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Spin polarization effect for Co_2 molecule*

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The density functional theory (DFT)(b3p86) of Gaussian 03 has been used to optimize the structure of the Co_2 molecule, a transition metal element molecule. The result shows that the ground state for the Co_2 molecule is a 7-multiple state, indicating a spin polarization effect in the Co_2 molecule. Meanwhile, we have not found any spin pollution because the wavefunction of the ground state is not mingled with wavefunctions of higher-energy states. So for the ground state of Co_2 molecule to be a 7-multiple state is the indicative of spin polarization effect of the Co_2 molecule, that is, there exist 6 parallel spin electrons in a Co_2 molecule. The number of non-conjugated electrons is the greatest. These electrons occupy different spacial orbitals so that the energy of the Co_2 molecule is minimized. It can be concluded that the effect of parallel spin in the Co_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 the other states of the Co_2 molecule are derived. The dissociation energy De for the ground state of Co_2 molecule is 4.0489eV, equilibrium bond length R_e is 0.2061 nm, and vibration frequency ω_e is 378.13 cm^{-1}. Its diatomic molecule force constants f_2, f_3, and f_4 are 2.4824 aJ·nm^{-2}, -7.3451 aJ·nm^{-3}, and 11.2222 aJ·nm^{-4}respectively(1 aJ=10^{-18} J). The other spectroscopic data for the ground state of Co_2 molecule $\omega_e\chi_e$, B_e, and α_e are 0.7202 cm^{-1}, 0.1347 cm^{-1}, and 2.9120× 10^{-1} cm^{-1} respectively. And $\omega_e\chi_e$ is the non-syntonic part of frequency, B_e is the rotational constant, α_e is revised constant of rotational constant for non-rigid part of Co_2 molecule.

Keywords: Co_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 cobalt is one of the most important chemical elements. But up to now, useful information concerning the molecular structure of Co_2, a transition metal molecule, 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 varieties 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 the growing theoretical interest.

Cobalt dimer is the molecule whose electronic ground state is not experimentally known. Kant and Strauss applied the third-law method to the determination of 1.69±0.26eV for the dissociation energy.[2] Matrix isolation resonance Raman spectroscopy by Dong *et al* determined ω_e=296.8±0.54cm^{-1}. No bond length value has yet been determined from experiment. A Badger's rule bond length estimate of 0.202nm exists; but as was the case with scandium dimer, it cannot depend on these types of molecules.[3] A number of density functional theory (DFT) and local spin-density approximation (LSDA) investigations have been recently undertaken and found the

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bond length to be between 1.92 and 0.202nm and the frequency to be between 414 and 445cm^{-1}.[4−6] The most recent non-DFT study of cobalt dimer was in 1983 by Shim and Gingerich, who optimized orbitals with HF/(8s6p3d) and performed a configuration interaction (CI) computation with 1084 determinants to find the relative ordering of the electronic states. Their study found the ground state to be $^5\Sigma_g^+$, with an approximate natural orbital occupation of $(3d\sigma_g)^{2.00}(3d\pi_u)^{3.09}$ $(3d\delta_g)^{3.02}(3d\delta_u^*)^{2.98}$ $(3d\pi_g^*)^{2.91}$ $(3d\sigma_u^*)^{2.00}$ $(4s\delta_g)^{1.94}$ $(4s\sigma_u^*)^{0.06}$. g is even number, u is odd number. Using this configuration, they reported R_e=0.256 nm, and ω_e =162cm^{-1}.[7] There is disagreement, then, between DFT and non-DFT methods that cannot be resolved fully until an experimental bond length is found and new *ab initio* studies are undertaken.

The occupation given by Shim and Gingerich could be verified by ultra high frequency (UHF), but no DFT functional could be converged to this occupation. There is considerable disagreement among the DFT functionals applied to the ground state occupation; all six functionals give the same orbital ordering but completely differently. LSDA, a functional which is not expected to perform well, predicts a ground $^5\Delta_g$ state. Christopher *et al*[8] in 2000 calculated the molecular structure of Co_2 by using the DFT, and concluded that the ground state of Co_2 was a 5-multiple state, equilibrium bond length R_e for the ground state of Co_2 molecule was 0.2438nm, the dissociation energy De was 0.16eV, and the vibration frequency ω_e was 223cm^{-1}. According to Dong *et al*,[9] the experimental vibration frequency ω_e is 297.34cm^{-1}; according to Weisshaar *et al*[3] the experimental equilibrium bond length R_e is 0.2020nm; according to Kant *et al*,[2] the experimental dissociation energy De is 1.95eV . Obviously, the gap between the former of 0.16eV and the latter of 1.95eV is considerable. But through calculation, we can conclude that the ground state of Co_2 is 7-multiple state, the equilibrium bond length R_e for the ground state of Co_2 molecule is 0.2061nm, the dissociation energy De is 4.0489eV, and the vibration frequency ω_e is 378.13cm^{-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 Co_2 molecule is a 7-multiple state, which indicates that there exists a spin polarization effect in Co_2 molecule.

