

# First-principles study of the stability and Jahn–Teller distortion of nickel clusters

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## Abstract

The density functional method for molecules has been employed to study the structural and magnetic properties of  $\text{Ni}_N$  ( $N = 2\text{--}13$ ) clusters. The calculated results show that the Jahn–Teller effect plays an important role in determining the ground state of certain geometric structures. Ground states have been assigned for these clusters. For  $\text{Ni}_5$  and  $\text{Ni}_7$ , new ground states have been found. The second derivative of the binding energy with cluster size shows that besides  $N = 13$ ,  $N = 10$  is also a magic number. Most importantly, it is found that from  $N = 6$  to 13, the spin moment is  $8\mu_B$  in all cases, which verifies the quantum confinement of  $4s$  electrons in small nickel clusters.

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## 1. Introduction

In the past three decades, transition-metal clusters (TMCs), due to their unique geometrical structures, physical, chemical, electronic and magnetic properties, have attracted much attention in scientific and

technological fields. Since the properties evolve with size and composition, suitably designed clusters with tailored properties are promising in the synthesis of nanostructures. Among the 30 kinds of pure TMCs, nickel clusters are the primary target of many research groups [1–9] because of their extensive catalytic and important magnetic properties. In comparison with the alkali metal clusters, the localized behavior of unfilled  $3d$  electrons of nickel clusters results in enormous complexity and dominates most of properties. Nickel

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clusters constitute one of the most studied sets of clusters and, therefore, are an excellent system for exploring new theoretical or experimental approaches.

Structural stability, electronic structure, and magnetic properties are three important linked problems in cluster research, since the magnetic moment depends on the electronic structure, which in turn depends on the geometry. Knowledge concerning these questions can give us additional insight into the physical and chemical properties. Unfortunately, it is very difficult to determine the geometry of nickel clusters consisting of less than 100 atoms, even though it is in this size range that nickel clusters exhibit the most interesting electronic, magnetic, and optical properties. Experimental determination of the cluster geometry is difficult, since most clusters are too large for spectroscopic probes but too small for diffraction probes. Theory is usually employed to determine the cluster geometry, but there are often several low-lying structural isomers whose energies are very close to that of the ground state [1,2]. Nevertheless attempts are being made, experimentally and theoretically, to obtain the geometries of nickel clusters.

On the experimental side, chemical-probe experiments have given very valuable, although indirect, information concerning the structure of these clusters. Parks and coworkers [3] have used the reactions of nickel clusters with ammonia and with water to predict the equilibrium geometric structure. Parks et al. [4] have probed the equilibrium geometric structure of small nickel clusters via molecular adsorption of nitrogen onto their surfaces. However, it is argued that the current experimental studies have not confirmed the coexistence of isomers [5]. On the theoretical side, the research techniques include molecular dynamics (MD) simulations, the embedded-atom method (EAM), first-principles calculation, and effective-medium-theory (EMT). The MD simulations to date are either based on the tight-binding framework or based on *ab initio* methods, which provide a good compromise between accuracy and computational speed. The EMT permits a fair estimation of binding energy. In general, for the smallest clusters, the best credible method is still first-principles calculations. Most of the *ab initio* calculations on  $\text{Ni}_N$  clusters have been performed within the framework of the self-consistent field at the nonlocal Hartree–Fock (HF) level of approximation [6–8], or the local

density approximation (LDA) based on computational schemes [9–11] such as the linearized-augmented-plane-wave, the linearized-muffin-tin-orbital etc. Because the size of the clusters and the complexity of the nickel atom do not allow a configuration interaction approach [6,7], the existing *ab initio* results are still somewhat inconsistent with respect to each other, and the true ground states are uncertain. Reuse et al. [12] carried out the first systematic study of the geometries of  $\text{Ni}_N$  ( $N = 2–6, 8, 13$ ) clusters using an approach based on a linear combination of atomic molecular-orbitals within the density functional formalism. They obtained calculated geometries, and the total spin magnetic moments for these nickel clusters.

It is well known that there are abundant low-lying structural isomers whose energies are very close to the ground state energy and that the Jahn–Teller effect [13] is important. Subsequently, Reuse et al. published studies for  $\text{Ni}_{13}$  [14],  $\text{Ni}_7$ , and  $\text{Ni}_8$  [1] clusters including the Jahn–Teller effect. A more complete study of the smallest  $\text{Ni}_N$  clusters is, however, still crucial for a comprehensive understanding of the property of these clusters.

