Change of magnetic properties of benzenes in multiple-decked sandwich clusters:

$Mn_n(C_6H_6)_{n+1}$ ($n = 1,2$)

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Abstract
Local magnetic moments in benzenes of a multiple-decked sandwich cluster, namely, $Mn_n(C_6H_6)_{n+1}$ $(n = 1, 2)$ are investigated using density functional theory. A significant increase in the magnetic moments of benzenes was found in the $2p_z$ orbitals. From the values of the local magnetic moments of $Mn(C_6H_6)_2$ and $Mn_2(C_6H_6)_3$, we find that the local magnetic moment of benzene in the centre of the chain is larger than that at the edge position. These results indicate a promising possibility of changing the magnetic properties of benzenes using a magnetic material.

1. Introduction

One active area in studies on electronic material devices in the last decade is spintronics, where one tries to exploit, in addition to the charge of the electron, its spin degree of freedom. A central problem here is the spin injection into non-magnetic materials, such as semiconductor materials. Studies on spin injection, from ferromagnetic materials to semiconductor materials, are now being done worldwide.

Recently, studies on spin injection have been geared towards spin injection from ferromagnetic materials to non-magnetic materials such as graphite and organic materials. Moreover, these studies are being done down to nano/atomic scale, where it is necessary to understand in more detail how spin injection occurs [1, 2]. Good materials for testing these ideas are organometallic compounds of multiple-decked sandwich clusters, namely, $M_n(C_6H_6)_{n+1}$ (M = transitions metal atoms). They have been synthesized in the laboratory by, e.g.,

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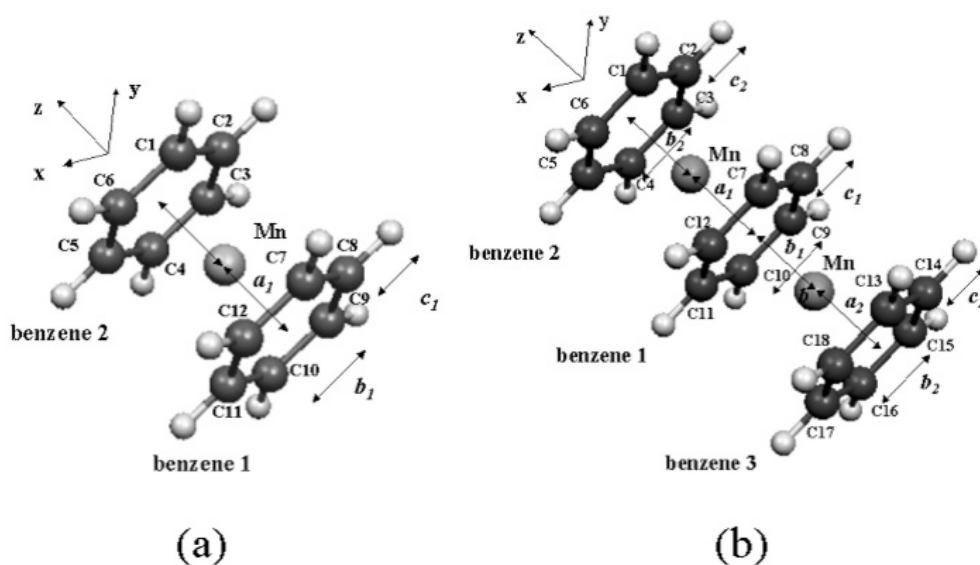
Figure 1. The model system of multiple-decked transition metal atom–benzenes sandwich clusters, $Mn_n(C_6H_6)_{n+1}$. (a) $Mn(C_6H_6)_2$ system, (b) $Mn_2(C_6H_6)_3$ system.

Cloke *et al* [3] and Hoshino *et al* [4], and have been the subject of many studies for the past few decades.

The electronic structures of these materials have been investigated by Miyajima *et al* [5], and it has been shown that these materials exhibit semiconducting and even conducting properties in the solid states [5]. The magnetic properties of these novel materials were investigated for the first time by Yasuike *et al*, when they investigated the spin state of the $V_2(C_6H_6)_3$ system. However, they could not exactly determine which state is more stable, the triplet or the singlet [6]. Pandey *et al* calculated the spin multiplicity [7][5] of $Mn_n(C_6H_6)_{n+1}$ (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and $n = 1, 2$) systems [7] and obtained agreements with electron spin resonant experiments done by Cloke *et al* [8]. However, the local magnetic moments in the transition metal atoms M and the benzenes, when they interact with each other to produce $Mn_n(C_6H_6)_{n+1}$ clusters, have not yet been analysed.

