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# Spin polarization effect of $Ni_2$ molecule*

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The density functional theory (DFT) method (b3p86) of Gaussian 03 is used to optimize the structure of the $Ni_2$ molecule. The result shows that the ground state for the $Ni_2$ molecule is a 5-multiple state, symbolizing a spin polarization effect existing in the $Ni_2$ molecule, a transition metal molecule, but no spin pollution is found because the wavefunction of the ground state does not mingle with wavefunctions of higher-energy states. So the ground state for $Ni_2$ molecule, which is a 5-multiple state, is indicative of spin polarization effect of the $Ni_2$ molecule, that is, there exist 4 parallel spin electrons in $Ni_2$ molecule. The number of non-conjugated electrons is greatest. These electrons occupy different spatial orbitals so that the energy of the $Ni_2$ molecule is minimized. It can be concluded that the effect of parallel spin in the $Ni_2$ molecule is larger than that 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 of the ground state and other states of the $Ni_2$ molecule are derived. The dissociation energy $D_e$ for the ground state of the $Ni_2$ molecule is 1.835 eV, equilibrium bond length $R_e$ is 0.2243 nm, vibration frequency $\omega_e$ is 262.35 $cm^{-1}$. Its force constants $f_2$, $f_3$ and $f_4$ are 1.1901 aJ.$nm^{-2}$, –5.8723 aJ.$nm^{-3}$, and 21.2505 aJ.$nm^{-4}$ respectively. The other spectroscopic data for the ground state of the $Ni_2$ molecule $\omega_e\chi_e$, $B_e$ and $\alpha_e$ are 1.6315 $cm^{-1}$, 0.1141 $cm^{-1}$, and $8.0145\times10^{-4}$ $cm^{-1}$ respectively.

**Keywords:** $Ni_2$, 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 nickel is one of the most important chemical elements. But up to now, useful information concerning the molecular structure of $Ni_2$ is limited. The difficulties in the theoretical treatment of transition metal systems originate from the near degeneracy effects due to 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 to be made to use 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 arouses the theoretical interest increasingly.

Christopher *et al*[2] in 2000 calculated the molecular structure of $Ni_2$ by using the density functional theory (DFT) method, and they concluded that nickel dimer had a ground $^1\Sigma_g^+$ state. Therefore, a debate on this nickel dimer ground state is induced. The manifold state with 0.84 eV of the ground state is composed of about 59 distinct electronic configurations, of which 41 configurations are degenerate.[3] Early experimental work indicated that $Ni_2$ had a $^3\Gamma_u$ or $^3\Gamma_g$ ground state, though $^3\Sigma_g^+$, $^3\Sigma_g^-$, $^1\Sigma_g^+$, and $^1\Sigma_u^-$ states were extremely close to each other in energy.[4,5] By using the R2PI, Pinegar *et al*[6] obtained a low resolution spectrum and assigned a Hund's case (c) ground state of $\Omega = O_g^+$ or $O_u^-$ , estimating $4_g$ ,$4_u$ and $5_u$ as ground state possibilities. They[6] found the bond length to be 2.01545±0.0004Å, and in the earlier work[7] the dissociation energy was given as 2.068±0.01 eV. Wang

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*et al*[8] used matrix isolation resonance Raman spectroscopy to determine $\omega_e = 259.2 \pm 3.0\,cm^{-1}$. Latter, Spain and Morse[3] employed a point charge and spin-orbit model based on ligand-field theory in their research and reported that the ground state was $O_g^+$ and that the states in question were an equal mixture of $^1\Sigma_g^+$ and $^3\Sigma_g^-$ states in Hund's case(a) notation. Obviously, since this is a multireference case, the single configuration DFT method cannot be expected to characterize $Ni_2$ perfectly.