In general, the density functional method with its useful local density approximation and its relatively simple computational scheme provides an alternate theoretical tool for studying transition-metal complexity and the results obtained so far are comparable or better than those obtained at the HF level. The first-principles cluster method referred to as the density functional for molecules (DMol) [21] is an accurate and efficient local density functional calculation for molecules and has been applied to many problems in molecular clusters, such as chemisorption, surface reconstruction, and the ground state of highly correlated TMCs. Recently, Nayak et al. [5] have studied the structure of  $\text{Ni}_7$  using the DMol method together with MD simulations. They have used the Hedin–Lundqvist/Janak–Moruzzi–Williams local correlation functions and double numerical basis sets with 4p polarization functions in their calculations. More recently, using the DMol cluster method, Zhang et al. [15,16] have studied the structural stability of  $\text{La}_N$  clusters and Wang et al. [17,18] have successfully studied the electronic structures of icosahedral  $\text{Ti}_N$  clusters.

In order to clarify the stable structures for  $\text{Ni}_N$  ( $N = 2–13$ ) clusters, we have performed a global min-

imization of the total energy using the first-principles cluster method. We have found that high symmetry clusters have heavy degeneracy and that the Jahn–Teller effect is prominent. Above all, for clusters of 5 and 7 atoms, we have found new ground states. To our knowledge, the existing first-principles calculations of  $\text{Ni}_N$  ( $N = 9\text{--}12$ ) clusters are not sufficient, and there are only results based on tight-binding molecular dynamics (TBMD) simulations [19] and the EAM study [20]. In this Letter, we present our research results for the smallest  $\text{Ni}_N$  ( $2 \leq N \leq 13$ ) clusters.

## 2. Computational details

The DMol cluster method can yield accurate and efficient self-consistent calculations using a rapidly convergent three-dimensional numerical integration scheme [21]. As is known, the basis sets and the exchange-correlation function used in the localized-orbital method can affect the calculated results to some extent. The inner orbitals such as 3s and 3p sometimes are important for the ground-state properties of nickel clusters. We chose a double-numerical basis with polarized functions (DNP), which froze only the 1s, 2s, 2p orbitals in the present study. The size of the DNP basis sets is comparable to that of the Gaussian 6–31 G\*\* sets, but the numerical basis set is much more accurate than a Gaussian basis set of the same size. Experimental evidence on the high reactivity of nickel clusters suggests that their ground states have open shells. In the density functional approach, this means that spin polarized calculations are required to find the correct electronic configuration of the ground state.

First of all, using several kinds of exchange-correlation functionals, we have performed all-electron test calculations on the  $\text{Ni}_2$  dimer. The functionals used in the test include the following: the Perdew–Wang (1992) (PWC) functional [22]; the Perdew–Wang (1991) (PW91) with the Becke (B88) exchange functional (denoted as BP together); the Lee–Yang–Parr (LYP) correlation functional with B88 (denoted as BLYP together); and the Perdew, Burke, Enzerhof (PBE) functional. The first of these functionals, belongs to the LDA, and is a recent parameterization of the Ceperley and Alder data, which corrects some Vosko–Wilk–Nusair functional problems through fitting. The others are all general gradient approximation

Table 1

Calculated atomic bond lengths  $a_0$  (in Å) and binding energies  $E_b$  (in eV) of the  $\text{Ni}_2$  dimer in the ground state

	PWC	BP	BLYP	PBE	Expt.
$a_0$	2.064	2.096	2.112	2.096	$2.1545 \pm 0.0004$
$E_b$	−6.62893	−5.99681	−5.63756	−5.97857	$−2.042 \pm 0.002$

(GGA) corrections. The popular B88 functional [23] is often used in conjunction with the PW91 functional or the LYP [24] correlation functional. The PBE [25] functional is another GGA functional in which all the parameters are fundamental constants. The results of test calculations are summarized in Table 1. The binding energy of the cluster system is defined as the difference in the total energy between the interacting atom system and the free-atom system.

From Table 1, it is obvious that the results of GGA are much closer to the experimental data than those of LDA. The results of BLYP are closest to the experimental data in binding energy and bond length. It should also be noted that the BLYP functional has been applied successfully to several other systems, including carbon nanotubes,  $\text{Ti}_N$  clusters [17,18],  $\text{La}_N$  clusters [15,16]. In consideration of above calculated results and these applications, we adopted the BLYP exchange-correlation functional in the present study.

