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Spin polarization effect for Cr_2 molecule*

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Density functional theory (DFT) (B3P86) of Gaussian 03 has been used to optimize the structure of the Cr_2 molecule, a transition metal element molecule. The result shows that the ground state for the Cr_2 molecule is a 13-multiple state, indicating that there exists a spin polarization effect in the Cr_2 molecule. Meanwhile, we have not found any spin pollution because the wave function of the ground state does not mingle with wave functions of higher-energy states. So the ground state for Cr_2 molecule being a 13-multiple state is indicative of spin polarization effect of the Cr_2 molecule among transition metal elements, that is, there are 12 parallel spin electrons in the Cr_2 molecule. The number of non-conjugated electrons is greatest. These electrons occupy different spatial orbitals so that the energy of the Cr_2 molecule is minimized. It can be concluded that the effect of parallel spin in the Cr_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 Cr_2 molecule are derived. The dissociation energy De for the ground state of the Cr_2 molecule is 0.1034 eV, equilibrium bond length Re is 0.3396 nm, and vibration frequency ω_e is 73.81 cm^{-1}. Its force constants f_2, f_3 and f_4 are 0.0835, −0.2831 and 0.3535 $aJ \cdot nm^{-4}$ respectively. The other spectroscopic data for the ground state of the Cr_2 molecule $\omega_e\chi_e$, B_e and α_e are 1.2105, 0.0562 and $7.2938 \times 10^{-4} cm^{-1}$ respectively.

Keywords: Cr_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 chromium is one of the most important chemical elements. But up to now, useful information concerning the molecular structure of Cr_2 has been limited. The difficulties in theoretically treating 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 appropriately describe the d bonds of these systems by using 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, the *ab initio* molecular orbital method 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 the theoretical interest increasingly.

Christopher *et al*[2] in 2000 calculated the molecular structure of Cr_2 by using the DFT, and they concluded that a chromium dimer had a ground $^1\Sigma_g^+$ state with a [core] $(3d\pi_u)^4(3d\sigma_g)^2(4s\sigma_g)^2(3d\delta_g)^4$ electron configuration and a $^7S + {}^7S$ dissociation limit. Thus, it has formally a "strong" bond order of six, of which the significance is questionable, given its low dissociation energy.[3] The bond length determined by laser-induced fluorescence (LIF) is 0.16788 nm,[4] the frequency determined by negative-ion photoelectron spectroscopy is $480.6 \pm 0.5\ cm^{-1}$,[5] and a second-law estimate of the dissociation energy[6] is 1.44 ± 0.05 eV. It is thought that the potential energy surface of the chromium dimer may have two minima, one is closed-shell and has been observed by experiment (the aforementioned $^1\Sigma_g^+$ state), and the other is antiferromagnetically coupled in the 3d orbitals and its actual existence is in doubt (as in Mn_2 before).[7] This study

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and the latest studies focus on the formally closed-shell case. Research by Edgecombe and Becke using the spin-projected DFT with a (14s9p5d2f) basis and the Becke–Lee–Yang–Parr (BLYP), the B3P86 (which stands for Becke 1993, Perdew 1986), and the local spin density approximation (LSDA) functionals found lengths of 0.148–0.150 nm to be in relative disagreement with experiment.[8] A conventional DFT with the LSDA functional predicted $R_e = 0.1634$ nm, which falls within the range of this study.[9]

The chromium dimer is an infamous problem in quantum chemistry, so it comes as no surprise that recent high-level theoretical studies are abundant. Scuseria and Schaefer studied the system at a coupled cluster (CC) level and determined a coupled cluster single and double (CCSD) bond length of 0.1562 nm and a CCSD (T) bond length of 0.1604 nm at frequencies 886 and 766 cm^{-1}, respectively.[10,11] Bauschlicher and Partridge reported the outer minimum in the potential energy surface at 0.254 nm which could be verified by unrestricted Becke-3-Lee-Yang-Parr (B3LYP) and B3P86 functionals; unrestricted BLYP and restricted B3LYP found the minimum of shorter bond length.[12] Anderson,[13] Roos and Anderson *et al*[14] used the complete active space second-order perturbation (CASPT2) method to find $R_e = 0.169$ or 0.171 nm and $\omega_e = 514$ or 590 cm^{-1}, depending on whether the relativistic effects were included or not, respectively. Most recently a very large (about 1.3 billion configuration state functions) multi-reference configuration interaaction/multi-reference averaged couple pari functional (MRCI/MRACPF) study by Dechsel *et al*[15] determined $R_e = 0.172$ nm, $\omega_e = 339$ cm^{-1}, and a dissociation energy of 1.09 eV. That such a large study did not accord with measurement for the geometry or frequency suggests that more theoretical work is still needed.

