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Spin polarization effect for Fe_2 molecule

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This paper uses the density functional theory (DFT)(B3p86) of Gaussian03 to optimize the structure of Fe_2 molecule. The result shows that the ground state for Fe_2 molecule is a 9-multiple state, which shows spin polarization effect of Fe_2 molecule of transition metal elements for the first time. Meanwhile, we have not found any spin pollution because the wavefunction of the ground state does not mingle with wavefunctions with higher energy states. So, that the ground state for Fe_2 molecule is a 9-multiple state is indicative of the spin polarization effect of Fe_2 molecule of transition metal elements. That is, there exist 8 parallel spin electrons. The non-conjugated electron is greatest in number. These electrons occupy different spacious tracks, so that the energy of the Fe_2 molecule is minimized. It can be concluded that the effect of parallel spin of the Fe_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 Fe_2 molecule are derived. Dissociation energy D_e for the ground state of Fe_2 molecule is 2.8586ev, equilibrium bond length R_e is 0.2124nm, vibration frequency ω_e is 336.38 cm^{-1}. Its force constants f_2, f_3, and f_4 are 1.8615aJ·nm^{-2}, –8.6704aJ·nm^{-3}, 29.1676aJ·nm^{-4} respectively. The other spectroscopic data for the ground state of Fe_2 molecule $\omega_e\chi_e$, B_e, α_e are 1.5461 cm^{-1}, 0.1339 cm^{-1}, 7.3428×10^{-4} cm^{-1} respectively.

Keywords: Fe_2, spin polarization, density functional theory, potential function
PACC: 3420, 3520G

1. Introduction

Currently it is a major research subject to analyse the molecular structures of the transition elements, especially those transition elements in the 4th and 5th periods. It is known that iron is one of the most important chemical elements. But up to now, useful information concerning the molecular structure of Fe_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 in 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 (MO) methods can barely reproduce the equilibrium geometries which have been accepted as being less sensitive to the level of calculations. Thus, the transition metal dimer is a challenging system which is of growing theoretical interest.

Christopher J. Barden and co-workers calculated molecular structure of Fe_2 by using density functional theory (DFT) in 2000:[2] he concluded that the ground state of Fe_2 is 7 multiple state, equilibrium bond length R_e for the ground state of Fe_2 molecule is 0.2645nm, dissociation energy D_e is 0.40ev, vibration frequency ω_e is 435 cm^{-1}. According to Moskovits and Dilella,[3] the experimental vibration frequency ω_e is 299.7 cm^{-1}. Obviously, the gap between the former and the latter is considerable. But by means of calculation, we have concluded that the ground state of Fe_2 is a 9-multiple state, equilibrium bond length R_e for the ground state of Fe_2 molecule is 0.2124nm, dissociation energy D_e is 2.8586eV, vibration frequency ω_e is 336.38 cm^{-1}. It can be seen that our calculation is much closer to the experimental result. Besides, this is the first time it has been shown that the ground state of Fe_2 molecule is a 9-multiple state, which indicates that spin polarization effect exists in the Fe_2 molecule of transition metal elements.

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It is difficult to confirm the ground state of the Fe_2 molecule. It might be related to the delocalization effect of the electron d of $3d^64s^2$. Using the DFT (B3p86) of Gaussian 03, we have optimized the structure of Fe_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 multiple states of Fe_2 molecule are very close to each other, but even so, the 9-multiple state is the ground state of Fe_2. It follows that in Fe_2 molecule there exists the spin polarization effect. Besides, we have confirmed that there exist spin polarization effects in Ti_2, Tc_2 and Ni_2 molecules after we studied the structures of Ti_2, Tc_2 and Ni_2 molecules.[4−6] We are currently doing research on the diatomic molecules of the other transition metal elements and their clusters.[7]