Christopher *et al*[2] in 2000 concluded that the ground state of $Ni_2$ was a 1-multiple state, the equilibrium bond length $R_e$ for the ground state of $Ni_2$ molecule was 0.2175 nm, the dissociation energy $D_e$ was –0.05 eV, and the vibration frequency $\omega_e$ was $307\,cm^{-1}$. Wang *et al*[8] found the experimental vibration frequency $\omega_e$ to be $262.2\,cm^{-1}$, Pinegar *et al*[6] showed the experimental equilibrium bond length $R_e$ to be 0.2155 nm, and Morse *et al*[7] gave the experimental dissociation energy $D_e$ as 2.067 eV. Obviously, the gap between the former of –0.05 eV and the latter of 2.067 eV is considerable. But from the calculations, we have concluded that the ground state of $Ni_2$ is a 5-multiple state, the equilibrium bond length $R_e$ for the ground state of $Ni_2$ molecule is 0.2243 nm, the dissociation energy $D_e$ is 1.835 eV, and the vibration frequency $\omega_e$ is $262.35\,cm^{-1}$. It can be seen that our calculations are very close to the measurements except for the bond length. What should be pointed out here is that, to the best of our knowledge, it is the first time that the ground state of $Ni_2$ molecule has been found to be a 5-multiple state, which implies that there exists the spin polarization effect in a $Ni_2$ molecule, a transition metal molecule.

We understand that it is difficult to confirm that the ground state of $Ni_2$ molecule arises from the delocalization effect of the d electron of $3d^84s^2$. Making use of the DFT method (B3p86) of Gaussian 03, we have optimized the structure of the $Ni_2$ molecule and obtained its potential energy function. The result shows that the corresponding minimal energies of 1-, 3-, 5-multiple states of the $Ni_2$ molecule are very close to each other, but even so, the 5-multiple state is the ground state of $Ni_2$. It follows that in a $Ni_2$ molecule there exists a spin polarization effect. Besides, we confirm that there exist the spin polarization effects also in $Ti_2$, $Tc_2$ and $Fe_2$ molecules after we have studied the structures of these molecules. In addition, we have conducted the research on the diatomic molecules of the other transition metal elements and their clusters.

It is universally received that the multiplicity of the ground state of diatomics for light elements is relatively low, for example, 2s + 1 = 1–4, because of the interaction of electronic configurations, particularly, the effect of electron pairing. However, the recent work[9] indicates that it is quite another story 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, while for $Pu_2$ , $Pu_3$ and $Pu_4$ the numbers of unpaired electrons are 12, 18 and 24, respectively; the possible multiplicities are 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 decreases with multiplicity increasing, 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 for U clusters. What this means is that the electrons prefer to take the form of parallel spin in $Pu_n$ and U clusters. This sort of non-equilibrium behaviour in electron spin is called spin-polarization effect. One of the major current research subjects is the spin-polarization in the actinide molecules. The potential functions of the compounds of heavy elements have also aroused the interest of many investigators.[10–14]

## 2. Theoretical methodology and calculation

The electronic configuration of Ni atom is $3d^84s^2$. So we can infer that the ground electronic configuration of Ni atom is $^3F_{4,3,2}$. The $Ni_2$ molecule composed of $^3F + ^3F$ might have 1-, 3-, or 5-multiple states. According to the calculations, the ground state of $Ni_2$ molecule is a 5-multiple state of the parallel spins of 4 electrons, which shows the spin polarization effect of the electrons in the molecule.

According to Ref.[15], $Ni_2$ molecule belongs in $D_{\infty h}$ molecule group, and the electronic configuration of Ni atom is $^3F$. Also according to Ref.[15], the atom groups can be decomposed into the direct summation of molecule groups $D_{\infty h}$ when two atoms form a linear molecule, that is,

$$^3F_g = {}^3\Sigma_g^- + {}^3\pi_g + {}^3\Delta_g + {}^3\Phi g.$$

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

$$^3F_g \times {}^3F_g = (^3\Sigma_g^- + {}^3\pi_g + {}^3\Delta_g + {}^3\Phi_g)$$

