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Spin polarization effect for Mn_2 molecule

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The density functional theory method (DFT) (b3p86) of Gaussian 03 has been used to optimize the structure of the Mn_2 molecule. The result shows that the ground state of the Mn_2 molecule is an 11-multiple state, indicating a spin polarization effect in the Mn_2 molecule, a transition metal element molecule. Meanwhile, we have not found any spin pollution because the wavefunction of the ground state does not mingle with wavefunctions of higher-energy states. So the ground state for Mn_2 molecule being of an 11-multiple state is the indicative of spin polarization effect of the Mn_2 molecule among those in the transition metal elements: that is, there are 10 parallel spin electrons in a Mn_2 molecule. The number of non-conjugated electrons is the greatest. These electrons occupy different spacious orbitals so that the energy of the Mn_2 molecule is minimized. It can be concluded that the effect of parallel spin in the Mn_2 molecule is larger than the effect of the conjugated molecule, which is obviously related to the effect of electron d delocalization. In addition, the Murrell–Sorbie potential functions with the parameters for the ground state and other states of the Mn_2 molecule are derived. The dissociation energy D_e for the ground state of the Mn_2 molecule is 1.4477 eV, equilibrium bond length R_e is 0.2506 nm, vibration frequency ω_e is 211.51 cm^{-1}. Its force constants f_2, f_3, and f_4 are 0.7240 aJ·nm^{-2}, −3.35574 aJ·nm^{-3}, 11.4813 aJ·nm^{-4} respectively. The other spectroscopic data for the ground state of the Mn_2 molecule $\omega_e\chi_e$, B_e, α_e are 1.5301 cm^{-1}, 0.0978 cm^{-1}, 7.7825× 10^{-4} cm^{-1} respectively.

Keywords: Mn_2, spin polarization, density functional theory, potential function
PACC: 3420, 3420B, 3520D,3520G

1. Introduction

Currently it is a major research subject to analyse the molecular structures of transition elements, especially those in the 4th and 5th periods. It is known that manganese is one of the most important chemical elements. But up to now, useful information concerning the molecular structure of Mn_2 is limited. The difficulties in the theoretical treatment of transition metal systems result from the near-degeneracy effects from the formation of d bonds, the strong dynamical correlation effects from the tightly packed electrons in the d shell, and the non-negligible relativistic effects.[1] To properly describe the d bonds of these systems by means of the *ab initio* method, a heavy computational effort is required: a multireference based theory with a large active space and an extended basis set. A transition metal dimer is theoretically one of the most interesting electronic systems, because it has various kinds of spin configurations that are comprised of the orbitals with different angular momenta in a limited energy region. Even though a dimer consists of only one metallic bond, *ab initio* molecular orbital methods can barely reproduce the equilibrium geometries that have been accepted as being less sensitive to the level of calculations. Thus, the transition metal dimer is a challenging system that attracts growing theoretical interest.

Manganese dimer is a peculiar van der Walls molecule, a system that is quite complicated for a theory to describe. An average of third-law estimates for the dissociation energy is reported by Morse as 0.74 eV.[2] Because the experimental work has not been particularly successful, the experimental result of dissociation energy obtained cannot be used. Kirkwood *et al*[3] assigned ω_e as 68.1 cm^{-1} using matrix isolation resonance Raman spectroscopy. Cheeseman *et al*[4] examined the system at various temperatures using electronic spin resonance, and used $S = 4$ and $S = 5$ states of the molecule to approximate the bond length to 0.34 nm. No high-level non-density functional theory research has been undertaken for Mn_2. In 1964, Nesbet[5] used restricted Hartree–Fock (RHF) method and a Heisenberg formalism to predict the bonding to be antiferromagnetic and the bond length to be 0.288 nm, in good agreement with our density functional theory results. Shillady *et al*[6] performed an unrestricted Hartree–Fock (UHF) computation and obtained the bond length to be 0.35 nm. Fujima and

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Yamaguchi[7] used a spin-polarized $X-$ method to find antiferromagnetic bond length to be 0.34 nm. In sharp contrast to these relatively good estimates of the bond length, the bond distance for the single state of manganese dimmer was reported to be only 0.166 nm by Nayak *et al.*[8] In the non-DFT research, all dissociation energy predictions were less than 0.79 eV, in the DFT study of Nayak *et al*[8] the dissociation energies were negative, suggesting an unbound system.