Overall, in this study, the bond length is somewhat overestimated by the DFT, but the frequency and the dissociation energy are somewhat underestimated by the DFT. Christopher *et al*[2] in 2000 calculated the molecular structure of Cr_2 by using the DFT, and they concluded that the ground state of Cr_2 was a 1-multiple state, the equilibrium bond length Re for the ground state of Cr_2 molecule was 0.1595 nm, the dissociation energy D_e was -2.37 eV, and the vibration frequency ω_e was 942 cm^{-1}. According to Casey and Leopold,[5] the experimental vibration frequency ω_e is 480.1 cm^{-1}, according to Bondybey and English,[4] the experimental equilibrium bond length Re is 0.1679 nm, and according to Hilpert *et al*,[6] the experimental dissociation energy D_e is 1.44 eV. Obviously, the gap between the former (-2.37 eV) and the latter (1.95 eV) is considerable. But through calculation, we have concluded that the ground state of Cr_2 is a 13-multiple state, the equilibrium bond length Re for the ground state of Cr_2 molecule is 0.3396 nm, the dissociation energy D_e is 0.1034 eV, and the vibration frequency ω_e is 73.81 cm^{-1}. It can be seen that our calculations are much closer to the experimental results except the bond length and the vibration frequency. Besides, this is the first time, so far as we know, to show that the ground state of Cr_2 molecule is a 13-multiple state, which indicates that there exists a spin polarization effect in a Cr_2 molecule, a transition metal molecule.

It is difficult to confirm the ground state of Cr_2 molecule, which might be related to the delocalization effect of the d electron of $3d^5 4s^1$. Making use of the density functional theory method (DFT) (B3P86) of Gaussian 03, we optimize the structure of the Cr_2 molecule and obtain the potential energy function of this molecule. The result shows that the corresponding minimal energies of 1-, 3-,5-,7, 9-,11-, 13-multiple states of the Cr_2 molecule are very close to each other, but even so, the 13-multiple state is the ground state of Cr_2. It follows that in a Cr_2 molecule there exists a spin polarization effect. Besides, we can confirm that there exist the spin polarization effects in Ti_2, Tc_2, Fe_2 and Ni_2 molecules after we have studied the structures of Ti_2, Tc_2, Fe_2 and Ni_2 molecules. We carry out the research also on the diatomic molecules of the other transition metal elements and their clusters.

It is generally known that the multiplicity of the ground state of diatomics for light elements is usually comparatively low, for example, $2s + 1 = 1 - 4$, because of the interaction between the electronic configurations, particularly, the effect of electron pairing. However, the recent work[16] 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, and the most stable configurations are of the multiplicities of 13, 19, 25 for Pu_2, Pu_3 and Pu_4, respectively. It

is similar to the case of U clusters. What does this imply? It means that the electrons prefer to take parallel spins in Pu_n and U clusters. This sort of non-equilibrium in electron spins is called the 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 have also aroused the interest of many scientists.[17−21]

2. Theoretical method and calculation

The electronic configuration of Cr atom is $3d^5 4s^1$. So we can infer that the ground electronic configuration of Cr atom is $^7S_3$. The Cr_2 molecule composed of $^7F + ^7F$ might have $1-, 3-, 5-, 7-, 9-, 11-$, or 13-multiple states. According to the calculations, the ground state of Cr_2 molecule is a 13-multiple state of the parallel spins of 12 electrons, which shows the spin polarization effect of the electrons in the molecule.

According to Ref.[22], Cr_2 molecule belongs to $D_{\infty h}$ molecule group, and the electronic configuration of Cr atom is $^7S_3$. According to Ref.[22], 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,

$$^7S_g = ^7\Sigma_g^+.$$

So the direct product of two Cr atoms with a spherical symmetry is

$$^7S_g \times ^7S_g = ^7\Sigma_g^+ \times ^7\Sigma_g^+ = ^{1,3,5,7,9,11,13}\Sigma_g^+,$$

where $^{1,3,5,7,9,11,13}\Sigma_g^+$ are the possible electronic configurations of Cr_2 molecule. By using density functional method (B3P86) of Gaussian03, 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., the total s expectation values and calculated values of spins).