$$
\begin{aligned}
&\times({}^3\Sigma_g^- + {}^3\pi_g + {}^3\Delta_g + {}^3\Phi_g)\\
&= {}^{1,3,5}\Sigma_g^+ + {}^{1,3,5}\pi_g + {}^{1,3,5}\Delta_g + {}^{1,3,5}\Phi_g^+\\
&\quad + {}^{1,3,5}\pi_g + {}^{1,3,5}\Sigma_g^+ + {}^{1,3,5}\Sigma_g^- + {}^{1,3,5}\Delta_g\\
&\quad + {}^{1,3,5}\pi_g + {}^{1,3,5}\Phi_g + {}^{1,3,5}\Delta_g + {}^{1,3,5}\Gamma_g\\
&\quad + {}^{1,3,5}\Delta_g + {}^{1,3,5}\pi_g + {}^{1,3,5}\Phi_g + {}^{1,3,5}\Sigma_g^+\\
&\quad + {}^{1,3,5}\Sigma_g^- + {}^{1,3,5}\Gamma_g + {}^{1,3,5}\pi_g + {}^{1,3,5}H_g\\
&\quad + {}^{1,3,5}\Phi_g + {}^{1,3,5}\Delta_g + {}^{1,3,5}\Gamma_g + {}^{1,3,5}\pi_g\\
&\quad + {}^{1,3,5}H_g + {}^{1,3,5}\Sigma_g^+ + {}^{1,3,5}\Sigma_g^- + {}^{1,3,5}I_g\\
&= {}^{1,3,5}\Sigma_g^+(4) + {}^{1,3,5}\Sigma_g^-(3) + {}^{1,3,5}\pi_g(6)\\
&\quad + {}^{1,3,5}\Delta_g(5) + {}^{1,3,5}\Phi_g(4) + {}^{1,3,5}\Gamma_g(3)\\
&\quad + {}^{1,3,5}I_g + {}^{1,3,5}H_g(2),
\end{aligned}
$$

where ${}^{1,3,5}\Sigma_g^+$, etc are the possible electronic configurations of $Ni_2$ molecule. By using the DFT method (B3p86)of Gaussian03, all the possible molecule states can be optimized (see Table 1, where the theoretical bond lengths in nm, the lowest energy levels of the molecules in H.a.u., the total s expectance values, and calculated values of spins can be found.).

**Table 1.** Optimum results of $Ni_2$ molecule.

| Multiplicity | $R_e$/nm | $E$/H.a.u. | Expectance of spin $S_1$ | Calculation of spin $S_2$ |
|---|---|---|---|---|
| 1 | 0.2575 | –3017.4597 | 0 | |
| 3 | 0.2462 | –3017.5795 | 2 | 2 |
| 5 | 0.2243 | –3017.6067 | 6 | 6 |

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 wavefunctions 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 calculated value of $S_2$. $S_1$ should equal s(s+1), where s is the total spin value of the $Ni_2$ molecule. In general, the result is acceptable if the error does not exceed 10%.

In Table 1, H.a.u.(Hartree atom unit) is an energy unit (1 H.a.u.= $27.212 \times 1.6 \times 10^{-19}$J). From Table 1 we can find that the energy of 5-multiple state of the $Ni_2$ molecule is lowest, so the 5-multiple state is the ground state of the $Ni_2$ molecule. As the multiplicity increases, the number of unpaired electrons increases gradually, that is, in the $Ni_2$ molecule, the greater the number of unpaired electrons is, the lower its energy will be —the state with the lowest energy is most stable. This condition is known as spin polarization effect. The pairing of electrons may reduce the energy of the system. However, the commutative integral of parallel spin electrons is positive, which also leads to a reduction in energy of the system. It shows that in transition element molecules, the effect of parallel spin 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-multiple states of the $Ni_2$ molecule are very close to each other. According to our calculations, the ground state of the $Ni_2$ molecule is a 5-multiple state. That the ground state of $Ni_2$ molecule is a 5-multiple state shows that there exists a spin polarization effect in the $Ni_2$ molecule, a diatomic molecule of transition metal element. The dissociation energy of the ground state of the $Ni_2$ molecule (5-multiple state) is $D_e = 1.835$ eV. From Table 1, we can also find that expectance values and the calculated values of total spin of 3- and 5-multiple states are absolutely the same except for the 1-multiple state that does not emerge in the optimum result. It shows that there is no spin pollution in the DFT calculations for the $Ni_2$ molecule, and that the wavefunction of the ground state does not mingle with any wavefunction of higher-energy state.