Christopher *et al*[9] in 2000 calculated the molecular structure of Mn_2 by using DFT, and concluded that the ground state of Mn_2 is 1-multiple state, the equilibrium bond length R_e for the ground state of Mn_2 molecule is 0.1645 nm, with no dissociation energy D_e in his results, and the vibration frequency ω_e is 732 cm^{-1}. According to Kirkwood *et al*,[3] the experimental vibration frequency ω_e is 68.1 cm^{-1}, and according to Cheeseman *et al*,[4] the experimental equilibrium bond length R_e is 0.3400 nm. Obviously, the gap between the former of 0.1645 nm and the latter of 0.3400 nm is considerable. But by means of calculation, we have concluded that the ground state of Mn_2 is 11-multiple state, the equilibrium bond length R_e for the ground state of Mn_2 molecule is 0.2506 nm, the dissociation energy D_e is 1.4477 eV, and the vibration frequency ω_e is 211.51 cm^{-1}. It can be seen that our calculation is much closer to the experimental results. Besides, this is the first time, so far as we know, to show that the ground state of Mn_2 molecule is 11-multiple state, which indicates that spin polarization effect exists in Mn_2 molecule, a transition metal molecule.

It is difficult to confirm the ground state of Mn_2 molecule. It might be related to the delocalization effect of the d electron of $3d^54s^2$. Making use of the density functional theory method (DFT) (B3p86) of Gaussian 03, we have optimized the structure of the Mn_2 molecule and obtained the potential energy function of this molecule. The result shows that the corresponding minimal energies of 1-, 3-, 5-, 7-, 9-, 11-multiple states of the Mn_2 molecule are very close to each other, but even so, the 11-multiple state is certainly the ground state of Mn_2. It follows that in Mn_2 molecule there exists the spin polarization effect. Besides, we have confirmed that there exist the spin polarization effects in Ti_2, Tc_2, Fe_2 and Ni_2 molecules after we studied the structures of Ti_2, Tc_2, Fe_2 and Ni_2 molecules.[10−13] We have made research also on the diatomic molecules of the other transition metal elements and their clusters.[14]

It is generally known that the multiplicity of the ground state of diatomics for light elements is usually comparatively low, for example, $2s+1=1\sim4$, because of the interaction of electronic configurations, particularly, the effect of electron pairing. However, the recent work[15] indicates that this is not the case for heavy elements. For example, for molecules Pu_n $(n=2,3,4)$, the ground state of plutonium Pu is ^7F_g with 6 of unpaired electrons, the unpaired electrons for Pu_2, Pu_3 and Pu_4 will be 12, 18 and 24, respectively; the possible multiplicities will be $2s+1=1$, 3, 5, 7, 9, 11, and 13 for Pu_2, $2s+1=1$, 3, 5, 7, 9, 11, 13, 15, 17, and 19 for Pu_3, $2s+1=1$, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, and 25 for Pu_4. The energy will decrease with multiplicity, the most stable configurations are of the multiplicities of 13, 19, 25 for Pu_2, Pu_3 and Pu_4, respectively. It is similar for U clusters. What does this imply? It means that the electrons prefer to take parallel spin in Pu_n and U clusters. This sort of non-equilibrium in electron spins is called spin-polarization effect. One of the major current research subjects is the spin-polarization in the molecules of actinide elements. The potential functions of the compounds of heavy elements also attract the interest of many scientific workers.[16−18]

2. Theoretical methodology and calculation

The electronic configuration of Fe atom is $3d^54s^2$ where $4s^2$ is fully occupied. From $3d^5$, we can infer that the ground electronic configuration of Fe atom is $^6S_{5/2}$. The Mn_2 molecule composed of $^6S+{}^6S$ might have 1-, 3-, 5-, 7-, 9- or 11-multiple state. According to the calculations, the ground state of Mn_2 molecule is 11-multiple state of the parallel spins of 10 electrons, which shows the spin polarization effect of the electrons in the molecule.