Both in experiment and in theory, the determination of the ground state of the  $\text{Ni}_2$  dimer has been the subject of much controversy. The latest experiments [26] on  $\text{Ni}_2$  clusters, using resonant two-photon ionization spectroscopy, show a ground-state bond length of  $2.1545 \pm 0.0004$  Å for  $^{58}\text{Ni}_2$ , and a revised value for the binding energy of  $−2.042 \pm 0.002$  eV. We find the ground-state binding energy to be  $−5.63756$  eV, which is much lower than the experimental data, and a bond length of 2.112 Å, which is close to the experimental data. It is well known that the density functional method sometimes estimates too low for the binding energy but gives good bond distances. Our calculations show the total spin to be  $S = 1$ , which is consistent with earlier matrix isolation measurements [27] and many theoretical predictions [12]. However, the most recent jet-cooled study of the  $\text{Ni}_2$  dimer indicated that the ground state was a mixture of triplet and singlet states. These differences are extremely small but still need further work.

For accurate calculations, we chose an octupole scheme for the multipolar expansion of the charge

density and Coulomb potential. In the optimizations, the energy gradient and atomic displacement converge to  $1 \times 10^{-4}$  Hartree/Bohr and  $1 \times 10^{-4}$  Å, respectively. The charge density in the self-consistent iterations converges to  $1 \times 10^{-6}$  e/Å<sup>3</sup>, which corresponds to a total energy convergence of  $1 \times 10^{-5}$  Hartree.

As the number of possible configurations increases very rapidly with the cluster size, it is obvious that one cannot explore all possible configurations. In general, clusters with higher symmetry and fewer low coordination surface atoms are expected to be more stable. The initial geometry was therefore constructed according to a certain symmetry. We then examined almost all candidate configurations for up to 13 atoms appearing in the literature. In order to determine the ground state of each cluster, by relaxation, starting from those configurations, we have employed Jahn–Teller theory [13], which states that an electronic system occupying an energy level with degeneracy is unstable and a structural distortion will occur to remove that degeneracy, especially in those systems whose highest-occupied molecular orbital (HOMO) is not fully occupied. For almost every cluster size, we performed various distortion involving moving one or several atoms along the main axis of the cluster. If the configuration

of the cluster belongs to a point group with a single main axis, this operation does not change the symmetry. It is important that all of these structural distortions are small, just enough to lift the energy level degeneracy. It should be noted, however, that for a cubic point group with several main axes, the above operation would lower the symmetry of the cluster.