It is difficult to confirm the ground state of Co_2 molecule. It might be related to the delocalization effect of the d electron of $3d^54s^2$. Making use of the DFT (B3p86) of Gaussian 03, we can optimize the structure of the Co_2 molecule and obtain the potential energy function of this molecule. The result shows that the corresponding minimal energies of 1-, 3-, 5-, 7-multiple states of the Co_2 molecule are very close to each other, but even so, the 7-multiple state is the ground state of Co_2. It follows that in Co_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 have made 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 of electronic configurations, particularly, the effect of electron pairing. However, the recent work[10] 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 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 U clusters. What this implies is 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 actinides. The potential functions of the compounds of heavy elements also arouse the interest of many scientific workers.[11−16]

2. Theoretical method and calculation

The electronic configuration of Co atom is $3d^74s^2$, where $4s^2$ is fully occupied. From $3d^7$, we can infer that the ground electronic configuration of Co atom is $^4F_{9/2}$. The Co_2 molecule composed of $^4F+^4F$ might have 1-, 3-, 5-, or 7-multiple states. According to the calculations, the ground state of Co_2 molecule is a 7-

multiple state of the parallel spins of 6 electrons, which shows a spin polarization effect of the electrons in the molecule.

According to Ref.[17], Co_2 molecule belongs to $D_{\infty h}$ molecule group, and the electronic configuration of Co atom is ${}^4F_{9/2}$. According to Ref.[17], 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,

$$ {}^4F_{\rm g} = {}^4\,\Sigma_{\rm g}^- + {}^4\,\pi_{\rm g} + {}^4\,\Delta_{\rm g} + {}^4\,\Phi{\rm g}.$$

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

$$\begin{aligned}
{}^4F_{\rm g}\times{}^4F_{\rm g} =& ({}^4\Sigma_{\rm g}^- + {}^4\,\pi_{\rm g} + {}^4\,\Delta_{\rm g} + {}^4\,\Phi{\rm g}) \times ({}^4\Sigma_{\rm g}^- + {}^4\,\pi_{\rm g} + {}^4\,\Delta_{\rm g} + {}^4\,\Phi{\rm g}) \\
=& {}^{1,3,5,7}\Sigma_{\rm g}^+ + {}^{1,3,5,7}\,\pi_{\rm g} + {}^{1,3,5,7}\,\Delta_{\rm g} + {}^{1,3,5,7}\,\Phi{\rm g} + {}^{1,3,5,7}\,\pi_{\rm g} + {}^{1,3,5,7}\,\Sigma_{\rm g}^+ + {}^{1,3,5,}\,\Sigma_{\rm g}^- + {}^{1,3,5,7}\,\Delta_{\rm g} \\
&+ {}^{1,3,5,7}\,\pi_{\rm g} + {}^{1,3,5,7}\,\Phi_{\rm g} + {}^{1,3,5,7}\,\Delta_{\rm g} + {}^{1,3,5,7}\,\Phi_{\rm g} + {}^{1,3,5,7}\,\Delta_{\rm g} + {}^{1,3,5,7}\,\pi_{\rm g} + {}^{1,3,5,7}\,\Phi_{\rm g} \\
&+ {}^{1,3,5,7}\,\Sigma_{\rm g}^+ + {}^{1,3,5,7}\,\Sigma_{\rm g}^- + {}^{1,3,5,7}\,\Phi_{\rm g} + {}^{1,3,5,7}\,\pi_{\rm g} + {}^{1,3,5,7}\,H_{\rm g} + {}^{1,3,5,7}\,\Phi_{\rm g} + {}^{1,3,5,7}\,\Delta_{\rm g} \\
&+ {}^{1,3,5,7}\,\Phi_{\rm g} + {}^{1,3,5,7}\,\pi_{\rm g} + {}^{1,3,5,7}\,H_{\rm g} + {}^{1,3,5,7}\,\Sigma_{\rm g}^+ + {}^{1,3,5,7}\,\Sigma_{\rm g}^- + {}^{1,3,5,7}\,I_{\rm g} \\
=& {}^{1,3,5,7}\Sigma_{\rm g}^{5,7}\pi_{\rm g}(6) + {}^{1,3,5,7}\,\Delta_{\rm g}(5) + {}^{1,3,5,7}\,\Phi_{\rm g}(4) + {}^{1,3,5,7}\,\Phi_{\rm g}(3) + {}^{1,3,5,7}\,I_{\rm g} + {}^{1,3,5,7}\,H_{\rm g}(2),
\end{aligned}$$