It is generally known that the multiplicity of ground state of diatomics for light elements is usually comparatively low, for example, $2s+1=1\sim4$, which is because of the interaction of electronic configuration, particularly, the effect of electron pairing. However, recent work[8] 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 ones, 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 are the implications of this situation? It means that the electrons prefer parallel spin in Pu_n and U clusters. This sort of non-equilibrium for electron spin is called spin-polarization effect. One of the major current research subjects is the spin-polarization for the actinides element molecules. The potential functions of compounds of heavy elements are also interesting domains for many scientific workers.[9−11]

2. Theoretical techniques and calculation

The electronic configuration of Fe atom is $3d^64s^2$ where $4s^2$ is a fully occupied. From $3d^6$, we can infer that the ground electronic configuration of Fe atom is $^5D_4$. The Fe_2 molecule composed of $^5D+{}^5D$ might have 1, 3, 5, 7 or 9 multiple states. According to the calculations, the ground state of Fe_2 molecule is a 9-multiple state of the parallel spin of 8 electrons, which shows the spin polarization effect of the electron in the molecule.

According to Atomic and Molecular Reaction Statics,[12] Fe_2 molecule belongs to $D_{\infty h}$ molecule group, and the electronic configuration of Fe atom is $^5D_4$. According to the Group Theoretical Derivation of Molecular Electronic States,[12] the atom group can be dissolved into the direct summation of molecule group $D_{\infty h}$ when two atoms form a linear molecule. That is,

$$^5D_g = {}^5\Sigma_g^+ + {}^5\Pi_g + {}^5\Delta_g.$$

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

$$\begin{aligned}
{}^5D_g \times {}^5D_g =& ({}^5\Sigma_g^+ + {}^5\Pi_g + {}^5\Delta_g) \times ({}^5\Sigma_g^+ + {}^5\Pi_g + {}^5\Delta_g)\\
=& {}^{1,3,5,7,9}\Sigma_g^+ + {}^{1,3,5,7,9}\Pi_g + {}^{1,3,5,7,9}\Delta_g + {}^{1,3,5,7,9}\Sigma_g^+ + {}^{1,3,5,7,9}\Sigma_g^+\\
&+ {}^{1,3,5,7,9}\Sigma_g^- + {}^{1,3,5,7,9}\Delta_g + {}^{1,3,5,7,9}\Pi_g + {}^{1,3,5,7,9}\phi_g + {}^{1,3,5,7,9}\Delta_g\\
&+ {}^{1,3,5,7,9}\Pi_g + {}^{1,3,5,7,9}\phi_g + {}^{1,3,5,7,9}\Sigma_g^+ + {}^{1,3,5,7,9}\Sigma_g^- + {}^{1,3,5,7,9}\Gamma_g\\
=& {}^{1,3,5,7,9}\Sigma_g^+(4) + {}^{1,3,5,7,9}\Sigma_g^-(2) + {}^{1,3,5,7,9}\Pi_g(3) + {}^{1,3,5,7,9}\Delta_g(3) + {}^{1,3,5,7,9}\phi_g(2) + {}^{1,3,5,7,9}\Gamma_g,
\end{aligned}$$

where ${}^{1,3,5,7,9}\Sigma_g^+(4)$, ${}^{1,3,5,7,9}\Sigma_g^-(2)$, ${}^{1,3,5,7,9}\Pi_g(3)$, ${}^{1,3,5,7,9}\Delta_g(3)$, ${}^{1,3,5,7,9}\phi_g(2)$ or ${}^{1,3,5,7,9}\Gamma_g$ are the possible electronic configuration of Fe_2 molecule. Using DFT (B3p86)of Gaussian03, we have optimized all the possible molecule states (See Table 1 for the theoretical bond lengths in nm, the lowest energy levels of the molecules in H.a.u., and the total expectance values and calculation values of spin. Here H.a.u. (Hartree atom unit) is energy unit, 1H.a.u.=$27.212\times1.6\times10^{19}$J.)