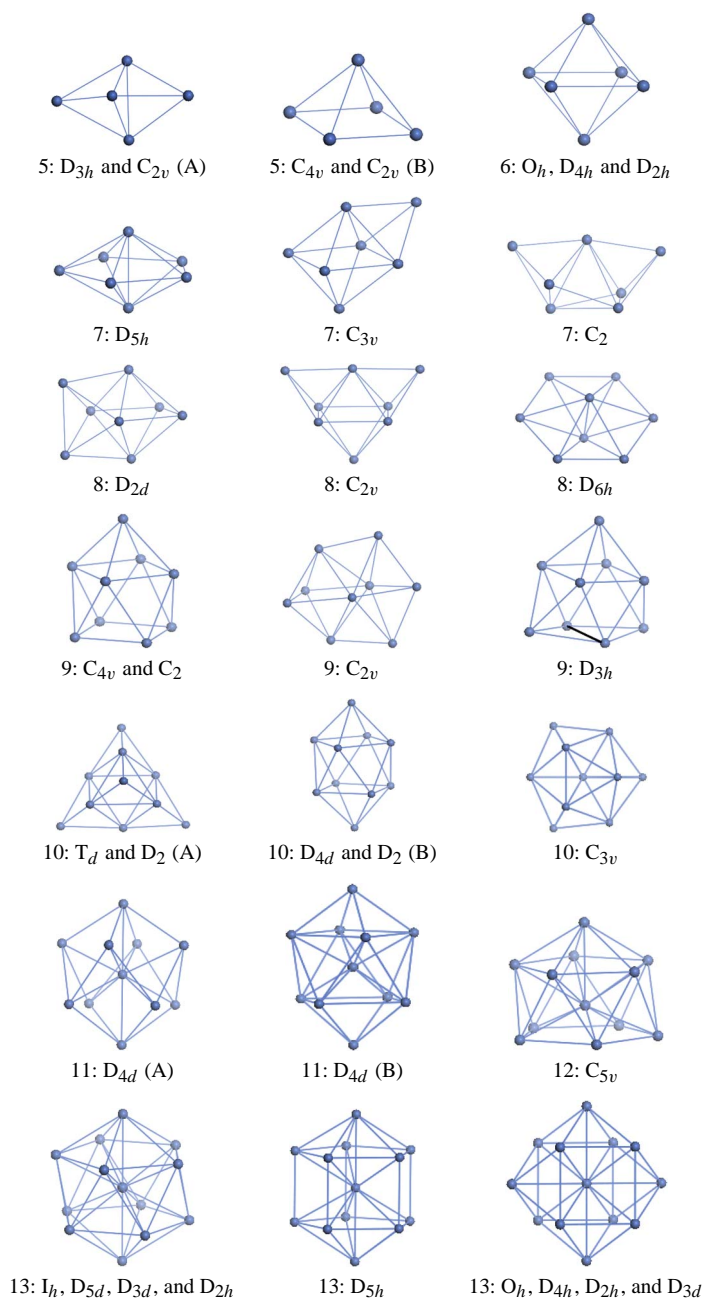
### 3. Results and discussions

The calculated results are summarized in Table 2 and some sketches of the geometric structures are shown in Fig. 1. As mentioned by Alonso [28], for the TMCs, the equilibrium geometry is determined by competition between two factors. One is that a compact structure has the maximum number of bonds. The other factor is that the directional bonding is compatible with the orientation and the filling of the d orbital. The two factors both enhance the binding energy. The first factor above means that, normally, the larger the number of bonds, the more stable the cluster. In Table 2, besides a few special clusters, we give only those structures with a high number of bonds. The

Table 2

Calculated results for different structures of Ni<sub>N</sub> ( $N = 2$ –13) clusters. The table lists the symmetry, binding energy  $E_b$  (in eV), the HOMO state, the energy difference  $\Delta E$  between the LUMO and HOMO, the electron occupation number  $n$  in the HOMO, and the total spin moment  $\mu_s$  (in  $\mu_B$ )

$N$	Sym	$E_b$	HOMO	$\Delta E$	$n$	$\mu_s$	$N$	Sym	$E_b$	HOMO	$\Delta E$	$n$	$\mu_s$
3	D <sub>3h</sub>	−9.16767	E''	0.368	1	2		C <sub>2v</sub>	−35.38311	A1	0.161	1	8
	C <sub>2v</sub>	−9.27671	A1	0.131	1	2		C <sub>4v</sub>	−35.84272	E	0.371	2	8
4	T <sub>d</sub>	−13.39243	T2	0.458	1	4		C <sub>2</sub>	−35.85273	B	0.255	1	8
	C <sub>3v</sub>	−13.37616	E	0.019	1	4	10	T <sub>d</sub>	−40.49849	T1	0.507	3	8
	C <sub>s</sub>	−13.46724	A'	0.228	1	4		D <sub>2</sub> (A)	−40.49849	B3	0.506	1	8
	D <sub>2d</sub>	−13.47127	B2	0.222	1	4		C <sub>3v</sub>	−39.97942	A1	0.228	1	8
5	D <sub>3h</sub>	−17.62936	E''	0.227	2	4		D <sub>4d</sub>	−39.99117	E1	0.059	2	8
	C <sub>2v</sub> (A)	−17.77462	A2	0.302	1	4		D <sub>2</sub> (B)	−39.99273	B3	0.030	1	8
	C <sub>4v</sub>	−17.96244	E	0.663	2	6	11	D <sub>4d</sub> (A)	−43.34163	A2	0.224	1	8
	C <sub>2v</sub> (B)	−17.98921	B2	0.685	1	6		D <sub>4d</sub> (B)	−43.26211	B2	0.477	1	8
6	O <sub>h</sub>	−22.11106	T2U	0.252	2	8	12	C <sub>5v</sub>	−48.40911	E2	0.124	2	8
	D <sub>4h</sub>	−22.19598	EU	0.125	2	8	13	I <sub>h</sub>	−52.05962	HU	0.195	3	8
	D <sub>2h</sub>	−22.21052	B1U	0.119	1	8		D <sub>5d</sub> (i)	−52.71926	A2U	0.112	1	8
7	D <sub>5h</sub>	−26.68841	E1'	0.170	2	6		D <sub>3d</sub> (i)	−52.71943	A2U	0.124	1	8
	C <sub>3v</sub>	−26.87943	A1	0.371	1	8		D <sub>2h</sub> (i)	−52.44182	B1U	0.229	1	8
	C <sub>2</sub>	−26.63191	A	0.654	1	8		D <sub>5h</sub> (d)	−52.27069	A2''	0.134	1	8
8	D <sub>2d</sub>	−31.38768	E	0.487	2	8		O <sub>h</sub> (c)	−51.66657	T1G	0.129	2	8
	C <sub>2v</sub>	−31.27790	B2	0.245	1	8		D <sub>4h</sub> (c)	−51.74011	B2U	0.233	1	6
	D <sub>6h</sub>	−30.21057	E1U	0.154	1	6		D <sub>2h</sub> (c)	−51.87265	B3U	0.082	1	6
9	D <sub>3h</sub>	−35.82140	E'	0.139	1	8		D <sub>3d</sub> (c)	−51.88782	EU	0.16	2	6