where ${}^{1,3,5,7}\Sigma_{\rm g}^+$ are the possible electronic configurations of Co_2 molecule. By the use of density functional method (b3p86)of Gaussian03, all the possible molecule states can be optimized (see Table 1 for the theoretical bond lengths in nm, the lowest energy levels of the molecules in H.a.u., and the expectance values and calculated values of total 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 is mingled 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 expectance of total spin S_1 and the calculated value of total spin S_2. S_1 should equal $s(s+1)$, where s is the total spin value of the Co_2 molecule. In general, the result is acceptable if the error is not beyond 10%.

Table 1. Optimum results of Co_2 molecule.

Multiplicity	$R_{\rm e}$/nm	E/H.a.u.	Expectance of spin S_1	Calculation of spin S_2
1	0.18893	–2766.4721		0
3	0.19248	–2766.5056	2	2
5	0.19248	–2766.5639	6	6
7	0.20612	–2766.5693	12	12

In Table 1, H.a.u.(Hartree atom unit) 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 7-multiple state of the Co_2 molecule is the lowest, so the 7-multiple state is the ground state of the Co_2 molecule. As multiplicity increases, the number of unpaired electrons increases gradually, that is, in the Co_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 a reduction in the energy of the system. It shows that, in transition element molecules, the effect of spin parallel is larger than the effect of paired elec-

trons. It is obviously related to the delocalization of electron d. Meanwhile, we find that the minimal energy values of 1-, 3-, 5-, 7-multiple states of the Co_2 molecule are very close to each other. According to our thorough calculations, the ground state of the Co_2 molecule is a 7-multiple state. That the ground state of Co_2 molecule is a 7-multiple state shows that there exists a spin polarization effect in the Co_2 molecule, a diatomic molecule of transition metal element. The dissociation energy of the ground state of the Co_2 molecule (7-multiple state) is De=4.0489eV. From Table 1, we can find that expectances and the calculated values of total spins about 3-, 5- and 7-multiple states are absolutely the same except that 1-multiple state does not come up in the optimum result. It shows that there exists no spin pollution in the DFT calculations for the Co_2 molecule, and that the wavefunction of the ground state is not mingled with the wavefunction of higher-energy state.

3. Potential function and spectral data

Making use of DFT (b3p86) of Gaussian 03 program,[18] we can investigate 1-, 3-, 5-, and 7-multiple states of the Co_2 molecule and obtain a series of spot values of potential function. Using the least square fitting, we determine the function form of Murrell–Sorbie potential function,[19,20] which can be expressed as

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

In the above formula, $\rho = R - R_e$, where R is the interatomic distance and R_e its equilibrium value; 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 result).

Table 2. Parameters for Murrell–Sorbie potential function about the Co_2 molecule.

Multiplicity	De/eV	R_e/nm	$a_1/(0.1\text{nm})^{-1}$	$a_2/(0.1\text{nm})^{-2}$	$a_3/(0.1\text{nm})^{-3}$
7	4.0489	0.2061	1.8235	–0.2507	–0.5912
5	4.0106	0.1925	3.2247	1.6366	–0.0002
3	3.3525	0.1925	4.4519	6.5864	3.7921
1	5.7876	0.1889	2.1990	0.7571	1.2769

According to the Murrell–Sorbie potential function, from the above fitting data we can see from figure 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 fitting value. It means that the process of fitting is successful. The 7-multiple state is the ground state of the Co_2 molecule. In Figs.1–4, R is the distance between two atoms, in units of nm, and E is energy,in units of eV.

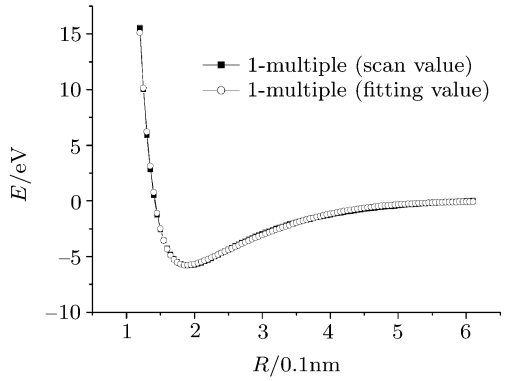


Fig.1. The potential curve of Co_2 molecule for 1-multiple.

