

Ab initio calculation of half-metallic ferrocene-based nanowire

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Half-metallic nanostructure is highly applicable in the field of Spintronics and electronic device technology. We examine the electronic properties of a ferrocene-based nanowire as a possible candidate for a half-metallic nanostructure using VASP and SIESTA. Ferrocene-based nanowire shows high stability in both binding energy simulation and molecular dynamics (MD) simulation. The density of states (DOS) and the projected DOS of the ferrocene-based nanowire indicate that one-dimensional clustering of ferrocene molecules can be explained because of p-d orbital hybridization between iron and carbon. Half-metallic property and energy dispersion at the Fermi level due to one-dimensional structure is also observed from the DOS results.

Introduction

Understanding electronic characteristics of one-dimensional nanostructures has become more important in the field of physics, since it provides valuable knowledge in useful applications such as electronic device technology. In this paper, we examine the electronic properties of a ferrocene-based nanowire as a possible candidate for an applicable one-dimensional nanostructure. Previously, ab initio calculations of transition metal-benzene (or CP) sandwich structures has been conducted to understand the orbital hybridization of the structure and its electronic properties using the tight binding Hamiltonian model [1],[2].

We expand a ferrocene molecule (iron-CP sandwich structure) to an infinite nanowire and conduct computer simulations using both VASP (Vienna Ab-initio Simulation Package) code and SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) package for an ab initio calculation with density functional theory (DFT). We, as a result, show that the binding energy of the ferrocene-based nanowire is large enough to sustain the structure, and the density of states of the structure at Fermi energy depends on spin of electrons indicating that this molecule-based nanostructure can be applicable to Spintronics devices.

Method

We perform DFT calculation with VASP code and SIESTA package (on the EDISON nanophysics website) using generalized gradient approximation (GGA+U in VASP, GGA-PBE in SIESTA) pseudo-potential and the double-zeta basis set. ENCUT 400ev option is used in VASP, and 200eV is used in SIESTA.

First, we find most stable atomic arrangement in a ferrocene molecule and a ferrocene-based nanowire. Relaxation of a ferrocene molecule is conducted in $20 \times 20 \times 20 \text{ \AA}^3$ unit cell, with a single K-point. Relaxation of a ferrocene-based nanowire is conducted in $20 \times 20 \times L_z \text{ \AA}^3$ unit cell, which is made up of one ferrocene molecule and one iron atom above the molecule, with a single K-point. We try many different values of L_z so that determine optimum positions of atoms giving minimum total energy. Then, we obtain binding energy with the relaxed arrangement using both VASP and SIESTA, and conduct molecular dynamics (MD) by setting one step as 1fs to figure out if the nanowire can exist stably in nature using VASP.

Second, we obtain the density of states(DOS) and the projected density of states(PDOS) of the ferrocene-based nanowire for two different spin

states of electrons. The DOS and PDOS results are almost consistent as we change sampling methods in various ways including multi-stacked supercell or the number of K-points in c direction. In the Results section, we present the results of the case that we use the (1x1x21) grid in the Monkhost-Pack scheme comparing the results of VASP and SIESTA.

Results

Ferrocene has sandwich-like molecular structure which consists of two cross sited Cyclopentadienyls (CPs) and one iron between CPs (FIG. 1(a)). We added one iron atom onto the ferrocene molecule to make a unit cell of a one-dimensional ferrocene-based nanowire. The relaxed distance between the CPs is 3.33 Å in one ferrocene molecule and 3.42 Å in the nanowire structure. The latter does not change when we expand the unit cell to a multi-stacked supercell by putting more molecules on the top of the original unit cell.

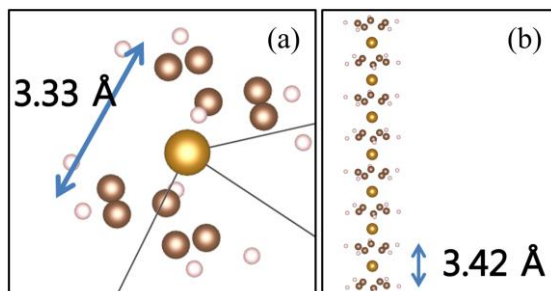


FIG. 1. (a) Relaxed ferrocene molecule (b) Relaxed ferrocene-based nanowire

We compare two energies to determine whether the one-dimensional nanowire is more stable than two molecules optimally distant from each other. The optimal distance between them (D) is found with the same method used for relaxation. We call the binding energy of the two molecules as ‘binding energy 1 (E_{b1})’ and the binding energy of the ferrocene-iron-ferrocene structure as ‘binding energy 2 (E_{b2})’ (FIG.2). The VASP calculation result is $E_{b1} = -0.1\text{eV}$ and $E_{b2} = -1.6\text{eV}$ while the SIESTA result is $E_{b1} = -0.4\text{eV}$ and $E_{b2} = -2\text{eV}$. The difference between E_{b1} and E_{b2} is about 1.5eV, which indicates that the stacked nanowire structure

can be more stable system than the system in which two molecules keep distance from each other to minimize their total energy. We can also see high stability of the ferrocene-based one-dimensional structure from the MD results (FIG. 3.). Above room temperature (500K), the ferrocene-based nanowire maintains its structure after 1ps (FIG. 3(b)).