## 3. Potential function and spectral data

Making use of the DFT method (B3p86) of Gaussian03 program,[16] we have studied 1-multiple, 3-multiple, 5-multiple states of the $Ni_2$ molecule and obtained a series of spot values of potential function. Using the least-square fitting, we determine the function form of Murrell–Sorbie potential function,[17,18] 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, and $a_1$, $a_2$ and $a_3$ are the 1st, 2nd and 3rd order moduli respectively. They can be obtained through fitting as listed in Table 2.

**Table 2.** Parameters for Murrell–Sorbie potential function of $Ni_2$ molecule.

| Multiplicity | $D_e$/eV | $R_e$/nm | $a_1/10\text{nm}^{-1}$ | $a_2/10^2\text{nm}^{-2}$ | $a_3/10^3\text{nm}^{-3}$ |
|---|---|---|---|---|---|
| 1 | 0.993 | 0.2575 | 3.002 | 2.643 | 1.056 |
| 3 | 1.344 | 0.2462 | 1.564 | –0.232 | 0.596 |
| 5 | 1.835 | 0.2243 | 1.604 | –0.738 | 0.770 |

According to the parameters for Murrell–Sorbie potential function of the $Ni_2$ molecule we can acquire the corresponding fitting curves for the 1, 3, and 5 multiple states. Each state has two curves, one for the scan value, and the other for fitting value; they accord with each other well, which means that the process of fitting is successful. The 5-multiple state is the ground state of the $Ni_2$ molecule. In Figs.1–3, $R$ is the distance between two atoms ( in units of Å), and $E$ is energy (in units of eV).