In this paper, by using the density functional theory we calculate the local magnetic moments of benzenes in $M_n(C_6H_6)_{n+1}$ (M = Mn, $n = 1, 2$) cluster systems. By focusing on the orbitals of benzenes and the position of benzene in the $Mn_n(C_6H_6)_{n+1}$ cluster, some conclusions may be drawn regarding changing the magnetic properties of benzenes.

2. Model and method

The model system that we used to describe the multiple-decked transition metal atom–benzenes sandwich clusters $Mn(C_6H_6)_2$ and $Mn_2(C_6H_6)_3$ is shown in figure 1. These optimized structures are obtained by performing a series of density functional theory (DFT) based total energy calculations using the Gaussian 2003 program [9], adopting Becke's three-parameter functional [10], Perdew and Wang's gradient-corrected correlation functional [11], and Dunning [12], Hay and Wadt's basis sets [13]. Here, a_i ($i = 1, 2$) are the distances from

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[5] The spin multiplicity is given by the equation $2S + 1$, where S is the total spin.

the transition metal atom to the hexagonal centre of benzene. For the $Mn(C_6H_6)_2$ system, the two benzenes are symmetric with respect to the Mn atom and $a_1 = 1.704$ Å. For the $Mn_2(C_6H_6)_3$ system, benzene 2 and benzene 3 are symmetric with respect to benzene 1, and $a_1 = 1.762$ Å, $a_2 = 1.629$ Å. b_i are the distances between the two C atoms in the benzenes. For the $Mn(C_6H_6)_2$ system $b_1 = 1.428$ Å and for the $Mn_2(C_6H_6)_3$ system $b_1 = 1.439$ Å and $b_2 = 1.432$ Å. c_i are the distances between the C and the H in the benzenes. For the $Mn(C_6H_6)_2$ system $c_1 = 1.084$ Å, for the $Mn_2(C_6H_6)_3$ system $c_1 = 1.083$ Å and $c_2 = 1.0852$ Å. Ci $(i = 1, 2, 3, \ldots)$ are carbon atoms. The benzene rings are parallel to the xy-plane while the z-axis is perpendicular to the plane of the benzenes.

We have examined the $\langle \mathbf{S} \cdot \mathbf{S} \rangle$ values, and compared them to the $S(S + 1)$ values for each total spin of the $Mn(C_6H_6)_2$ and $Mn_2(C_6H_6)_3$ systems, to check for spin contamination. For the ground state of the $Mn(C_6H_6)_2$ system, the $\langle \mathbf{S} \cdot \mathbf{S} \rangle$ value is 0.761, while $S(S + 1) = 0.75$. For the ground state of the $Mn_2(C_6H_6)_3$, the $\langle \mathbf{S} \cdot \mathbf{S} \rangle$ value is 2.0921, while $S(S + 1) = 2.0$. These values are much smaller than the maximum value that can be allowed, 10%.[6] This also further shows that the results that we have obtained here are reliable enough for investigating the behaviour of the spins of these materials.

To investigate the changes in the magnetic moment of the 3d transition metal atoms and the benzenes, the first step is to calculate the magnetic moments of the 3d transition metal atom Mn system and the benzenes system. Next, we compare these results with those where the transition metal atoms M and the benzenes are in $Mn(C_6H_6)_2$ and $Mn_2(C_6H_6)_3$ systems.

The magnetic moment is determined by $m = \mu_B(\rho_\alpha - \rho_\beta)$, where one alpha electron corresponds to a magnetic moment of 1 μ_B, while one beta electron corresponds to a magnetic moment of -1 μ_B. ρ_α gives the alpha spin densities (electrons with spin up), while ρ_β gives the beta spin densities (electrons with spin down), and μ_B is the Bohr magneton. The magnetic moments with positive values have the same direction as those of the alpha electrons, while those with negative values have the same direction as those of the beta electrons.

3. Results and discussion

The magnetic moments for Mn in the isolated case (free ion) can be understood from the electronic properties of the 3d atoms, where all of the elements in the 3d series, except Cr, have the $3d^m4s^2$ configuration (m = number of electrons). The magnetic moment of Mn is 5 μ_B as a result of five electrons with spin alpha occupying the five 3d orbitals. When Mn is absorbed into two benzenes in $Mn(C_6H_6)_2$, we find that the magnetic moment of Mn decreases to 1.1695 μ_B/Mn atom. The magnetic moments of the two benzenes in $Mn(C_6H_6)_2$ increase (in magnitude of the negative value) to -0.1694 μ_B. In the $Mn_2(C_6H_6)_3$ system, we find that the magnetic moment of Mn decreases to 1.414 μ_B/Mn atom, and the magnetic moments of the benzenes in $Mn_2(C_6H_6)_3$ increase to -0.2250 μ_B for benzenes 2 and 3, and -0.3933 μ_B for benzene 1. From the values of the local magnetic moments of the benzenes, one can see that the position of the benzene in the chains of $Mn_2(C_6H_6)_3$ systems determines the corresponding magnetic moment of the benzene. A benzene that is positioned at the centre due to interactions with two Mn atoms has a high magnetic moment, compared to those at the edges.

