Possible magnetic states in buckybowl molecules

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Abstract

Possible magnetic properties are studied in the buckybowl molecules: the sumanene and a part of $C_{60}$. The Hubbard model is applied to the systems. We find that the molecular structure determines the magnetism in the sumanene. On the other hand, the edge state is found along the zigzag edge of a part of $C_{60}$. Therefore, the novel property, transition from molecular magnetism to the magnetism like in nanographene, is found.

Keywords: magnetic states, buckybowl, sumanene, $C_{60}$, Hubbard model
1. INTRODUCTION

Nanographene materials [1,2] have been studied intensively. The recent Nobel prize paper [3] on graphene has promoted experimental and theoretical investigation on nanocarbon materials, too. Unique magnetic properties along the zigzag edge of the graphene nanoribbon [1] have been predicted. On the other hand, defects on the fullerene C$_{60}$ [4] may give possible unique electronic states. Further, we have studied magnetic properties of stacked nanographene sheets by the cluster calculations with the Hubbard model [5-7].

The buckybowl molecule "sumanene" [8,9] has been synthesized experimentally. The molecule has a curved shape, and is a part of the structure of C$_{60}$. The molecule has π-electrons on the curved surface. The electronic properties have been calculated [10], and their uniqueness has been revealed. Therefore, it is also interesting to study possible magnetic properties. In addition, we consider a part of C$_{60}$, where three pentagons and six hexagons are added around the outer part of the sumanene. A zigzag line appears, so magnetic properties can be compared with those of graphene nanoribbons [1].

In this paper, possible magnetic properties are studied in the buckybowl sumanene and a part of C$_{60}$ with the zigzag edge like in nanographene. The Hubbard model [5-7] is applied to π-electrons on the curved molecules. We will discuss that the molecular structure determines the magnetism in the sumanene, while the edge state gives magnetism along the zigzag edge of a part of C$_{60}$. Therefore, the novel property, transition from molecular magnetism to the magnetism in nanographene, appears.

This paper is organized as follows. In section 2, we explain the model. In section 3, we report magnetism of the sumanene. In section 4, we discuss about a part of C$_{60}$. The paper is closed with a short summary in section 5.

2. MODEL AND METHOD

We treat half-filled π-electron systems on buckybowl molecules by the Hubbard model. This is a well known model for description of localized magnetic properties of itinerant electrons.
The model is as follows:

\[ H = -t \sum_{\langle i,j \rangle,\sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}) + U \sum_i (c_{i,\uparrow}^\dagger c_{i,\uparrow} - \frac{n_{\text{el}}}{2})(c_{i,\downarrow}^\dagger c_{i,\downarrow} - \frac{n_{\text{el}}}{2}), \]  

where \( c_{i,\sigma} \) annihilates a \( \pi \)-electron of spin \( \sigma \) at the \( i \)th site; \( t > 0 \) is the hopping integral between the nearest neighbor \( i \)th and \( j \)th sites; the sum with \( \langle i, j \rangle \) is taken for all the pairs of the nearest neighbor sites; \( n_{\text{el}} \) is the average electron density of the system. Here, \( n_{\text{el}} = 1 \) for the half filled electrons. The term \( U \) is the strength of repulsive force between up and down spins at the \( i \)th site. When \( U \) is larger than \( t \), the electrons favor to localize, and magnetic states are realized. When \( t \) is larger than \( U \), the magnetic character is suppressed due to the strong itinerant property. We adopt the Hartree-Fock approximation to this model [5-7]:

\[ c_{i,\uparrow}^\dagger c_{i,\uparrow} c_{i,\downarrow}^\dagger c_{i,\downarrow} \Rightarrow \langle c_{i,\uparrow}^\dagger c_{i,\uparrow} \rangle c_{i,\downarrow}^\dagger c_{i,\downarrow} + c_{i,\uparrow}^\dagger c_{i,\downarrow} \langle c_{i,\uparrow}^\dagger c_{i,\downarrow} \rangle - \langle c_{i,\uparrow}^\dagger c_{i,\downarrow} \rangle \langle c_{i,\uparrow}^\dagger c_{i,\downarrow} \rangle. \]  

The magnetic moment at the \( i \)th lattice site is calculated as:

\[ m_i = \frac{1}{2}(\langle c_{i,\uparrow}^\dagger c_{i,\uparrow} \rangle - \langle c_{i,\downarrow}^\dagger c_{i,\downarrow} \rangle). \]  

3. MAGNETIC STATES OF SUMANENE

The sumanene molecule has a curved shape, where a hexagon is located at the center of the molecule. Figure 1 shows the molecular structure. The pentagons and hexagons are alternated among the central hexagon. The molecule has the \( C_3 \) symmetry. The central hexagon has bond alternation of the single and double bonds. Three surrounding hexagons have two double bonds. There are three nonequivalent edge atoms due to the symmetry. They are named as A, B, and C. It is assumed that \( \pi \) electron is active at the site A. In other words, the site A is terminated with one hydrogen atom, not with two H atoms. This assumption is necessary for the appearance of the magnetism.