Table 1. Optimum results of Cr_2 molecule.

Multiplicity	R_e/nm	E/H.a.u.	Expectation of spin S_1	Calculation of spin S_2
1	0.15531	–2089.7748		0
3	0.15638	–2089.7195	2	2
5	0.19384	–2089.7592	6	6
7	0.20037	–2789.7472	12	12
9	0.23932	–2089.7635	20	20
11	0.27484	–2089.8584	30	30
13	0.33963	–2089.8593	42	42

The spin pollution is an error in the unlimited *ab initio* calculation. It often comes about in the total energy because the wave function of the ground state mingles with the wave function 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 with the value of calculation S_2. S_1 should equal $s(s+1)$, where s is the total spin value of the Cr_2 molecule. In general, the result is acceptable if the error is not beyond 10%. In Table 1, H.a.u. (Hartree atom unit) is an energy unit, and 1 H.a.u. $= 27.212 \times 1.6 \times 10^{-19}$J. From Table 1 we can find that the energy of 13-multiple state of the Cr_2 molecule is lowest, so the 13-multiple state is the ground state of the Cr_2 molecule. As the multiplicity increases, the unpaired electrons increase gradually, that is, in the Cr_2 molecule, the greater the number of the unpaired electrons is, the lower its energy will be. The state with the lowest energy is most stable. This condition is known as the spin polarization effect. The pairing of electrons may reduce the energy of the system. However, the commutative integral of spin parallel electrons is positive, which also leads to a reduction in energy of the system. It 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 $1-, 3-, 5-, 7-, 9-, 11-$, 13-multiple states of the Cr_2 molecule are very close to each other. According to our thorough calculations, the ground state of

the Cr_2 molecule is the 13-multiple state. That the ground state of Cr_2 molecule is the 13-multiple state shows that there exists the spin polarization effect in the Cr_2 molecule, a diatomic molecule of transition metal element. The dissociation energy of the ground state of the Cr_2 molecule (13-multiple state) is De = 0.1034 eV. From Table 1, we can also find that the expectation values and the calculated values of total spin about $3-, 5-, 7-, 9-, 11-$, 13-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 Cr_2 molecule, and that the wave function of the ground state does not mingle with the wave function of higher-energy state.

3. Potential function and spectral data

Making use of density functional theory (DFT) (B3P86) of Gaussian 03 program,[23] we have calculated the 1-multiple, 3-multiple, 5-multiple, 7-multiple, 9-multiple, 11-multiple, and 13-multiple states of the Cr_2 molecule and obtained a series of spot values of potential function. Using the least square fitting, we can determine the function form of Murrell–Sorbie potential function,[24,25] 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, $\rho = R - Re$, where R is the interatomic distance and Re its equilibrium value; De is the molecular energy of dissociation; a_1, a_2, and a_3 are the 1st, 2nd and 3rd order moduli respectively. They can be conducted through fitting (see Table 2 for the results). According to parameters for Murrell–Sorbie potential function about the Cr_2 molecule we can acquire the respective fitting curves for 1, 3, 5, 7, 9 , 11, and 13 multiple states. Every state has two curves, one is for the scan value, and the other is for the fitting value. This means that the process of fitting is successful. The 13-multiple state is the ground state of the Cr_2 molecule. In Figs.1–7, R is the distance between two atoms, in units of nm, and E is energy in units of eV.

Table 2. Parameters for Murrell–Sorbie potential function about the Cr_2 molecule.

Multiplicity	D_e/eV	R_e/nm	$a_1/(0.1\text{nm})^{-1}$	$a_2/(0.1\text{nm})^{-2}$	$a_3/(0.1\text{nm})^{-3}$
13	0.1034	0.3396	3.5744	3.8693	1.4555
11	2.2552	0.2748	2.4474	-1.5984	5.5109
9	1.1588	0.2393	3.9929	3.4855	0.0006
7	3.9576	0.2004	3.4197	4.4017	2.6108
5	7.1905	0.1938	3.6328	5.3595	3.3028
3	10.5083	0.1564	2.8344	1.7365	4.3810
1	15.8752	0.1553	2.2657	-0.2206	1.5808

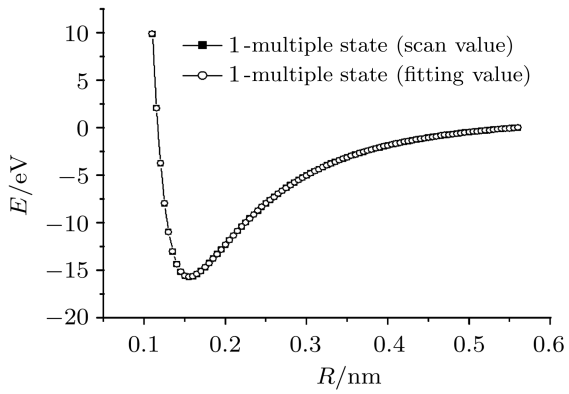


Fig.1. The potential curve of Cr_2 molecule for 1-multiple state.