Fig. 1. Some structural sketches and their symmetries of  $Ni_N$  ( $N = 5-13$ ) clusters.

second factor above promotes the occurrence of the Jahn–Teller effect and results in the known complexity of TMCs.

For the  $Ni_3$  cluster we have tried two structures ( $C_{2v}$  and  $D_{3h}$ ). The  $C_{2v}$  is a distorted form of  $D_{3h}$ .

We have found that the structure with  $C_{2v}$  symmetry (isosceles triangular) and average bond length of 2.2798 Å has the lowest energy. The case of  $Ni_3$  is of special significance because of the existing controversy between theory and experiment. Moskovits and

Dilella [29] found the geometry of  $\text{Ni}_3$  in solid argon to be  $C_{2v}$  triplet with an apex angle estimated to be between  $90^\circ$  and  $100^\circ$ . Studies using both TBMD simulations [19] and EAM [20] for  $\text{Ni}_3$  indicated that the  $D_{3h}$  (equilateral triangle) structure was the most stable. Reuse et al. [12] suggested a  $C_{2v}$  ground state with triplet state and an apex angle of  $61^\circ$ . In good agreement with Reuse et al., our results indicate that the ground state is a  $C_{2v}$  structure with  $S = 1$  and an apex angle of  $57.198^\circ$ . At the same time, we have found that the binding energy of the equilateral triangle configuration is 0.11 eV higher than that of our  $C_{2v}$  structure.

For  $\text{Ni}_4$ , we have investigated the tetrahedron structure. The  $C_{3v}$ ,  $C_s$ , and  $D_{2d}$  structures are all distortions from the tetrahedron  $T_d$  form. The  $T_d$  structure, a regular tetrahedron, has a triplet HOMO state partially filled, and its binding energy is little higher than that of the  $C_s$  structure with a singlet HOMO state. The  $D_{2d}$  structure (a rhombus bent into a butterfly structure), another distortion tetrahedron [12] has the lowest binding energy and  $S = 2$ . We conclude that the  $D_{2d}$  and  $C_s$  structures are the energetically lowest two isomers, and that they have the same spin.

Most theoretical calculations of  $\text{Ni}_5$  [12,20] have found that the ground state to be a trigonal bipyramid ( $D_{3h}$  symmetry). In our work, we tried the two structure  $D_{3h}$  and  $C_{4v}$ . The  $C_{2v}$  (A) is a distortion from  $D_{3h}$ , and  $C_{2v}$  (B) from the square pyramid  $C_{4v}$ . The  $D_{3h}$  and  $C_{4v}$  structures have both twofold HOMO states fully filled. The Jahn–Teller distortion from  $D_{3h}$  to  $C_{2v}$  (A) has lifted the twofold degeneracy and lowered the binding energy. Similarly, from  $C_{4v}$  to  $C_{2v}$  (B), the twofold degeneracy of  $C_{4v}$  is also lifted. The lowest energy structure is just the  $C_{2v}$  (B) distortion of the square pyramid structure, the base being a rhombus rather than a square. The binding energy is 0.027 eV lower than that of the  $C_{4v}$  structure. This conclusion agrees with that of the TBMD study by Menon et al. [19], who called this structure  $C_{2v}$  (B) as a distortion  $T_d$ . In our case, the distortion structure of  $D_{3h}$  is 0.215 eV less favorable than that of  $C_{4v}$ . It is interesting to note that the number of bonds in  $C_{2v}$  (B) is fewer than in  $C_{2v}$  (A). We have further calculated the average bond lengths (2.351 Å for (B) and 2.373 Å for (A)), which shows that  $C_{2v}$  (B) is more compact than  $C_{2v}$  (A). In addition, the tetragonal pyramid of  $\text{Ni}_5$  permits undistorted d-orbital combinations to form though it

has fewer bonds. In contrast, the trigonal bipyramid  $C_{2v}$  (A) configuration optimizes the number of bonds but forces d orbitals into a symmetry which is not optimal for their bonding (the d orbitals in an atom have square symmetry). Therefore, the  $C_{2v}$  (B) with fewer bonds is more stable than  $C_{2v}$  (A). The  $C_{2v}$  (B) studied in the present work is thus a new ground state of the  $\text{Ni}_5$  cluster obtained here for the first time by a first-principles calculation.

