known that real lattice dimerization in gold nanowires are perceptible just immediately before the breakage of the wires. While exploring the role of scalar relativity, it has been observed that scalar relativity decreases the dimerization amplitude of each of the linear metastable gold nanowires compared to its non-relativistic counterpart. Another interesting observation is the greater stabilization of Au₅ and Au₇ in constrained relaxation search compared to that of the unconstrained relaxation scheme in relativistic method. The dramatic even–odd oscillations are observed in the values of the dimerization amplitudes, HOMO–LUMO energy gap, and second differences of wire energies. The results are very stable and consistent up to Au₉.

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1. Introduction

Recent years have witnessed an unprecedented surge of interest in nanostructured materials that heralds a technological revolution in molecular electronic devices and applications in the related field [1–4]. This upsurge of interest has brought in particular quantum wires, namely, metallic nanowires and linear atomic chains into the focus of mainstream research. Of the several quantum wires studied so far, gold nanowires and linear gold atomic chains have attracted a considerable degree of attention due to their amazing versatility of structural features [5–9]. The physical properties of one dimensional (1D) and quasi-1D materials are strongly determined by certain quantum effects, viz. electron–phonon coupling and electron–electron corre-

lation. The most striking consequence of these quantum effects is the Peierls instability [10]. It is well known that 1D lattice can not escape itself from the abysmal depth of Peierls instability which in turn triggers spontaneous symmetry breaking and imparts a driving force to the dimerization of the lattice. Apart from these quantum effects, relativistic effect also plays a very crucial role to determine the properties of gold. Theoretical chemistry of gold at the relativistic level has been explored extensively [11–14]. Relativistic effect arises when electrons move fast round a heavy nucleus (like gold) and can be explained by Dirac equation. Relativistic effect can generally be categorized into two major parts, one is the scalar relativistic (SR) effect which includes mass–velocity and Darwin corrections and the other one is the spin–orbit interaction.

Historically, Ohnishi et al. [15] first visualized monatomic gold wires between two gold electrodes by transmission electron microscopy (TEM) and provided direct

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experimental information about their structures. The experimental results indicate that bond length between two gold atoms is 3.5–4.0 Å which is much larger than Au–Au separation at the bulk and the wire is stable in spite of strong Rayleigh instability. In another pioneering work, Yanson et al. [16] have described the breaking of atomic-scale gold contacts leading to the formation of gold chains which are one atom thick and four atoms long. After that in a remarkable experiment, Kondo et al. [17] generated gold nanowire of length up to 15 nm. Soon after these discoveries, a great many theoretical effort has been devoted to address the puzzling structural features of gold nanowire using first-principle calculations as prime investigating tool. De Maria and Springborg [18] proposed that for monatomic gold chain it is more preferable to dimerize than to remain equally spaced when the bond length is 2.8 Å and longer. Their work is further supported by Nakamura et al. [19] who proposed the importance of this dimerization of gold nanowires at larger bond lengths over that at shorter one. They also reported the structural stability of single and double rows of Au atoms, using first-principle density functional calculations. Such a dimerization at larger bond lengths leads to the breakage of the wire (as reported in Refs. [20,21]). Sánchez-Portal et al. [21] further showed that a planar zigzag geometry is more stable than its linear analog for monatomic Au wires. They also provided an explanation for the large inter atomic distances as evidenced from TEM measurement.

Apart from the study of the monatomic gold wires, several works have also been done for gold clusters [22–25]. Häkkinen et al. [22] investigated the atomic and electronic structures of neutral and anionic gold clusters using the density functional theory with scalar relativistic *ab initio* pseudo potentials and a generalized gradient correction. Some of the properties calculated for those clusters have shown the dramatic even–odd effect. Their work was in good agreement with the later works of Wang et al. [23] where the even–odd effect was clearly observed. Recently, Xiao et al. [24] have carried out DFT calculations to study gold clusters up to 55 atoms. They also observed that zigzag monatomic Au nanowire is more stable than their linear analogs which are in accordance with the earlier predictions [21]. Further, they [24] also suggested a substantial lattice dimerization in these gold nanowires for a finite chain of length up to 2 nm and have accounted for the disappearance of the same in the infinite limit.

Albeit zigzag structure is the stable form of Au wire, but under the condition of extreme tension i.e., prior to breaking of the wire, it becomes linear. Moreover, the earlier works [19,21] also suggested that lattice dimerization is perceptible just immediately before the rupture of the wire. It is also noticeable that unconstrained relaxation search in *ab initio* scheme fails to account true lattice dimerization in these nanowires [24]. The focus of the present study involves a search for true lattice dimerization in the linearized gold nanowires of finite chain length and how dimerization amplitude is modified due to scalar relativistic

effect. Moreover, we also intend to see whether the results of geometry optimization for unconstrained relaxation truly reflect the global minima in the energy landscape of these nanowires. The explicit role of scalar relativistic effect on the lattice dimerization and the concomitant change in the HOMO–LUMO energy gap, binding energies and second differences of wire energies of these metastable systems are also being addressed.

2. Computational details

All the calculations have been implemented in the Amsterdam density functional package (ADF 2006.01) [26]. The linear gold nanowires, viz. Au₄, Au₅, Au₆, Au₇, Au₈ and Au₉ are optimized using both scalar relativistic and non-relativistic methods in unconstrained relaxation approach. The zero-order regular approximation (ZORA) [27] is adopted for all the calculations in the relativistic method. In unconstrained relaxation no definite periodicity in bond length is observed for these nanowires which indicate that true lattice dimerization is not perceptible. Hence in order to search for true dimerization, constrained relaxation scheme has been adopted. In this scheme, the shortest bond length of the optimized geometry for each of the linear gold nanowires is fixed while the longer bond length is varied. The exchange–correlation functional used in all these calculations of these nanowires is BLYP which contains Becke [28] exchange and Lee–Yang–Parr (LYP) [29] correlation functional. For all the geometry optimizations and the single point energy calculations TZP is chosen as the basis set which consists of a triple zeta basis augmented with one polarization function. All the quantum chemical calculations performed involve spin restricted calculations for the even numbered gold nanowires (Au₄, Au₆ and Au₈) and spin polarized one for the odd numbered nanowires (Au₅, Au₇ and Au₉).

3. Results and discussion

The ZORA approximation to Dirac equation has been successfully implemented previously [30] to molecules neglecting the spin-orbit interaction. This is what is referred to as the scalar relativistic approximation which plays a significant role in the study of these nanowires. The ZORA Hamiltonian yields satisfactory results in atomic orbitals, particularly for valence orbitals [27].

Table 1 illustrates a comparison of the energy values for all the linear gold nanowires in unconstrained and constrained relaxation searches in both non-relativistic and relativistic methods. Interestingly it has been observed that the geometries of Au₅ and Au₇ are more stable under constrained relaxation scheme relative to their unconstrained analogs in relativistic method. In unconstrained relaxation search, the geometries are lacking any definite periodicity in the bond lengths. Hence a constrained relaxation search has been carried out to find a true lattice dimerization in these linear nanowires.

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