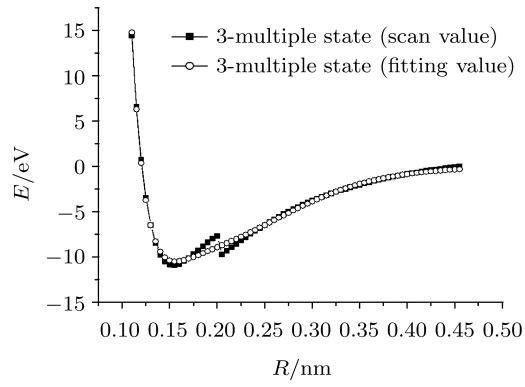


Fig.2. The potential curve of Cr_2 molecule for 3-multiple state.

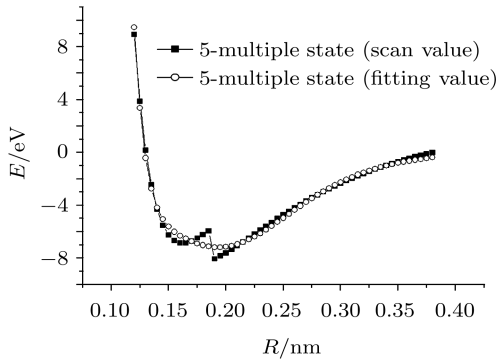


Fig.3. The potential curve of Cr_2 molecule for 5-multiple state.

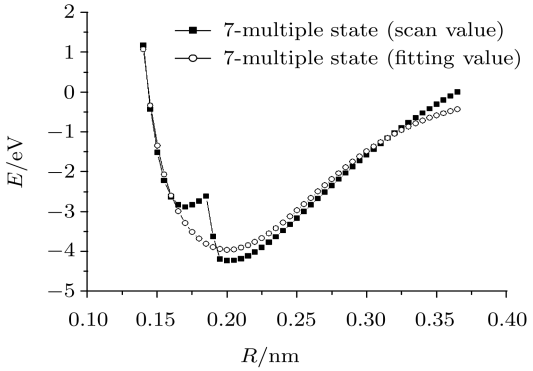


Fig.4. The potential curve of Cr_2 molecule for 7-multiple state.

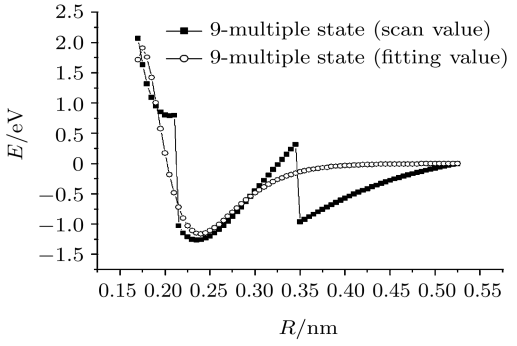


Fig.5. The potential curve of Cr_2 molecule for 9-multiple state.

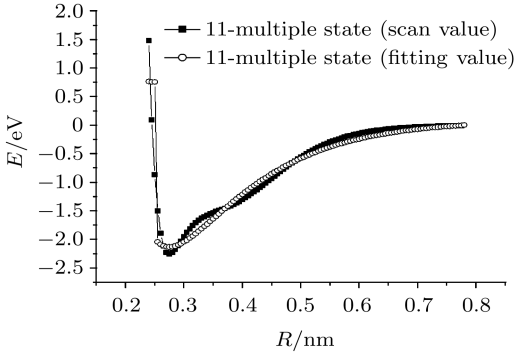


Fig.6. The potential curve of Cr_2 molecule for 11-multiple state.