The initial configuration of  $\text{Ni}_6$  is a tetragonal bipyramid. Both  $D_{4h}$  and  $D_{2h}$  are distortion tetragonal bipyramids derived from the octahedron ( $O_h$  symmetry). The rectangular octahedron ( $O_h$ ) has a threefold HOMO state partially occupied, and is unstable according to Jahn–Teller theory. The distortion from  $O_h$  to  $D_{4h}$  has changed the threefold to twofold degeneracy, fully occupied. The further distortion from  $D_{4h}$  to  $D_{2h}$  has completely lifted the twofold degeneracy. The  $D_{2h}$  structure is energetically the lowest isomer, with a bond length ranging from 2.372 to 2.400 Å. This is in qualitative agreement with the predictions of Menon et al. [19] and Almlöf et al. [30] who considered Jahn–Teller distortions in octahedral  $\text{Ni}_6$ .

In the case of  $\text{Ni}_7$ , we have considered a capped octahedron, a pentagonal bipyramid, and a tri-capped tetrahedron structure. They all have the same number of bonds. The capped octahedron ( $C_{3v}$ ) and the pentagonal bipyramid ( $D_{5h}$ ) have similar binding energy. The latter has a twofold HOMO state fully occupied and is only 0.0273 eV/atom higher in total energy than the  $C_{3v}$  structure. It is well known that the structure, which has a fully occupied HOMO state, is relatively stable, although there is degeneracy in the HOMO state. Consequently we suggest that the capped octahedron ( $C_{3v}$ ) and the pentagonal bipyramid ( $D_{5h}$ ) are two nearly degenerate isomers. Some theoretical calculations have predicted the ground state to be a pentagonal bipyramid, but other density functional calculations [1,5,31] and EAM results [20] have suggested that these two types of structures are nearly degenerate isomeric forms. The corresponding average binding energies per atom were found to differ by only 0.03–0.07 eV/atom, i.e., very similar to our findings. Compared with  $C_{3v}$ , the tri-capped tetrahedron structure ( $C_2$  symmetry) has the same spin and singlet HOMO state, but its binding energy is 0.25 eV higher than that of the  $C_{3v}$  structure, which may be regarded as a third isomer [20] for  $\text{Ni}_7$ .



For  $\text{Ni}_8$ , we have selected three configurations ( $\text{D}_{2d}$ ,  $\text{D}_{6h}$  and one bi-capped octahedron). The  $\text{D}_{2d}$  structure, called [20] ‘bisdisphenoid’, has the lowest binding energy and a twofold HOMO state fully filled. This conclusion is in best agreement with both experiment [6] and an EAM study by Grigoryan et al. [20]. The bi-capped octahedron  $\text{C}_{2v}$  has a singlet HOMO state and a slightly higher binding energy compared to  $\text{D}_{2d}$ . The  $\text{D}_{6h}$  structure is unstable because of the higher binding energy and twofold HOMO state partially occupied. We have not found more stable distortion structures for either  $\text{D}_{2d}$  or  $\text{D}_{6h}$ . It is worth noting that the number of bonds in the  $\text{D}_{6h}$  structure is the highest for all the structures discussed here, but it is unstable. From the optimized structure of  $\text{D}_{6h}$  in Fig. 1, we can see that the coordination of the two apex atoms is up to 7, greater than half the coordination number of a face-center cube. Its 6-atom base must therefore be expanded, which could weaken the binding energy.

For  $\text{Ni}_9$ , three configurations have been studied ( $\text{C}_{2v}$ ,  $\text{D}_{3h}$ , and  $\text{C}_{4v}$ ). The  $\text{C}_2$  structure is a distortion of  $\text{C}_{4v}$ . The lowest energy structure obtained is the  $\text{C}_2$ , which has a singlet HOMO state. The  $\text{D}_{3h}$  and  $\text{C}_2$  have similar energy, but the  $\text{D}_{3h}$  has a twofold HOMO state, incompletely occupied. A Jahn–Teller distortion could possibly lift the degeneracy or make the HOMO state occupied fully, but further distortion of  $\text{D}_{3h}$  is rather difficult. The  $\text{C}_{2v}$  structure with a similar binding energy is also a low-lying isomer. From Fig. 1, we can see that the number of bonds in the  $\text{D}_{3h}$  configuration is greater by one than in  $\text{C}_{4v}$  or  $\text{C}_{2v}$  but  $\text{D}_{3h}$  is less stable than  $\text{C}_{4v}$  and  $\text{C}_{2v}$ . We hypothesize that one reason for this is that the  $\text{D}_{3h}$  structure makes the distortion of d orbitals have trigonal symmetry, and that the bond emphasized in Fig. 1 is too short being 0.1–0.138 Å shorter than most of the other bonds.

