

Ground state properties of a high-spin $\text{Mn}_{12}\text{O}_{12}$ molecule in an organic compound

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The electronic structure and the magnetism of a $\text{Mn}_{12}\text{O}_{12}$ molecule at ground state have been studied by density functional theory with a local spin density approximation. We have found that the magnetic moments of Mn ions in the tetrahedron and those of Mn ions in the crown of the $\text{Mn}_{12}\text{O}_{12}$ molecule align antiferromagnetically. The average moment per Mn ion is about $3.07\mu_B$ in the tetrahedron and $4.07\mu_B$ in the crown. The total spin amounts to $20.0\mu_B$ which is in agreement with recent experimental results. The significant difference of magnetic moments between Mn ions at two sites is attributed to the different exchange splitting of $3d$ orbitals. However, the charge difference between the two kinds of Mn ions is as small as 0.22 electrons. The charge density and the spin density exhibit strong directional dependence, which indicates the strong anisotropy in this molecule. © 1998 American Institute of Physics. [S0021-8979(98)40411-0]

The study of large molecular clusters of metal ions is a very important area of interest which is expanding rapidly.¹ Very recently, many new phenomena such as the quantum tunneling of magnetization, gigantic relaxation time and magnetic bistability²⁻⁸ were discovered in a so-called high-spin molecular organic compound— $\text{Mn}_{12}\text{O}_{12}$ acetate.^{9,10} These new observations have further enhanced the interest because of its suitability for the investigation of magnetic properties on nanoscale or mesoscopic dimensions, and its promise of use in data storage devices.

$\text{Mn}_{12}\text{O}_{12}$ acetate has a well-defined crystal structure which can be described as a $\text{Mn}_{12}\text{O}_{12}$ molecule surrounded by some organic ligands.^{9,10} The molecule contains two kinds of manganese ions bridged by oxygen. The inner four ions form a tetrahedron in the center of cluster (denoted by Mn_t) and the outer eight form a crown (denoted by Mn_c). A recent experiment¹¹ shows that the molecule has a large net spin $S = 10$, which is always oriented along the easy axis S_4 . Although a strong interplay could exist in the $\text{Mn}_{12}\text{O}_{12}$ molecule, the interaction between the molecules themselves is still weak because of the large distance. Many experiments^{2-8,10} have shown that at low temperature, the $\text{Mn}_{12}\text{O}_{12}$ molecule acts just like a high-spin magnet with clean discrete quantum numbers ($m_s = -10, \dots, +10$). So, unlike many other nanomagnetic materials, the magnetic behavior of $\text{Mn}_{12}\text{O}_{12}$ acetate should be mainly determined by the $\text{Mn}_{12}\text{O}_{12}$ molecule.

So far, in spite of some experimental observations²⁻¹³

having been made, there is still a lack of many theoretical studies^{14,15} for such an interesting material, especially studies of the electronic structure and the magnetism on a microscopic level. In this article, we report our results of first principle studies on the $\text{Mn}_{12}\text{O}_{12}$ molecule. We have employed the discrete variational method (DVM)^{16,17} based on density functional theory (DFT) with a local spin density approximation (LSDA)¹⁸ to study the ground state properties of the $\text{Mn}_{12}\text{O}_{12}$ molecule. In DVM, the Kohn-Sham equation (in atomic units),

$$(-\nabla^2/2 + V_C + V_{XC})\phi_{i\sigma} = \epsilon_{i\sigma}\phi_{i\sigma}, \quad (1)$$

with charge density $\rho_\sigma(\mathbf{r})$,

$$\rho_\sigma(\mathbf{r}) = \sum_i n_{i\sigma} |\phi_{i\sigma}(\mathbf{r})|^2 \quad (2)$$

is solved self-consistently where $\phi_{i\sigma}$ is the single particle wave function for the molecule with occupation $n_{i\sigma}$, V_C is the Coulomb potential of the nuclei and electrons, and V_{XC} is the exchange-correlation potential under LSDA. In the present calculation, the numerical atomic orbitals obtained by self-consistent LDA calculations for a single atom are used as the variational bases to expand the one particle wave functions. The discrete summation method of pseudo-random points in the three dimensional space and group theory are adopted to simplify the solution of the eigenvalue equations. The Coulomb potential is obtained by means of fitting charge density to a multipolar expansion which ensures that the DVM gives more precise results.¹⁷ In our calculation, the order of the multipolar expansion functions has

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TABLE I. The magnetic moments (m), Mulliken orbital occupation numbers (Occ.) and charges for the Mn cations in the $\text{Mn}_{12}\text{O}_{12}$ molecule. Symbols \uparrow and \downarrow indicate the spin-up and the spin-down states, respectively.