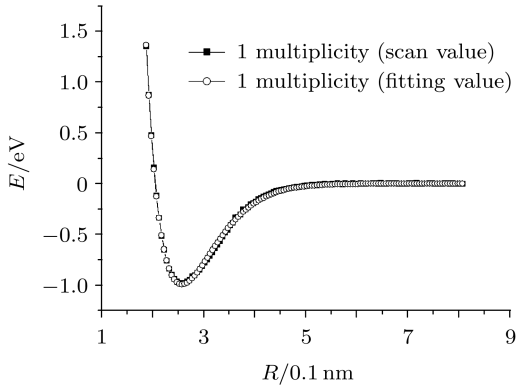



**Fig.1.** The potential curve of $Ni_2$ molecule for 1 multiplicity.

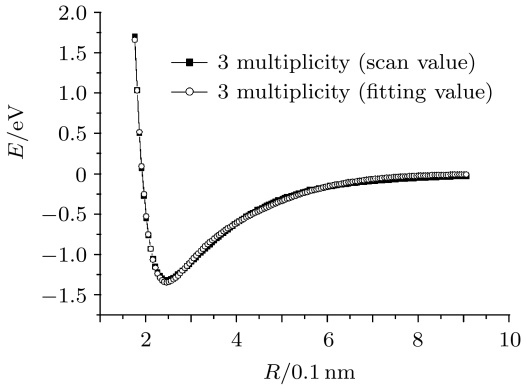



**Fig.2.** The potential curve of $Ni_2$ molecule for 3 multiplicity.

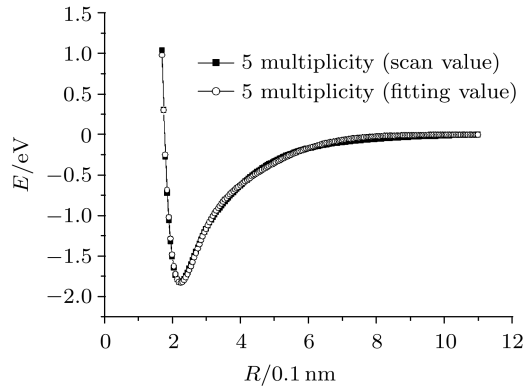



**Fig.3.** The potential curve of $Ni_2$ molecule for 5 multiplicity.

According to the relationship between the parameters $a_1, a_2$ and $a_3$ of the Murrell–Sorbie potential function and the spectroscopic data $\omega_e$, $\omega_e\chi_e$, $B_e$ and $\alpha_e$, and that between the force constants $f_2$, $f_3$ and $f_4$ and the spectroscopic data $\omega_e$, $\omega_e\chi_e$, $B_e$ and $\alpha_e$,[19,20] we can determine the spectroscopic data and force constants of the $Ni_2$ molecule as follows:

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

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 light speed in vacuum, $m$ is the atomic reduced mass, $B_e = h/8\pi^2\text{cm}$, and $R_e = (h/8\pi^2 cI_e)^{1/2}$.

We use the DFT method to calculate the mechanical parameters and spectral data for $Tc_2$, $Fe_2$ and $Ti_2$ molecules and other transition metal molecules. The results show that there exist spin-polarization effects in them. So we use a similar method to deal with the $Ni_2$ molecule.

**Table 3.** Mechanical parameters and spectral data for $Ni_2$ 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$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | 0.5924 | –2.0402 | 5.3869 | 4.7611 | 0.7665 | 0.0867 | 185.09 |
| 3 | 0.6263 | –2.8849 | 10.1446 | 7.8714 | 1.3764 | 0.0948 | 190.32 |
| 5 | 1.1901 | –5.8723 | 21.2505 | 8.0145 | 1.6315 | 0.1141 | 262.35 |

The following table shows a comparison among the experimental results, our results and others' calculated results.

**Table 4.** Comparison among the experimental results, our results and others' calculated results.

| | $R_e$/nm | $D_e$/eV | $\omega_e$/cm$^{-1}$ |
|---|---|---|---|
| This work | 0.2243 | 1.8350 | 262.35 |
| Experiment | 0.2155[6] | 2.0670[7] | 262.20 [8] |
| Christopher *et al*'s[2] | 0.2175 | –0.0500 | 307.00 |

Our method is the same as Christopher *et al*'s, but their basis sets are different. So our results are different from Christopher *et al*'s.

## 4. Conclusions

Making use of the DFT method (B3p86) of Gaussian 03 program, we have investigated the 1-, 3-, and 5-multiple states of the $Ni_2$ molecule. The results show that the ground state for the $Ni_2$ molecule is a 5-multiple state, which exhibits a spin polarization effect of the $Ni_2$ molecule, and is indicative of 4 parallel spin electrons in the $Ni_2$ molecule, where the number of non-conjugated electrons is greatest. These electrons occupy different spatial orbitals, and in this case, the energy of the $Ni_2$ molecule is minimal. It shows that the effect of parallel spins in the $Ni_2$ molecule is larger than the conjugation effect of electrons in the molecule, which is obviously related to the effect of the delocalization of the electron d. Dissociation energy of 5-multiple state (ground state) of $Ni_2$ molecule, $D_e$, is 1.835 eV, and the equilibrium bond length is 0.2243 nm. We have obtained the Murrell–Sorbie potential function of the $Ni_2$ molecule, its vibration frequency is 262.35 cm$^{-1}$, and its force constants $f_2$, $f_3$, and $f_4$ are 1.1901 aJ $\cdot$ nm$^{-2}$, –5.8723 aJ $\cdot$ nm$^{-3}$, and 21.2505 aJ $\cdot$ nm$^{-4}$ respectively. These results are very helpful for understanding the structural features of the transition metal molecules. We have already used the DFT method to calculate the parameters of $Tc_2$ and $Ti_2$ molecules and other transition metal molecules. The results show that there exist spin-polarization effects in them. So we have used a similar method to deal with the $Ni_2$ molecule and obtained some feasible results.

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