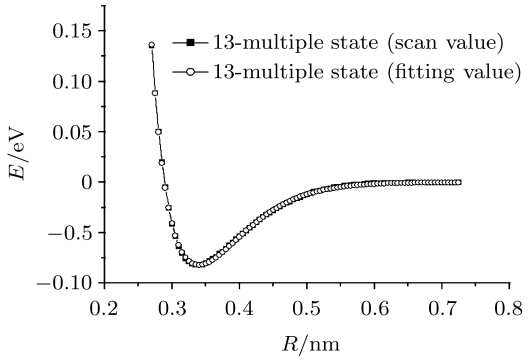


Fig.7. The potential curve of Cr_2 molecule for 13-multiple state.

According to the relationship between the parameters a_1, a_2, and a_3 of the Murrell–Sorbie potential function and the spectroscopic data ω_e, $\omega_e\chi_e$, B_e and α_e, and that between the force constants f_2, f_3 and f_4 and the spectroscopic data ω_e, $\omega_e\chi_e$, B_e and α_e,[26,27] we can determine the spectroscopic data and force constants of the Cr_2 molecule as follows:

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

$$f_3 = 6D_e(a_1a_2 - a_3 - a_1^3/3) = -3f_2/R_e(1+\alpha_e\omega_e/6B_e^3),$$

and

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

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

We have already used the density functional theory to calculate the mechanical parameters and the spectral data for Ni_2, Tc_2, Fe_2 and Ti_2 molecules and other transition metal element molecules. The results show that there exists a spin-polarization effect in them. So we use a similar method to deal with the Cr_2 molecule.

The following table is a comparison between the experimental results, our results and other calculated results.

Our method and Christopher's method are the same, but their basis sets are different. So our results are different from Christopher's results.

Table 3. The mechanical parameters and spectral data for Cr_2 molecule.

Multiplicity	$f_2/(\mathrm{aJ/nm^2})$	$f_3/(\mathrm{aJ/nm^3})$	$f_4/(\mathrm{aJ/nm^4})$	$\alpha_e/10^{-4}\mathrm{cm^{-1}}$	$\omega_e\chi_e/\mathrm{cm^{-1}}$	$B_e/\mathrm{cm^{-1}}$	$\omega_e/\mathrm{cm^{-1}}$
13	0.0835	–0.2831	0.3535	7.2938	1.2105	0.0562	73.81
11	3.3194	–31.0021	197.3637	7.1820	6.9797	0.0858	465.51
9	1.6658	–8.1356	17.7817	6.7535	2.3569	0.1132	329.77
7	1.8331	–3.4084	4.7175	1.0942	0.2585	0.1615	345.94
5	2.8551	1.2872	-44.1286	–5.3445	1.2802	0.1726	431.73
3	7.6788	–71.2121	545.9005	22.8430	5.8559	0.2652	708.03
1	14.1790	–90.9180	454.2786	10.4530	2.9573	2.6882	962.11

Table 4. Comparison between the experimental our results and other calculated results.

	R_e/nm	D_e/eV	$\omega_e/\mathrm{cm^{-1}}$
This work	0.3396	0.1034	73.81
Experiment	0.1679[4]	1.4900[6]	480.10[5]
Christopher[2]	0.1595	–2.3700	942.00

4. Conclusion

Making use of density functional theory (DFT) (B3P86) of Gaussian 03 program, we have investigated the $1-, 3-, 5-, 7-, 9-, 11-$, and 13-multiple states of the Cr_2 molecule. The result shows that the ground state for the Cr_2 molecule is the 13-multiple state, which shows a spin polarization effect in the Cr_2 molecule, and is indicative of the fact that there exist 12 parallel spin electrons in the Cr_2 molecule, where the number of non-conjugated electrons is largest. These electrons occupy different spatial orbitals, and in this case, the energy of the Cr_2 molecule is minimal. It shows that the effect of parallel spins in the Cr_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. Dissociation energy D_e of 13-multiple state (ground state) of Cr_2 molecule is 0.1034 eV, and the equilibrium bond length is 0.3396 nm. We have obtained the Murrell–Sorbie potential function of the Cr_2 molecule, its vibration frequency of $73.81\,\mathrm{cm^{-1}}$, and its force constants f_2, f_3 and f_4 of 0.0835, -0.2831 and $0.3535\,\mathrm{aJ.nm^{-3}}$ respectively. These results are very helpful for understanding the structural characteristics of the transition metal molecules. We have already used the DFT to investigate Ni_2 and Ti_2 molecules and other transition metal element molecules. The results show that there exists a spin-polarization effect in them. So we have used a similar method to deal with the Cr_2 molecule and obtained some feasible results.

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