The Hartree-Fock equation is solved with a certain initial condition for the electron number 21. This is the same as the carbon atom number. The magnetic solution is actually obtained. The magnetic moments at the sites A, B, and C are plotted against the Coulomb interaction strength \( U \) in Fig. 2. The interaction is changed within \( 0 < U < 2.5t \). The magnetic moment
appears at the site A [Fig. 2 (a)]. Its magnitude increases from about 0.2 of $U = 0$, as the strength $U$ becomes larger. The magnitude of the magnetic moments at the sites B and C [Figs. 2 (b) and (c)] is one-order smaller than that of the site A. The existence of magnetic moments at the sites B and C will not be observed. The appearance of the moment at the site A is related with the fact that the site is the outmost site of the pentagon ring of the molecule. On the other hand, the bond between the sites B and C is a double bond, so the singlet spin state is favorable and localized magnetic moments will disappear. This type of magnetic state reflects the alternation pattern of the single and double bonds, so it is one of molecular magnetic states.

Such molecular magnetism is closely related with the molecular magnetism in the trianglene [11,12]. The nonbonding molecular orbitals give rise to the magnetic nature of the trianglene, too. Possibly, electron-phonon couplings may give rise to distortions to molecular structures, namely the Jahn-Teller distortions. However, in the stage of this simple tight binding model, we do not have detailed knowledge of electron-phonon (molecular vibrations) couplings. Thus, we have limited the work to the magnetic solution of the Hubbard model. Inclusion of the molecular distortion can be done possibly by using the Su-Schrieffer-Heeger type interaction performed for the works of carbon nanotubes [13] and graphene frakes [14].

4.. MAGNETIC STATES IN A PART OF $C_{60}$

In this section, we consider magnetic states in a part of $C_{60}$, where three pentagons and six hexagons are added around the outer part of the sumanene [Fig. 1]. The new structure is shown in Fig. 3. The structural relation with the sumanene would be obvious. A zigzag line appears along the outmost part of the molecular structure, so magnetic properties can be compared with those of graphene nanoribbons [1]. This is another interest because bulk magnetic states have been predicted in graphene nanoribbons. Along the zigzag line of Fig. 3, there are four nonequivalent edge sites. They are named sites A to D. The site A is at the outmost site of the pentagon, and sites B, C, and D belongs to hexagons.
The calculated result of the magnetic state due to the Hartree-Fock approximation is summarized in Fig. 4. The magnetic moment at the site A (a), site B (b), site C (c), and site D (d) is displayed as a function of the Coulomb interaction strength $U$. We find the switch-on of the positive magnetic moments at the sites A and C, and the presence of the negative moments at the sites B and D. The absolute values of the moments increase as the strength $U$ becomes larger. The moments of the sites A and C seem to be finite at $U = 0$, because these sites locate at the outmost part of the molecule. On the other hand, the moments of the sites B and D are near to zero due to the three bonded nature of these sites. Such the alternation of the positive and negative magnetic moment along the zigzag edge of a part of $C_{60}$ would be by no means the realization of the edge state magnetism, which has been discussed in graphene nanoribbons [1]. The electrons of the magnetic moments occupy wavefunctions which have large amplitudes at and near the zigzag atoms in these systems.

At the first glance, the above qualitative behavior of the magnetic property seems similar with that of the nanographene. However, there is a quantitative difference. In nanographene ribbon with zigzag edges [1], the magnetic moment at the edge atoms (types of the sites A and C of Fig. 3) is larger than that at the neighboring sites (types of the sites B and D). So, ferrimagnetism occurs. In the present system, the absolute value of the magnetic moment of the sites A to D is of the similar magnitude. This is the quantitative difference from the graphene nanoribbons. In density functional calculations [15], magnetic moments at edge atoms are displayed only. It is possible that the similar alternation of the up and down spins has been obtained in the ab initio study [15]. The recent molecular dynamics simulations [16] correspond to this calculation, and stabilities of the molecules and structural transitions have been discussed.

Comparing magnetic properties between the sumanene and a part of $C_{60}$, the magnetic moment is suppressed at the sites B and C of the hexagons of the sumanene in Fig. 1, while magnetic moments are favored at the sites B, C, and D of the hexagons in Fig. 3. The magnetism of the sumanene is of the molecular nature [11,12], while that of the part of $C_{60}$ is like of the bulk magnetism of nanographene [1]. Therefore, by changing the system size,
transition from molecular magnetism to magnetism like nanoribbons with zigzag edges has been found.

It is known that the Hartree-Fock approximation tends to overestimate the possibility of broken symmetry magnetic solutions. Fluctuations from the mean field approximation could change the stabilities of solutions. More precise treatments may be done by quantum Monte Carlo or exact diagonalization method, as has been used for the extended Hubbard model on the C$_{20}$ molecule recently [17], for example. This would be one of the extensions to the future studies. This paper has provided an indication of the trend of change of magnetism when going from small molecules like the sumanene to larger ones like graphene nanoribbons.

5. SUMMARY

In summary, possible magnetic orders have been studied in the buckybowl molecules: the sumanene and a part of C$_{60}$. The Hubbard model has been applied to the systems. It has been found that the molecular structure determines the magnetism in the sumanene. On the other hand, the edge state is realized along the zigzag edge of a part of C$_{60}$. Therefore, the novel property, transition from molecular magnetism to the magnetism in nanographene, has been found.

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FIG. 1. The sumanene molecule. The symbols, A, B, and C, label symmetrically unequivalent edge atoms.

Figure Captions
FIG. 2. The magnetic moment at the site A (a), site B (b), and site C (c), as a function of the Coulomb interaction strength $U$ of the sumamine molecule.
FIG. 3. A part of $C_{60}$ with a zigzag line. The symbols, A, B, C, and D, label symmetrically unequivalent edge atoms.
FIG. 4. The magnetic moment at the site A (a), site B (b), site C (c), and site D (d), as a function of the Coulomb interaction strength $U$ of a part of $C_{60}$. 
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