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 excited states. High spin pollution will influence the molecular structure and the analysis of distributed numbers of molecules, especially the densities of spin. 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 Fe_2 molecule. In general, the result is acceptable if the error is not beyond 10%. From Table 1, we can find that the energy of the 9-multiple state of Fe_2 molecule is lowest, so the 9-multiple state is the ground state of the Fe_2 molecule. As the multiplicity increases, the unpaired electrons increase gradually. That is, in the Fe_2 molecule, the greater the number of unpaired electrons, the lower its energy will be—the state with the lowest energy is the stablest. This condition is known as the 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 reduction of the energy of the system. This shows that, in the 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 multiple states of Fe_2 molecule are very close to each other. According to our detailed calculations, the ground state of Fe_2 molecule is a 9-multiple state. The fact that the ground state of Fe_2 molecule is a 9-multiple state shows that there exists spin polarization effect in the Fe_2 molecule, the diatomic molecule of transition metal elements. The dissociation energy of the ground state of Fe_2 molecule (9-multiple state) is D_e=2.8586eV. From Table 1, we can find that the prospective values and the calculation values of total spin are absolutely the same for 3, 5, 7, 9 multiple states except that the 1-multiple state does not come up in the optimum result. It shows that there is no spin pollution in the DFT calculations for Fe_2 molecule, and that the wavefunction of the ground state does not mingle with the wavefunction of excited states.

Table 1. Optimum results of Fe_2 molecule.

Multiplicity	R_e/nm	E/H.a.u.	Expectance of spin S_1	Calculation of spin S_2
1	0.18884	–2528.0602	0	
3	0.19989	–2528.1540	2	2
5	0.20765	–2528.1727	6	6
7	0.18903	–2528.2623	12	12
9	0.21236	–2528.2756	20	20

3. Potential function and spectral data

Using DFT (B3p86) of the Gaussian03 program, we calculated the 1-multiple state, 3-multiple state, 5-multiple state, 7-multiple state, 9-multiple state of Fe_2 molecule and obtained a series of spot values of the potential function. Using the method of least square fitting, we found the function form of the Murrell–Sorbie potential function,[13,14] 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, $\rho = R - R_e, R$ is the interatomic distance and R_e is its equilibrium value, D_e is the molecular energy of the dissociation, a_1, a_2, a_3 are the modulus of one, two and three orders respectively. They can be found through fitting. See Table 2 for the result.

Table 2. Parameters for the Murrell–Sorbie potential function for Fe_2 molecule.

Multiplicity	D_e/eV	R_e/nm	$a_1/0.1\text{nm}^{-1}$	$a_2/0.1\text{nm}^{-2}$	$a_3/0.1\text{nm}^{-3}$
9	2.8586	0.2124	1.4942	–0.9159	0.6746
7	7.2800	0.1890	1.5868	–0.7346	0.5056
5	5.4664	0.2077	2.9256	3.1242	1.5842
3	5.9722	0.1999	3.0013	3.4641	1.8582
1	4.4329	0.1888	4.5301	7.1059	4.1721

According to the Murrell–Sorbie potential function from the above fitting data, we can see the relevant potential curve and the corresponding scan results of the multiple states (see Figs.1–5). Every state includes two curves: one for the scan value, and the other for fitting value. They accord with each other precisely. This means that the process of fitting is successful. 9-multiple state is the ground state of the Fe_2 molecule.

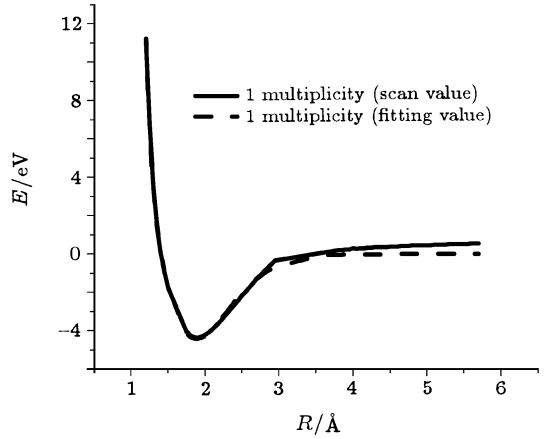


Fig.1. The potential curve of Fe_2 molecule for 1-multiplicity.