According to Ref.[19], Mn_2 molecule belongs to $D_{\infty h}$ molecule group, and the electronic configuration of Mn atom is $^6S_{5/2}$. According to Ref.[18], the atom groups can be dissolved into the direct summation of molecule groups $D_{\infty h}$ when two atoms form a linear molecule. That is, $^6S_g=\,^6\Sigma_g^+$.

So the direct product of two Mn atoms with spherical symmetry is

$$^6S_g\times{}^6S_g={}^6\Sigma_g^+\times{}^6\Sigma_g^+={}^{1,3,5,7,9,11}\Sigma_g^+,$$

where $^{1,3,5,7,9,11}\Sigma_g^+$ are the possible electronic configurations of Mn_2 molecule. By use of density func-

tional method (B3p86) of Gaussian 03, all the possible molecule states have been optimized (see Table 1 for the theoretical bond lengths in nm, the lowest energy levels of the molecules in H.a.u., and the total s expectance values and calculated values of spins).

Spin pollution is the error in the unlimited *ab initio* calculation. It often comes about in the total energy because the wavefunction of the ground state mingles with the wavefunction in higher-energetic states. High spin pollution will influence the molecular structure and the analysis of distributed numbers of molecules, especially the densities of spins. It also influences the constringency, especially the MP_n assignment. The spin pollution can be validated by comparing the total S_1 prospective value of spin and the value of calculation S_2. S_1 should equal $s(s+1)$, where s is the total spin value of the Mn_2 molecule. In general, the result is acceptable if the error is not beyond 10%.

Table 1. Optimum results of Mn_2 molecule.

Multiplicity	R_e/nm	E/H.a.u.	Expectance of spin S_1	Calculation of spin S_2
1	0.16512	−2302.7796		0
3	0.15637	−2302.7137	2	2
5	0.17527	−2302.7304	6	6
7	0.18603	−2302.7626	12	12
9	0.20936	−2302.7871	20	20
11	0.25056	−2302.8632	30	30

In Table 1, H.a.u. (Hartree atom units) is an energy unit, 1 H.a.u. $= 27.212\times1.6\times10^{-19}$J. From Table 1 we can find that the energy of the 11-multiple state of the Mn_2 molecule is the lowest, so the 11-multiple state is the ground state of the Mn_2 molecule. As the multiplicity increases, the unpaired electrons increase gradually, that is, in the Mn_2 molecule, the greater the number of the unpaired electrons is, the lower its energy will be —the state with the lowest energy is the most stable. This condition is known as spin polarization effect. Pairing of electrons may reduce the energy of the system. However, the commutative integral of spin parallel electrons is positive, which also leads to the reduction of the energy of the system. This shows that, in transition element molecules, the effect of spin parallel is larger than the effect of paired electrons. It is obviously related to the delocalization of electron d. Meanwhile, we find that the minimal energy values of 1-, 3-, 5-, 7-, 9-, 11-multiple states of the Mn_2 molecule are very close to each other. According to our through calculations, the ground state of the Mn_2 molecule is the 11-multiple state. That the ground state of Mn_2 molecule is 11-multiple state shows that there exists spin polarization effect in the Mn_2 molecule, a diatomic molecule of transition metal element. The dissociation energy of the ground state of the Mn_2 molecule (11-multiple state) is $D_e = 1.4477$ eV. From Table 1, we can find that prospective values and the calculated values of total spin in 3-, 5-, 7-, 9-, 11-multiple states are absolutely the same except that 1-multiple state does not come up in the optimum result. It shows that there is no spin pollution in the DFT calculations for the Mn_2 molecule, and that the wavefunction of the ground state does not mingle with the wavefunction of higher-energy state.