For  $\text{Ni}_{10}$ , we consider the following structures: tetra-capped octahedron ( $\text{T}_d$  symmetry),  $\text{C}_{3v}$  and  $\text{D}_{4d}$ . The  $\text{D}_2$  (A) is a distortion of  $\text{T}_d$  and  $\text{D}_2$  (B) of the  $\text{D}_{4d}$  symmetry structures. Of these geometries, the distortion  $\text{D}_2$  (A) structure of  $\text{T}_d$  symmetry is found to be the most stable, for it has the lowest binding energy and a singlet HOMO state. It is necessary to note that this distortion has completely lifted the threefold degeneracy of the HOMO state, though the binding energy does not show much reduction. The  $\text{D}_2$  (B) has also lifted the twofold degeneracy of the  $\text{D}_{4d}$  structure

and is the second isomers. The  $\text{C}_{3v}$  structure has no degeneracy in the HOMO state and is the third isomers of  $\text{Ni}_{10}$ . One additional comment should be made. The second derivative of cluster binding energy with respect to cluster size for  $\text{Ni}_{10}$  is 1.80262 eV, greater than zero, which suggests that  $N = 10$  is a so-called magic number, and that  $\text{Ni}_{10}$  is very stable, like  $\text{Ni}_{13}$ . This is the first time that the magic number  $N = 10$  has been found using a first-principles calculation and is consistent with the results of Grigoryan et al. [20].

For  $\text{Ni}_{11}$ , we have tried two  $\text{D}_{4d}$  structures:  $\text{D}_{4d}$  (A) and  $\text{D}_{4d}$  (B). The  $\text{D}_{4d}$  (A) structure has the lowest energy and a singlet HOMO state. The  $\text{D}_{4d}$  (B) structure is found to be quite similar in energy to that of the  $\text{D}_{4d}$  (A). It therefore appears that they are two nearly degenerate isomeric forms. The  $\text{Ni}_{12}$  cluster with  $\text{C}_{5v}$  symmetry has a fully occupied HOMO state with twofold degeneracy. However, it is difficult to distort  $\text{C}_{5v}$  into a more stable state whose HOMO state is not degenerate.

For  $\text{Ni}_{13}$ , there are three potential modes competing in cluster growth: icosahedral (i), decahedral (d) and cuboctahedral (c) isomers [32], and it is therefore essential to compare the results of structures. The four structures  $\text{D}_{5d}$  (i),  $\text{D}_{3d}$  (i),  $\text{D}_{2h}$  (i), and  $\text{I}_h$ , all belong to an icosahedral structure. Only  $\text{I}_h$  is a regular icosahedron; all the others are relaxed icosahedrons. The structures, excluding  $\text{I}_h$ , have similar binding energies and no degeneracy in the HOMO state. The  $\text{D}_{3d}$  (i) has the lowest binding energy, as was predicted by Reuse et al. [2]. The  $\text{I}_h$  structure has the highest binding energy and a degenerate HOMO of 5 with only three electrons. The  $\text{D}_{5d}$  (i),  $\text{D}_{2h}$  (i), and  $\text{D}_{3d}$  (i) structures can be considered as degenerate isomers of  $i\text{-Ni}_{13}$  while  $\text{I}_h$  is not stable. In the same way, for  $d\text{-Ni}_{13}$ ,  $\text{D}_{5h}$  (d) is stable. For  $c\text{-Ni}_{13}$ ,  $\text{D}_{2h}$  (c),  $\text{D}_{3d}$  (c) and  $\text{D}_{4h}$  (c) are degenerate isomers while  $\text{O}_h$  is not stable. Furthermore, it is clear that  $i\text{-Ni}_{13}$  clusters are of lower energy compared to the other two kinds of isomers, which indicates that  $\text{Ni}_{13}$  prefers to be  $i$ -isomer. Most of earlier theoretical studies [33] were based only on an icosahedral geometry. Although our studies have been carried out three geometries, nevertheless, our results find the icosahedral geometry to be the most stable, in agreement with experiment [4].