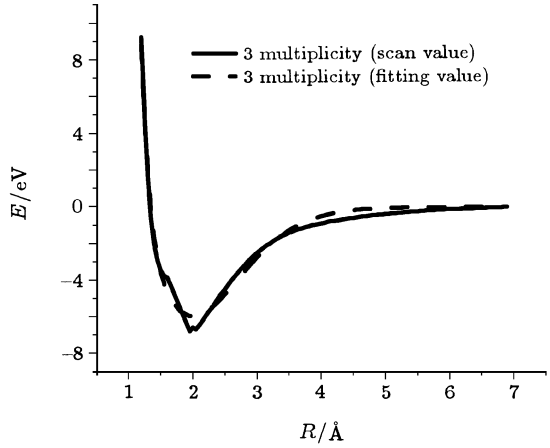


Fig.2. The potential curve of Fe_2 molecule for 3-multiplicity.

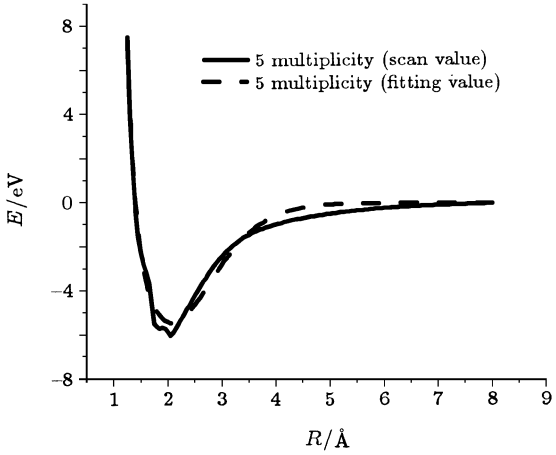


Fig.3. The potential curve of Fe_2 molecule for 5-multiplicity.

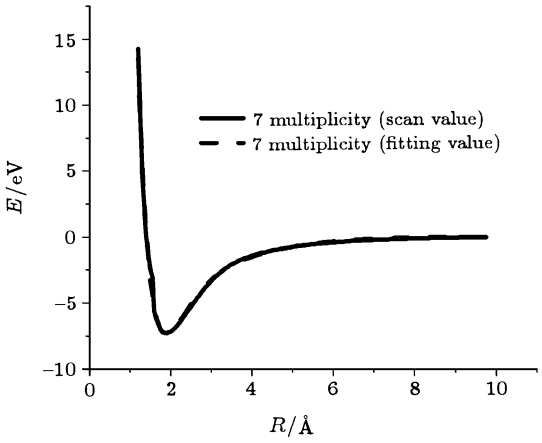


Fig.4. The potential curve of Fe_2 molecule for 7-multiplicity.

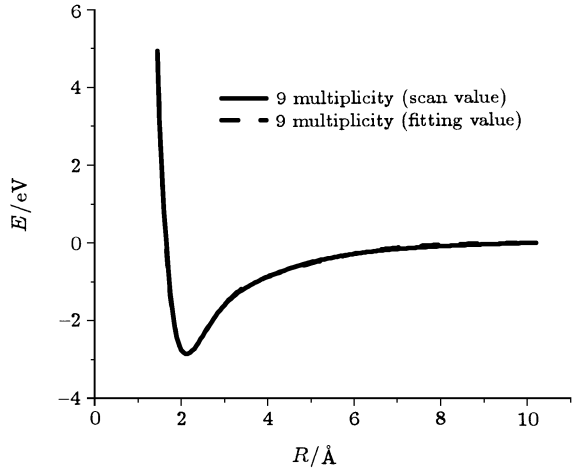


Fig.5. The potential curve of Fe_2 molecule for 9-multiplicity.