	Occ. (\uparrow)	Occ. (\downarrow)	Total Occ.	$m(\mu_B)$
Mn _i cations				
3d	3.62	0.55	4.17	+ 3.07
4s	0.01	0.01	0.02	0.00
			Charge + 2.82	Total + 3.07
Mn _c cations				
3d	0.14	4.22	4.36	− 4.07
4s	0.02	0.02	0.04	0.00
			Charge + 2.60	Total − 4.07

been chosen up to 2. The density of states (DOS) is obtained by using the Lorentzian broadening scheme, and the partial DOS (PDOS) is defined as:

$$D_{nl\sigma}^q = \sum_i P_{nl\sigma}^q \frac{\delta/\pi}{(\epsilon - \epsilon_{i\sigma})^2 + \delta^2}, \quad (3)$$

where $P_{nl\sigma}^q$ is the Mulliken population¹⁹ of the atomic orbital χ_{nl} of atom q in the molecular spin orbital $\phi_{i\sigma}$. The DOS of atom q with spin σ is obtained by a sum of n , l and i , and the total DOS of spin σ is given by the sum of all the atoms. To check the reliability of our method on the Mn-O system, we first study antiferromagnetically coupled MnO. We found magnetic moment of about $4.98\mu_B$ for the Mn cation, which is in agreement with experimental result.²⁰

For calculation of the $\text{Mn}_{12}\text{O}_{12}$ molecule, we adopted the experimental atomic distance,⁹ and put the z axis parallel to the easy axis. In Table I, we have presented magnetic moments, Mulliken orbital occupation numbers and charges for the Mn cations. From Table I, it can be seen the magnetic moment of the Mn_i cation is about $3.07\mu_B$ and that of the Mn_c cation is about $-4.07\mu_B$, which suggests that the two kinds of manganese ions are antiferromagnetically coupled. Considering the small contribution from the O anion, we get a total net spin amounting to $20.0\mu_B$ for the $\text{Mn}_{12}\text{O}_{12}$ molecule, which is exactly the same as the data derived from the experiment.¹¹ At the same time, we note that there is a large difference in Mulliken occupation numbers for the Mn 3d orbitals with spin up and with spin down. For the Mn_i cation, the electron occupation number in the 3d orbital with spin up is about 3.62, but it is only 0.55 in 3d orbital with spin down while, for the Mn_c cation, the electron occupation numbers of the 3d orbital with spin up and spin down are 0.14 and 4.22, respectively. In addition, for all the Mn ions, there are nearly no electrons in the 4s orbital, most of them have been transferred to oxygen atoms. The different occupation numbers show that the exchange splitting might have a significant difference for both kinds of Mn ions. In order to see this difference more clearly, we have presented the 3d PDOS of Mn cations as well as the total DOS of the $\text{Mn}_{12}\text{O}_{12}$ molecule in Fig. 1 and Fig. 2, respectively. From Fig. 1, the very large exchange splitting in the Mn 3d orbitals can be clearly observed, and both the spin-up and the spin-down PDOS have similar distribution. From PDOS, we can get the average value of the calculated exchange splitting, which is about 4.5

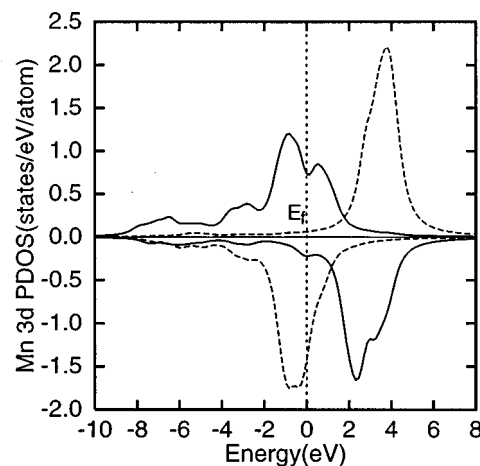


FIG. 1. The 3d PDOS for spin-up (upper panel) and spin down (lower panel) of the Mn_i cation (solid lines) and of the Mn_c cation (dashed lines). The Fermi level is shifted to zero.