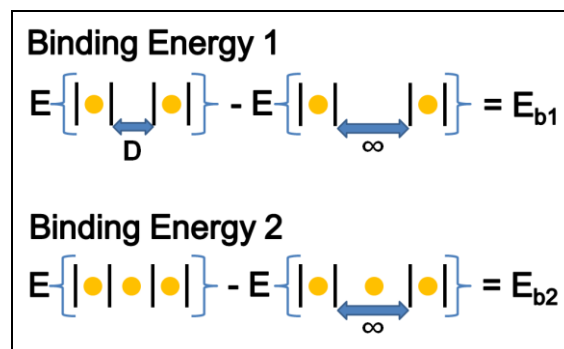


FIG. 2. Schematic diagram of binding energy. In VASP, $E_{b1} = -0.1\text{eV}$ when $D = 3.4\text{Å}$, and $E_{b2} = -1.6\text{eV}$. In SIESTA, $E_{b1} = -0.4\text{eV}$ when $D = 3.2\text{Å}$, and $E_{b2} = -2\text{eV}$. Binding energy shows that the system prefers ferrocene-iron-ferrocene structure to the structure where ferrocene molecules keep their distance (D) optimum from each other.

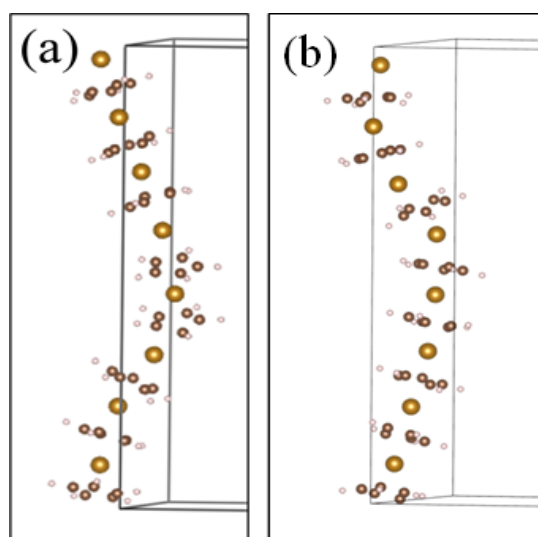


FIG. 3. MD calculation result shows stability of ferrocene-based nanowire in high temperature circumstance. (a) 500K, 374fs (b) 500K, 1012fs

The DOS results of the ferrocene-based nanowire depend on the methods used for simulation. First of all, the DOS result of VASP shows that it has positive density of states with one spin and zero density of states with opposite spin at the Fermi level.

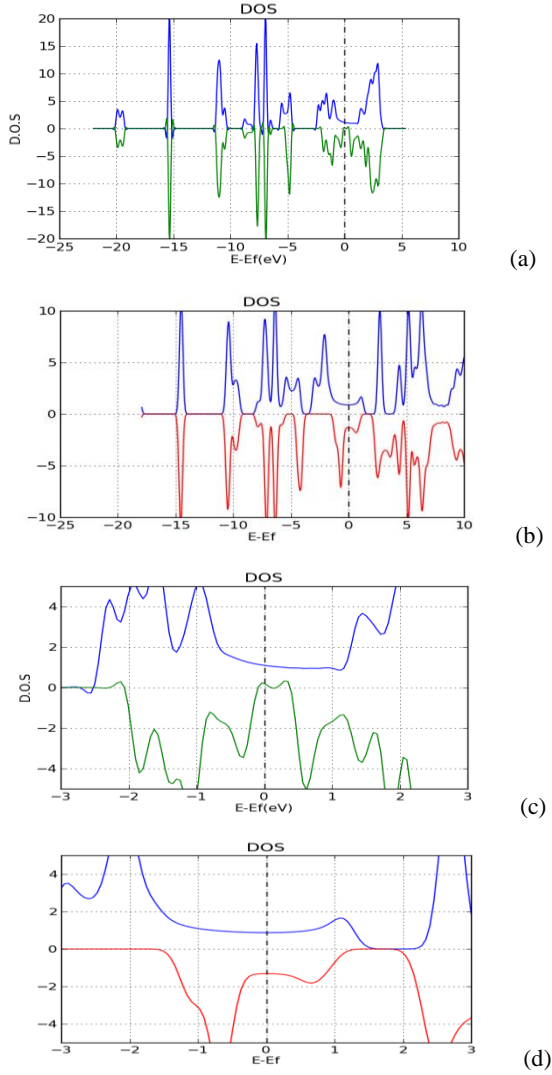


FIG. 4. (a)(c) VASP result of density of states (b)(d) SIESTA result. Negative DOS represents DOS of the electrons with opposite spin. The result of VASP suggests that the ferrocene-based nanowire can be a half-metal, but the result of SIESTA does not. (SIESTA DOS over the Fermi level comes from DZP option, which hardly affects on DOS near the Fermi level. The small bump crossing the DOS=0 line near $E-E_f=0$ seems to be a small error that comes from plotting algorithm of VASP)