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,[15,16] we can obtain the spectroscopic data and force constants for the Fe_2 molecule as follows:

$$
\begin{aligned}
f_2 &= D_e(a_1^2 - 2a_2),\\
f_3 &= 6D_e(a_1a_2 - a_3 - a_1^3/3),\\
f_4 &= D_e a_1^4 - 6f_2a_1^2 - 4f_3a_1,\\
f_2 &= 4\pi^2 m\omega_e^2 c^2,\\
f_3 &= -3f_2/R_e(1 + \alpha_e\omega_e/6B_e^3),\\
f_4 &= f_2/R_e^2[15 - (1 + \alpha_e\omega_e/6B_e^2)^2 - 8\omega_e\chi_e/B_e],
\end{aligned}
$$

where c is the velocity of light, m is the reduced mass of individual atoms, and the value of B_e is given by $B_e = h/8\pi^2 mc\ R_e^2 = h/8\pi^2 cI_e$ (Table 3).

Table 3. The mechanical parameters and spectral data for Fe_2 molecule.

Multiplicity	f_2/aJ/nm^2	f_3/aJ/nm^3	f_4/aJ/nm^4	$\alpha_e/10^{-4}\,cm^{-1}$	$\omega_e\chi_e/\,cm^{-1}$	$B_e/\,cm^{-1}$	$\omega_e/\,cm^{-1}$
9	1.8615	–8.6704	29.1676	7.3428	1.5461	0.1339	336.38
7	4.6506	–21.0168	70.5334	5.9517	1.4241	0.1690	531.68
5	1.8662	–2.7725	0.7714	0.0990	0.2464	0.1400	336.80
3	1.9899	–2.7162	2.7010	–0.3565	0.1319	0.1511	347.78
1	4.4816	–12.6576	-23.3502	2.5628	1.3965	0.1693	521.93

We used a similar method to calculate for the Ni_2 molecule, Tc_2 molecule and Ti_2 molecule and other transition metal element molecules. The results show that the spin-polarization effect exists in them. So we use a similar method to deal with the Fe_2 molecule.

Now by comparing our results with the experimental results as well as others' calculation results, we are able to see that ours is closer to the experimental results. See Table 4.

Table 4. Comparison of our work and experimental results.

	R_e/nm	D_e/eV	$\omega_e/\,cm^{-1}$
This work	0.2124	2.8586	336.38
Experiment	0.2020[17]	1.240[18]	299.70[3]
Christopher[2]	0.2645	0.400	435.00

4. Conclusion

Using DFT (B3p86) of the Gaussian03 program, we have calculated the 1, 3, 5, 7 and 9 multiple states of the Fe_2 molecule one by one. The result shows that the ground state of Fe_2 molecule should be the 9-multiple state. The minimal energy values of 1, 3, 5, 7 and 9 multiple states of Fe_2 molecule are very close to each other. Meanwhile, we have not found any spin pollution and the wavefunction of the ground state does not mingle with the wavefunction of excited states. The result shows that the ground state for the Fe_2 molecule is 9-multiple state, which shows the spin polarization effect of Fe_2 molecule of transition metal elements, and indicates the fact that there exist 8 parallel spin electrons in the Fe_2 molecule, where the nonconjugated electron is greatest in number. These electrons occupy different spacious tracks, and in this case, the energy of Fe_2 molecule is minimal. This shows that the effect of parallel spin of the Fe_2 molecule is larger than the conjugated effect of the electrons of the molecule, which is obviously related to the effect of the delocalization of electron d. Dissociation energy D_e of the 9-multiple state (ground state) of the Fe_2 molecule is 2.8586eV, and the equilibrium bond length is 0.2124nm. We have obtained the Murrell–Sorbie potential function of Fe_2 molecule, vibration frequency is $336.38\,cm^{-1}$, and the force constants f_2, f_3, and f_4 are 1.8615aJ·nm^{-2}, – 8.6704aJ·nm^{-3}, 29.1676aJ·nm^{-4} respectively. This result is very helpful for us to understand the structural characteristics of the transition metal molecules. We used a similar method to calculate Ni_2 molecule and Ti_2 molecule and other transition metal element molecules. The results show that the spin-polarization effect exists in them. So we use a similar method to deal with the Fe_2 molecule.

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