eV for Mn_i cations and 3.0 eV for Mn_c cations. The large difference of exchange splitting between Mn_c and Mn_i ions leads to the large difference of magnetic moments, although the total occupation numbers in 3d orbitals are almost the same. From the total DOS shown in Fig. 2, the large net spin resulting from the large orbital exchange splitting in the $\text{Mn}_{12}\text{O}_{12}$ molecule can be observed. The charges for the two kinds of Mn ions are different, but their difference is small, only about 0.22.

To check the dependence of magnetic moment on the atomic distance, we have performed the calculations with the atomic distance 15% larger or smaller than the experimental result. We found that the total magnetic moment of the $\text{Mn}_{12}\text{O}_{12}$ molecule remains the same. For each Mn ion, the magnetic moment changes only a few percent. These results indicate that the magnetic properties of the $\text{Mn}_{12}\text{O}_{12}$ molecule are insensitive to the atomic distance.

In Fig. 3 and Fig. 4, we have presented the charge density as well as the corresponding spin density contour plots on the plane perpendicular to the S_4 axis (denoted by σ_h) and the plane including the S_4 axis and that perpendicular to

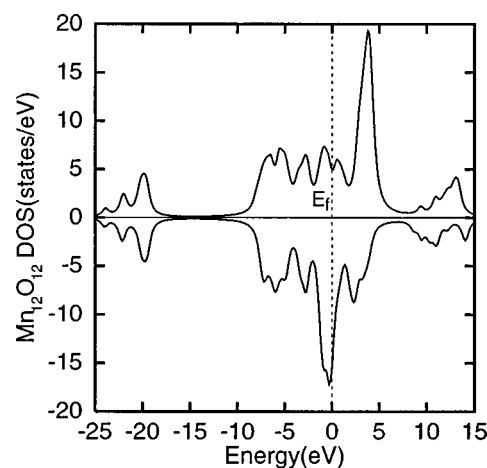


FIG. 2. The total DOS for spin up (upper panel) and spin down (lower panel) of the $\text{Mn}_{12}\text{O}_{12}$ molecule.

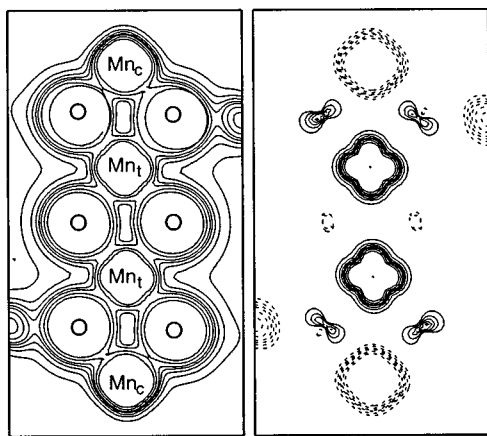


FIG. 3. Charge density (left panel) and spin density (right panel) contours of the $\text{Mn}_{12}\text{O}_{12}$ molecule on the plane perpendicular to the S_4 axis. The solid line stands for the positive value, and dashed line stands for the negative value.

σ_h (denoted by σ_v). On plane σ_h , it is obvious that, other than being spherical-like, the distribution of the charge density and the spin density for all Mn cations exhibits extremely strong directional dependence. However, on plane σ_v , the charge density and the spin density for Mn_c cations are spherically distributed, and those for Mn_t cations are only somewhat distorted from a spherical distribution. The strong directional dependence of the charge density and the spin density shows the large anisotropy of charge density and spin density in the $\text{Mn}_{12}\text{O}_{12}$ molecule which are mainly due to the distinction of neighboring atoms for Mn cations. So, it can