3. Potential function and spectral data

Making use of density functional theory method (DFT)(B3p86) of Gaussian 03 program,[20] we have calculated the 1-multiple, 3-multiple, 5-multiple, 7-multiple, 9-multiple, and 11-multiple states of the Mn_2 molecule and obtained a series of spot values of potential function. Using the least square fitting, we have determined the function form of Murrell–Sorbie potential function,[21,22] which can be expressed as

$$E(\rho) = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho).$$

In the above formula, $\rho = R - R_e$, where R is the interatomic distance and R_e its equilibrium value, D_e is the molecular energy of dissociation, a_1, a_2, a_3 are the 1st, 2nd and 3rd order moduli respectively. They can be obtained through fitting (see Table 2 for the result).

Table 2. Parameters for Murrell–Sorbie potential function about the Mn_2 molecule.

Multiplicity	D_e/ eV	R_e/nm	a_1/Å^{-1}	a_2/Å^{-2}	a_3/Å^{-3}
11	1.4477	0.2506	1.4850	−0.4581	0.6394
9	1.1127	0.2094	3.2360	−6.7839	0.0004
7	6.2188	0.1860	1.6313	−1.0162	1.2786
5	6.8027	0.1753	2.9644	3.4279	3.4334
3	3.7041	0.1564	10.7398	2.8669	1.3919
1	7.4332	0.1651	4.3931	5.6571	3.4740

According to the Murrell–Sorbie potential function, from the above fitting data we can see from the following figures the relevant potential curve and the corresponding scan results of the multiple states. Every state includes two curves, one for the scan value, and the other for the fitted value. It means that the process of fitting is successful. The 11-multiple state is the ground state of the Mn_2 molecule. In Figs.1–6, R is the distance between two atoms in units of Å, E is the energy, in units of eV.

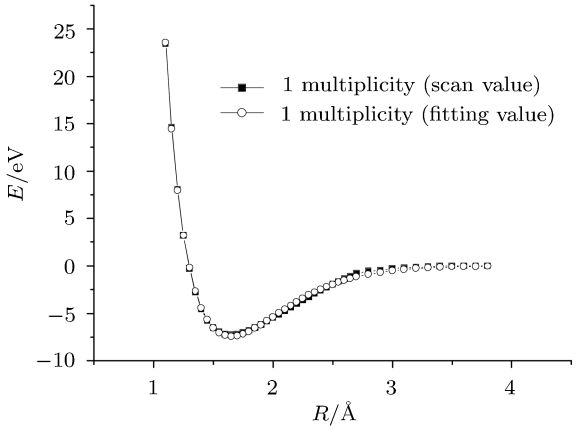


Fig.1. The potential curve of Mn_2 molecule for 1-multiplicity.

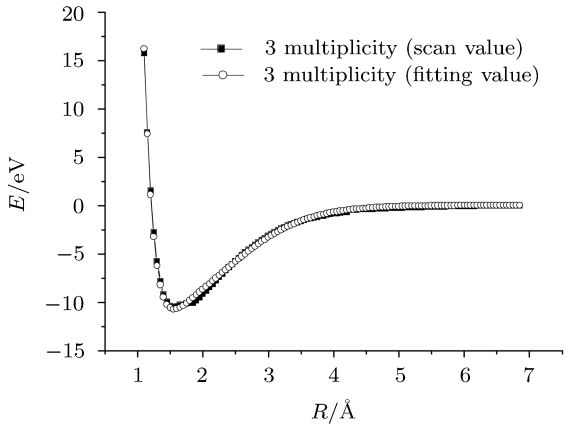


Fig.2. The potential curve of Mn_2 molecule for 3-multiplicity.