level. It means that the nanowire has a half-metallic property (FIG. 4(a)(c)). However, the DOS result of SIESTA contradicts the above conclusion, indicating that it is not a half-metal. At the Fermi level, the density of states are almost same regardless of the spin of electrons in the SIESTA result (FIG. 4(b)(d)). The projected DOS (PDOS) analysis can explain this inconsistency.

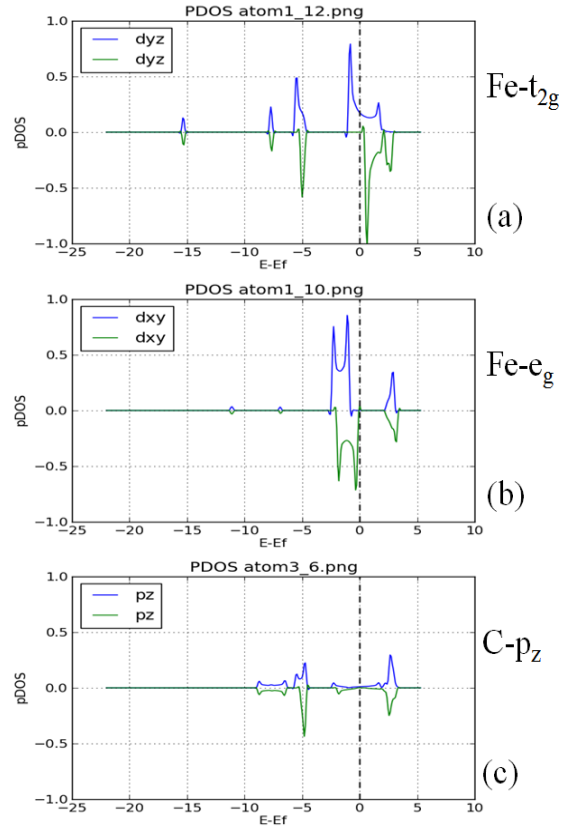


FIG. 5. VASP results of projected DOS. (a) Fe t_{2g} orbital, (b) Fe iron e_g orbital (c) C p_z orbital. The t_{2g} orbitals have higher energy level than the e_g orbitals because of their shapes and positions in one-dimensional wire structure. (See FIG. 7)

The VASP (FIG. 5) and the SIESTA PDOS results (FIG. 6) of the 3d orbitals of iron atom in the ferrocene-based nanowire are similar in shape. They both have double humped curves with the 2~3eV broadening width in the PDOS results of t_{2g} and e_g orbitals near the Fermi level. The double humped broadening comes from a one-dimensional arrangement of atoms because, in Hubbard model, the distribution of the eigenvalues of Hubbard matrix in one-dimensional atom

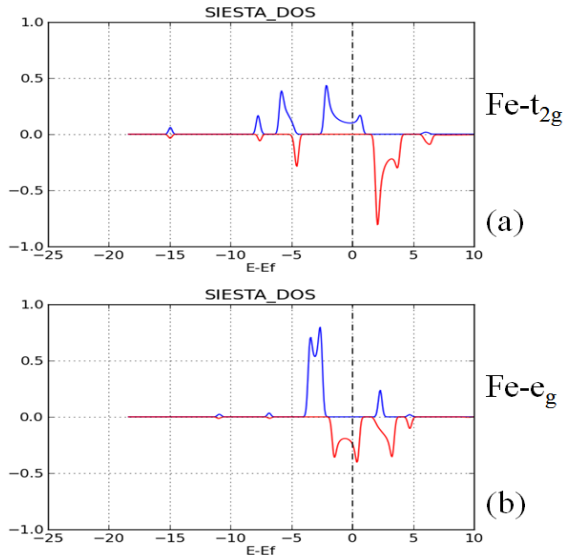


FIG. 6. SIESTA results of projected DOS. Exchange splitting at the Fermi level is larger than that of VASP data. (See FIG. 5(a)(b))