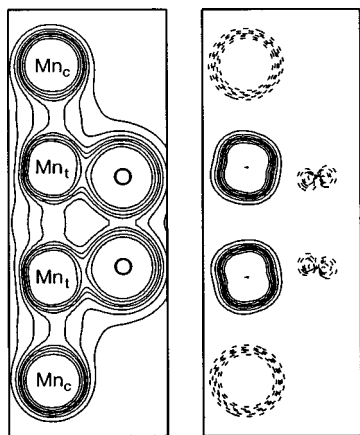


FIG. 4. Charge density (left panel) and spin density (right panel) contours of the $\text{Mn}_{12}\text{O}_{12}$ molecule on the plane including the S_4 axis. The solid line stands for the positive value, and the dashed line stands for the negative value.

be expected that there exists great magnetic anisotropy in $\text{Mn}_{12}\text{O}_{12}$ acetate.

In summary, the electronic and the magnetic properties of the $\text{Mn}_{12}\text{O}_{12}$ molecule at ground state have been investigated by the DVM with LSDA. We have found that the magnetic moments in the inner shell and the outer shell are antiferromagnetically aligned. The calculated total magnetic moment $20.0\mu_B$ for the $\text{Mn}_{12}\text{O}_{12}$ molecule is in good agreement with recent experimental data.¹¹ However, we did not find a significant difference in the occupation numbers for Mn_c and Mn_t . We attribute the large difference of magnetic moment for Mn_c and Mn_t ions to the different exchange splitting of $3d$ orbitals. The experimental observation of the strong anisotropy of $\text{Mn}_{12}\text{O}_{12}$ acetate^{10,12} has been confirmed by the strong anisotropy of the charge density and the spin density.

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- ¹D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, *Science* **265**, 1054 (1994).
- ²C. Paulsen, J.-G. Park, B. Barbara, R. Sessoli, and A. Caneschi, *J. Magn. Magn. Mater.* **140-144**, 379 (1995).
- ³B. Barbara, W. Wernsdorfer, L. C. Sampaio, J. G. Park, C. Paulsen, M. A. Novak, R. Ferré, D. Mailly, R. Sessoli, A. Caneschi, K. Hasselbach, A. Benoit, and L. Thomas, *J. Magn. Magn. Mater.* **140-144**, 1825 (1995).
- ⁴J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, *Phys. Rev. Lett.* **76**, 3830 (1996).
- ⁵E. M. Chudnovsky, *Science* **274**, 938 (1996).
- ⁶R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, *Nature (London)* **365**, 141 (1993).
- ⁷L. Thomas, F. Lioni, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, *Nature (London)* **383**, 145 (1996).
- ⁸J. M. Hernández, X. X. Zhang, F. Luis, J. Bartolomé, J. Tejada, and R. Ziolo, *Europhys. Lett.* **35**, 301 (1996).
- ⁹L. Lis, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **36**, 2042 (1980).
- ¹⁰R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.* **115**, 1804 (1993).
- ¹¹A. Caneschi, D. Gatteschi, and R. Sessoli, *J. Am. Chem. Soc.* **113**, 5873 (1991).
- ¹²M. A. Novak, R. Sessoli, A. Caneschi, and D. Gatteschi, *J. Magn. Magn. Mater.* **146**, 211 (1995).
- ¹³C. Paulsen, J.-G. Park, B. Barbara, R. Sessoli, and A. Caneschi, *J. Magn. Magn. Mater.* **140-144**, 1891 (1995).
- ¹⁴J. Villain, F. Hartman-Boutron, R. Sessoli, and A. Rettori, *Europhys. Lett.* **27**, 159 (1994).
- ¹⁵P. Politi, A. Rettori, F. Hartmann-Boutron, and J. Villain, *Phys. Rev. Lett.* **75**, 537 (1995).
- ¹⁶D. E. Ellis and G. S. Painter, *Phys. Rev. B* **2**, 2887 (1970).
- ¹⁷B. Delly and D. E. Ellis, *J. Chem. Phys.* **76**, 1949 (1982).
- ¹⁸P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1964).
- ¹⁹R. S. Mulliken, *J. Chem. Phys.* **23**, 1841 (1955).
- ²⁰D. Adler, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. 21.