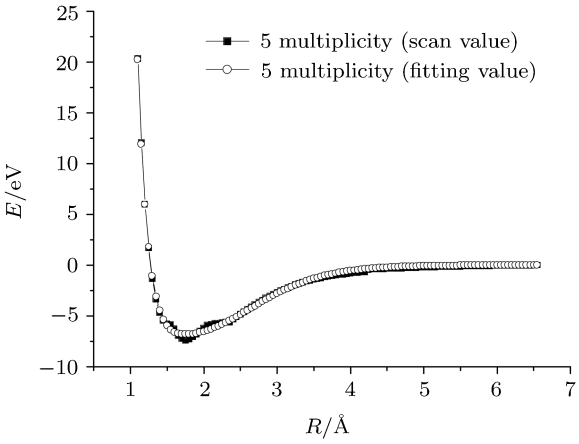


Fig.3. The potential curve of Mn_2 molecule for 5-multiplicity.

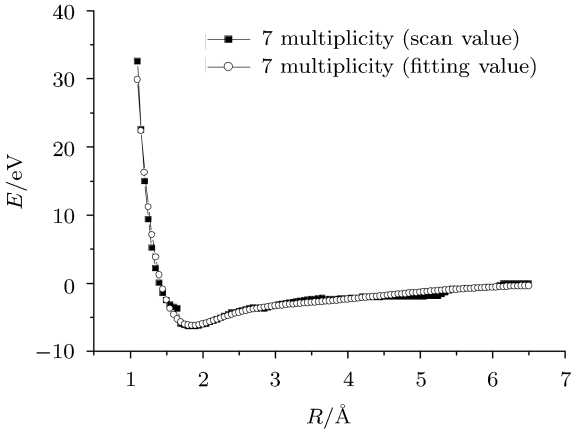


Fig.4. The potential curve of Mn_2 molecule for 7-multiplicity.

According to the relationship between the parameters a_1, a_2, a_3 of the Murrell–Sorbie potential function and the spectroscopic data ω_e, $\omega_e\chi_e$, B_e, α_e, and that between the force constants f_2, f_3, f_4 and the spectroscopic data ω_e, $\omega_e\chi_e$, B_e, α_e,[23,24] we can determine the spectroscopic data and force constants of the Mn_2 molecule as follows:

$$f_2 = D_e(a_1^2 - 2a_2) = 4\pi^2 m\omega_e^2 c^2,$$

$$f_3 = 6D_e(a_1a_2 - a_3 - a_1^3/3)$$
$$= -3f_2/R_e(1 + \alpha_e\omega_e/6B_e^3),$$
$$f_4 = D_e a_1^4 - 6f_2a_1^2 - 4f_3a_1$$
$$= f_2/R_e^2[15 - (1 + \alpha_e\omega_e/6B_e^2)^2 - 8\omega_e\chi_e/B_e],$$

where c is the velocity of light, m is the reduced mass of the atom, the value of B_e is given by $B_e = h/8\pi^2$ cm, and $R_e^2 = h/8\pi^2 cI_e$.

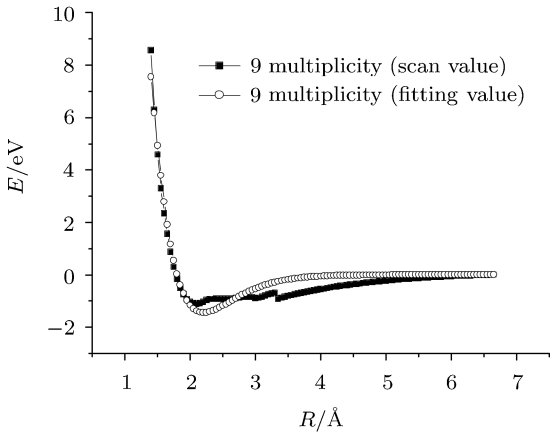


Fig.5. The potential curve of Mn_2 molecule for 9-multiplicity.