From the above analysis, it is clear that there are many low-lying states with very close-lying energies. The Jahn–Teller distortions, which lower the structural

symmetry, help determine the ground states for  $\text{Ni}_N$  clusters for  $N \leq 13$ . These distortions allow for the lowering of the energy through the removal of some of the degeneracy present in more symmetric geometries. In searching for the ground state, we find that the binding energy does not exhibit a smooth parabolic form when the cluster is expanded without changing the symmetry. This indicates that there are some false stable states very near the ground states for certain symmetries, which increases the difficulty of the calculation.

In the following, we discuss the magnetic moments of  $\text{Ni}_N$  clusters. Very recently, Zhou et al. [34,35] have studied the role of orbital polarization in low-dimensional transition metal systems, and Wan et al. [36] have demonstrated the effect of orbital polarization, surface enhancement, and quantum confinement in nanocluster magnetism. For the spin moment ( $\mu_s$ ) of  $\text{Ni}_{13}$ , Wan et al. obtained  $0.58 \mu_B/\text{atom}$  within a rather general tight-binding framework and Reuse et al. [12] obtained  $0.62 \mu_B/\text{atom}$  by the linear combination of atomic molecular-orbital approach. All these results are in good agreement with that of the present study; namely,  $\mu_s = 0.615 \mu_B/\text{atom}$  for  $\text{Ni}_{13}$ .

It is worth mentioning that our calculated results have shown that from  $N = 6$  to 13, the spin moment remains constant at  $8\mu_B$  (see Fig. 2), that is to say, the mean spin moments of the clusters decrease monotonically with size. Apsel et al. [37] found that the mean magnetic moment exhibited characteristic oscillations with respect to the nickel cluster size: in the range of  $N \leq 13$ , there was one pronounced minimum at  $N = 13$  and another less pronounced minimum at  $N = 6$ . At first sight our calculated results seems to be inconsistent with Apsel et al. Wan et al. [36], however, have already shown that it is the orbital moment that is responsible for this disagreement between the moment value and the oscillation of total moments with respect to the cluster size. Our results are crucial in reaching an understanding of the work of Wan et al. on the spin moment for  $N = 9$ –13. Within a simple electronic shell model [38], the spin moment (in  $\mu_B$ ) is equal to the number of unpaired electrons, i.e., the number of holes, which is equal in turn to the number of 4s electrons in the nickel atom. Fig. 2 therefore also indicates the total number of s electrons as a function of cluster size ( $2 \leq N \leq 13$ ). Our results exactly verify the findings of Wan et al., volume confinement

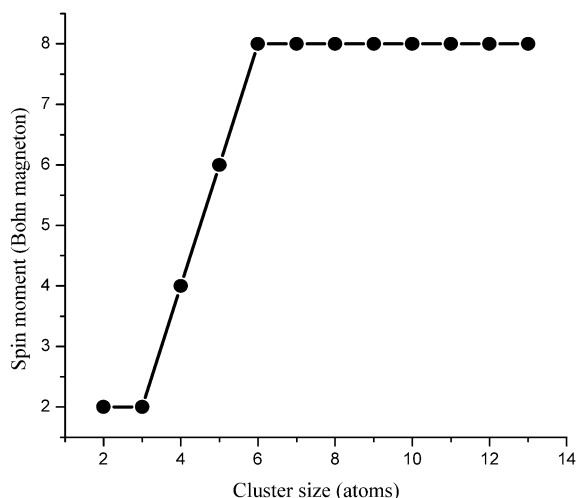


Fig. 2. Spin moment as a function of cluster size.

leads to a quantum terrace in the s electron occupation as a function of the cluster size, from  $N = 9$  to 13, and the total number of s electrons remains at eight independent of the cluster size. Our results therefore support Wan et al.'s findings. Furthermore our results show that the quantum terrace from  $N = 13$  to 9 may in fact extend to the 6-atom cluster.

#### 4. Conclusions

In summary, we have obtained optimized geometries of a number of low-energy geometrical isomers of  $\text{Ni}_N$  ( $N = 2$ –13) clusters using the DMol method based on density functional theory. The Jahn–Teller effect is shown to play an important role in optimizing the ground states. Reduced symmetry can easily lift the degeneracy of the HOMO state and there are many isomers near the ground state. For  $\text{Ni}_5$  and  $\text{Ni}_7$ , new ground states are found. As in the case of the 13-atom cluster,  $\text{Ni}_{10}$  is also a magic cluster. Above all, we obtained that from  $N = 6$  to 13, the spin moments are all  $8\mu_B$ , which exactly verifies the quantum confinement of 4s electrons in very smaller nickel clusters.

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