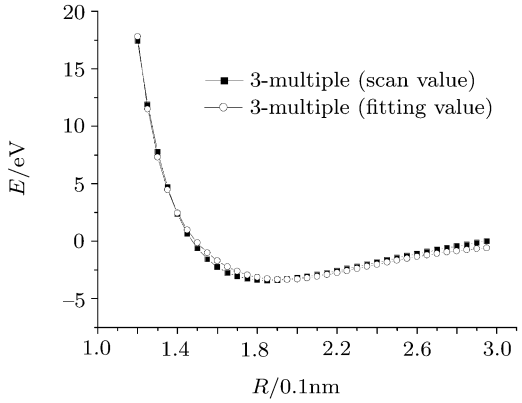


Fig.2. The potential curve of Co_2 molecule for 3-multiple.

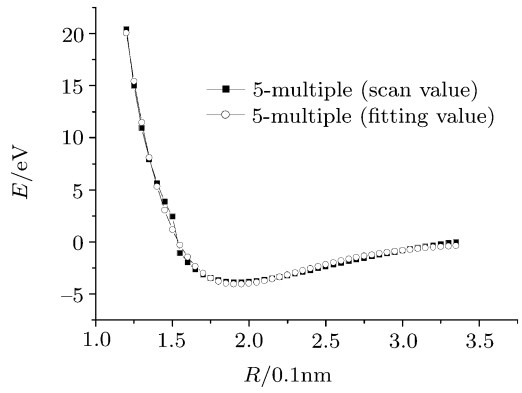


Fig.3. The potential curve of Co_2 molecule for 5-multiple.

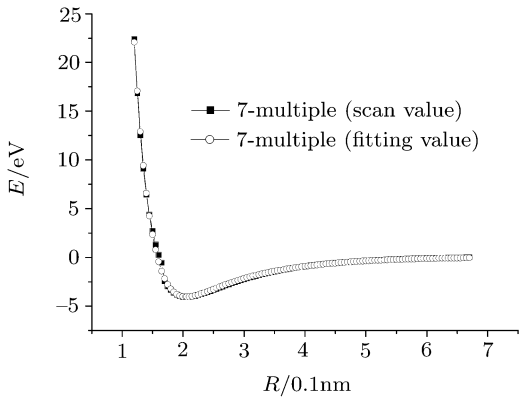


Fig.4. The potential curve of Co_2 molecule for 7-multiple.

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(see Table 3 for the result),[21,22] we can determine the spectroscopic data and force constants of Co_2 molecule as follows:

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

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

Table 3. The mechanical parameters and spectral data for Co_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}	ω_e/cm^{-1}
7	2.4824	–7.3451	11.2222	2.9120	0.7202	0.1347	378.13
5	4.6372	–23.0271	78.1639	6.0566	1.7356	0.1544	516.71
3	3.5701	–12.5093	9.2031	3.9376	1.2789	0.1544	453.47
1	3.0799	–17.5621	86.8002	9.4828	1.8599	0.1603	421.99

We have already used the DFT 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 there exists a spin-polarization effect in them. So we use the similar method to deal with the Co_2 molecule.

Now by comparing our results with the experimental results as well as other calculated results, 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	De/eV	ω_e/cm^{-1}
This work	0.2061	4.0489	378.13
Experiment	0.2020[3]	1.9500[2]	297.34 [9]
Christopher[8]	0.2438	0.1600	223.00

4. Conclusion

Making use of the DFT (b3p86) of Gaussian 03 program, we have calculated the 1-, 3-, 5-, and 7-multiple states of the Co_2 molecule. The result shows that the ground state for the Co_2 molecule is a 7-multiple state, which exhibits a spin polarization effect of the Co_2 molecule, and is indicative of the fact that there exist 6 parallel spin electrons in the Co_2 molecule, where the number of non-conjugated electrons is the greatest . These electrons occupy different spacial orbitals, and in this case, the energy of the Co_2 molecule is minimal. It shows that the effect of parallel spins in the Co_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 De of 7-multiple state (ground state) of Co_2 molecule is 4.0489eV, and the equilibrium bond length is 0.2061nm. We have obtained the Murrell–Sorbie potential function of the Co_2 molecule, its vibration frequency is 378.13cm^{-1}, and its force constants f_2, f_3, and f_4 are 2.4824 aJ·nm^{-2}, –7.3451 aJ·nm^{-3}, and 11.2222 aJ·nm^{-4} respectively. These results are very helpful for understanding the structural characteristics of the transition metal molecules. We have already used the DFT to investigate the 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 use the similar method to deal with the Co_2 molecule and obtain some reliable results.

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