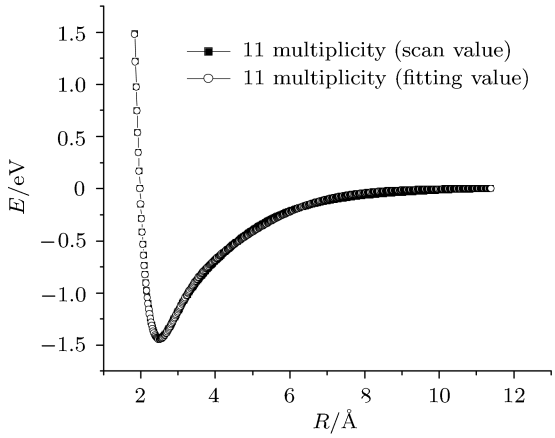


Fig.6. The potential curve of Mn_2 molecule for 11-multiplicity.

There are the mechanical parameters and spectral data for Mn_2 molecule in Table 3.

Table 3. The mechanical parameters and spectral data for Mn_2 molecule.

Multiplicity	f_2/(aJ/nm^2)	f_3/(aJ/nm^3)	f_4/(aJ/nm^4)	$\alpha_e/10^{-4}$ cm^{-1}	$\omega_e\chi_e$/cm$^-$	B_e/cm^{-1}	ω_e/cm^{-1}
11	0.7240	−3.3557	11.4813	7.7826	1.5301	0.0978	211.5087
9	4.2857	−35.5639	210.6175	10.9559	5.0357	0.1401	514.67
7	4.6765	−26.2049	103.3787	8.6902	2.3194	0.1774	537.62
5	2.1056	−12.7856	124.7550	16.9128	0.1691	0.1998	360.69
3	65.0501	−1365.6595	21544.69	18.7445	30.9438	0.2509	2004.83
1	9.5099	−49.1843	206.6681	7.3232	1.7528	0.2251	766.55

We have already used the density functional theory method to calculate the mechanical parameters and spectral data for Ni_2, Tc_2, Fe_2 and Ti_2 molecules and other transition metal element molecules. The results show that spin-polarization effect exists in them. So we use a similar method to deal with the Mn_2 molecule.

Now by comparing our results with the experimental results as well as the calculated results of other researchers, we can see that our results are closer to the experimental results (see Table 4).

Table 4. Comparison between the experimental and our results.

	R_e/nm	D_e/eV	ω_e/cm^{-1}
This work	0.2506	1.4477	211.51
Experiment	0.3400[4]		68.10[3]
Christopher[9]	0.1645		732.00
Morse[2]		0.7400	

4. Conclusion

Making use of density functional theory method (DFT)(B3p86) of Gaussian 03 program, we have calculated the 1-, 3-, 5-, 7-, 9- and 11-multiple states of the Mn_2 molecule. The result shows that the ground state of the Mn_2 molecule is 11-multiple state, indicates the existence of spin polarization effect in the Mn_2 molecule, and is indicative of the fact that there exist 10 parallel spin electrons in the Mn_2 molecule, where the number of non-conjugated electrons is the greatest. These electrons occupy different spacious orbitals, and in this case the energy of the Mn_2 molecule is minimal. It shows that the effect of parallel spins in the Mn_2 molecule is larger than the conjugated effect of the electrons in the molecule, which is obviously related to the effect of the delocalization of the electron d. The dissociation energy D_e

of 11-multiple state (ground state) of Mn_2 molecule is 1.4477 eV, and the equilibrium bond length is 0.2506 nm. We have obtained the Murrell–Sorbie potential function of the Mn_2 molecule, its vibration frequency is 211.51 cm^{-1}, and its force constants f_2, f_3, and f_4 are 0.7240 $aJ{\cdot}nm^{-2}$, -3.3557 $aJ{\cdot}nm^{-3}$, 11.4813 $aJ{\cdot}nm^{-4}$ respectively. These results are very helpful for understanding the structural characteristics of the transition metal molecules. We have already used the density functional theory method to calculate the Ni_2 and Ti_2 molecules and other transition metal element molecules. The results show that spin-polarization effect exists in them. So we use the similar method to deal with the Mn_2 molecule and obtain some feasible results.

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