The decreased magnetic moment in Mn and increased magnetic moments in the two benzenes can be explained as follows. As an example, we consider the $Mn(C_6H_6)_2$ system. In the calculations, the electron populations for the Mn free ion, the two benzenes, and the $Mn(C_6H_6)_2$ system are 15, 84, and 99, respectively. In the Mn free ion we have ten alpha electrons and five beta electrons. However, when this ion is absorbed into two benzenes,

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6 http://www.ccl.net/cca/documents/dyoung/topics-orig/spin_cont.html

the population of alpha electrons decreases from 10.0 to 8.0291, while that of beta electrons increases from 5.0 to 6.8596. The magnetic moment of Mn in the $Mn(C_6H_6)_2$ system for which we are making calculations is $8.0291 - 6.8596 = 1.1695 \mu_B$. In the two-benzenes system also, we can see that the population of alpha electrons decreases from 42.0 to 41.9710, and the population of beta electrons increases from 42.0 to 42.1404. The magnetic moment of the two benzenes in the $Mn(C_6H_6)_2$ system for which we are making calculations is $41.9710 - 42.1404 = -0.1694 \mu_B$.

The filling of electrons in the orbitals of Mn and the benzenes in the $Mn(C_6H_6)_2$ system causes electrons to transfer from alpha to beta in the orbitals, and thus is responsible for the decreasing magnetic moment of the Mn and the increasing magnetic moment of the benzenes. As an illustration, in the metal Mn, the major contribution of the increasing number of beta electrons comes from the two-electron transfer of the 4s orbital of Mn. In the free ion Mn, the energy level for the 4s orbital is below the vacuum level, and two electrons occupy this orbital. In the interacting systems, the energy level for the 4s orbital is higher than the vacuum level. The two electrons in this orbital transfer to (occupy) 3d orbitals that have lower energy levels. In the 3d orbitals, we find an increased number of beta electrons and a decreased number of alpha electrons. After checking the electron configurations in the orbitals for both alpha and beta electrons, we find the magnetic moment of Mn in the $Mn(C_6H_6)_2$ system mainly comes from the $3d_{xz}$ orbital. Furthermore, for both $Mn(C_6H_6)_2$ and $Mn_2(C_6H_6)_3$ systems, we find increased magnetic moment in the $2p_z$ orbitals of the benzenes; but negligible spin polarization is found in the twelve 1s, 2s, $2p_x$, and $2p_y$ orbitals of the two benzenes. The interaction between the $2p_z$ orbitals of the benzenes and the 3d orbitals of the Mn is expected to be responsible for these spin polarizations. Checking the magnetic moments of the $2p_z$ orbitals between the carbon atoms of the two benzenes in $Mn(C_6H_6)_2$ system, we find that C3, C6, C9, and C12 have magnetic moments of $-0.0426 \mu_B$, while C1, C2, C4, C5, C7, C8, C10, and C11 have magnetic moments of $-0.0076 \mu_B$. The magnetic moments of C3, C6, C9, and C12 are 5.6 times the magnetic moments of C1, C2, C4, C5, C7, C8, C10, and C11. Interaction between half of the nodal cone of the $2p_z$ orbitals of C3, C6, C9, and C12 and half of the nodal cone of the $3d_{x^2-y^2}$ orbital gives rise to the increasing magnetic moment of the $2p_z$ orbitals. Due to the small overlap between the $2p_z$ orbitals and the $3d_{xy}$ orbital, the contribution of the $3d_{xy}$ orbital to the $2p_z$ orbitals of C1, C2, C4, C5, C7, C8, C10, and C11 is small.

4. Summary

By using density functional theory we investigated the local magnetic moments of multiple-decked sandwich cluster systems, namely, $Mn_n (C_6H_6)_{n+1}$ ($n = 1, 2$). We found that the magnetic moments of the $2p_z$ orbitals of the benzenes increase in these systems. From the differences between the positions of the benzenes in the $Mn_2(C_6H_6)_3$ systems, we found that the benzene with the highest magnetic moment is at the centre of that cluster. These results indicate a promising possibility of changing the magnetic properties of benzenes using a magnetic material through the $2p_z$ orbitals. These studies may contribute to investigations of spin injection from transition metals, e.g., Mn, to non-magnetic materials on the nanoscale, where we propose refilling of electrons in the 3d orbitals of the metal atom and the benzenes to be responsible for the spin polarization and increasing magnetic moment of the benzenes.

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