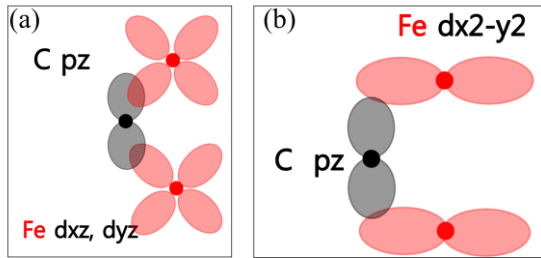


FIG. 7. Schematic diagram for p-d orbital bonding (a) t_{2g} - p_z bonding acts as the strongest bonding (b) e_g - p_z bonding acts as the secondary bonding. Since the t_{2g} orbitals of Fe and C atoms are relatively close each other, t_{2g} orbitals have wider energy broadening in DOS than e_g orbitals have. (see FIG. 5.)

arrangement gives a double humped curve. We can also see the double humps in the p_z orbitals of the carbon atoms in the nanowire (FIG. 5(c)). Therefore, we can conclude that the iron 3d orbitals (both t_{2g} and e_g orbitals) are strongly connected with the carbon p_z orbitals, producing the double humped curves in their DOS. The broadening width of t_{2g} DOS double hump is about one and a half times of that of e_g broadening width. It means that t_{2g} - p_z bonding (off diagonal terms in Hamiltonian matrix) is stronger than that of e_g - p_z bonding. It is consistent with our intuition for the

reason that the t_{2g} orbital of Fe and C atom are closer than the e_g orbital of Fe and C atom (FIG. 7).

The main reason of the inconsistency of VASP and SIESTA results is the difference of exchange splitting magnitude of the iron 3d orbital DOS. The SIESTA DOS gives larger exchange splitting in t_{2g} and e_g DOS than the VASP DOS. As a consequence, a slight change in DOS of t_{2g} and e_g makes change in Fermi level, giving the difference between half-metallic and metallic states (FIG.8).

Many sources affect the exchange splitting. In this case, intrinsic limitation of the SIESTA package would be the main reason that it overestimates the exchange splitting gaps. The SIESTA uses an orbital-based basis when it constructs wavefunction. This basis set has a limit to expressing the Khon-Sham Hamiltonian wavefunction. Especially when the wavefunction is a plane wave, the SIESTA solution becomes less accurate. Since the ferrocene-based nanowire can have one-dimensional wavefunction going along the z-direction, the SIESTA results is less credible than the VASP results. Thus, it is still possible that the ferrocene-based nanowire can be a half-metal.

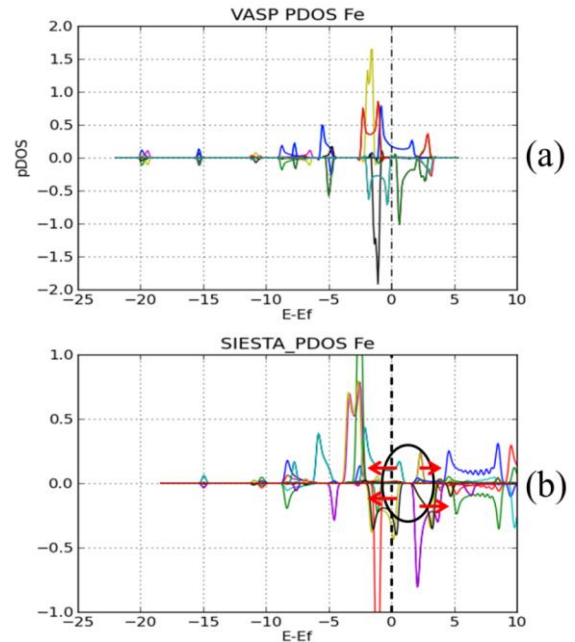


FIG. 8. (a) VASP result of projected DOS of iron atom. (b) SIESTA result. Fermi energy in SIESTA DOS goes down making metallic state due to broadening in exchange splitting gap. (See FIG. 6)

CONCLUSION

In this study, we investigated the ferrocene-based nanowire as a possible candidate for an applicable one-dimensional nanostructure, using VASP and SIESTA simulation packages. According to the binding energy results and MD calculations, the ferrocene-based nanowire can be a stable state, putting aside the feasibility of synthesis of the nanostructure. The DOS result of VASP predicts that the nanowire is a half-metal, but the SIESTA DOS result indicates that it is close to a metal. We conclude that the VASP result is more reasonable because SIESTA has an intrinsic problem in solving the Kohn-Sham Hamiltonian that has a plane wave as its eigenfunction.

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REFERENCES

- [1] Hongming WENG, Taisuke OZAKI, and Kiyoyuki TERAOKA, *Journal of the Physical Society of Japan* Vol. 77, No. 6, June, 2008, 064301
- [2] K. Miyajima, S. Yabushita, M. B. Knickelbein, and A. Nakajima: *J. Am. Chem. Soc.* 129 (2007) 8473.