

## A Density Functional Study of Structure and Stability of $\text{Ni}_8$ , $\text{Ni}_8^+$ and $\text{Ni}_8^-$ Cluster

Patrizia Calaminici<sup>1a</sup>, Marcela R. Beltrán<sup>b</sup>,

<sup>a</sup>Departamento de Química  
CINVESTAV

Av. Instituto Politécnico Nacional 2508  
A.P. 14-740, México D.F. 07000 México

<sup>b</sup>Universidad Nacional Autónoma de México,  
Instituto de Investigaciones de Materiales,  
Mexico City, D.F. 01000 México

Received 11 October, 2005; accepted 1 November, 2005

*Abstract:* Density functional calculations of neutral, cationic and anionic nickel octamer are presented. The structure optimization and frequency analysis were performed on the local density approximation (LDA) level with the exchange correlation functional by Vosko, Wilk and Nusair (VWN). Improved calculations for the stability were based on the generalized gradient approximation (GGA) where the exchange correlation functional of Perdew and Wang (PW) was used. For neutral, cationic and anionic cluster several isomers and different spin multiplicities were investigated in order to find the lowest structures. Structural parameters, relative energies, binding energies, harmonic frequencies, adiabatic ionization potential and electron affinity will be presented. The calculated values are compared with available experimental data.

*Keywords:* Density Functional Theory, Transition Metal Clusters, Nickel Clusters, Structures, Relative Energy.

*This manuscript is dedicated to the memory of Professor Jaroslav Koutecky for his very important achievements and unforgettable contribution in the study of transition metal clusters.*

---

<sup>1</sup>Corresponding author. E-mail: pcalamin@mail.cinvestav.mx

## 1 Introduction

The study of transition metal (TM) clusters has become an increasingly interesting topic in the past three decades from both experimental and theoretical point of views due to their particular physical, chemical, electronic and magnetic properties related to their peculiar geometrical structures, and to their role on the development of these properties toward the bulk (see for example Refs. [1, 2, 3, 4, 5, 6] and references therein). In this sense the knowledge of their properties furnishes information how the transition from atom or molecule to the solid state may occur. The determination of structural properties and the growth pattern of the clusters therefore offer a first step toward the understanding of the development of a solid. If we classify solids by their bonding properties we can distinguish three categories with strong bonding usually referred to be as ionic, semiconducting or metallic solids. Among the  $3d$  TM clusters, Ni systems have received most of attention both experimentally and theoretically [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. In particular the localized behavior of the unfilled  $3d$  electrons in nickel clusters results in a big complexity which has animated many groups to study how this effects dominates in most of the properties of these systems. From the theoretical point of view, nickel clusters have constituted one of the most studied sets of clusters since they are excellent systems for exploring new theoretical approaches and several manuscripts have been already published. Even if to review the full literature about this topic is not a purpose of the present work, in order to get an idea of the different theoretical approaches applied in the study nickel clusters, we would like to address the reader to the following papers and their therein references [10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. Despite many articles have published on the different isomers of neutral small nickel clusters less attention has been paid to the study of structure and properties of cationic and anionic systems. In this letter a particular effort was done in order to answer some of the questions related to the structure and electronic properties of cationic and anionic nickel octamer. In the following sections we present the structures of several isomers of  $Ni_8$ ,  $Ni_8^+$  and  $Ni_8^-$  cluster obtained from all-electron Linear Combination Gaussian Type Orbital-Kohn-Sham Density Functional Theory (LCGTO-KS-DFT) calculations. Different topologies and spin multiplicity were considered in order to scan as much as possible each potential energy surface (PES) and find the lowest energetic structures. The stability of the structures is tested by a frequency analysis. Structural parameters, harmonic frequencies, binding energy, ionization potential and electron affinity are reported. The calculated values are compared with available data from the literature. We believe this is the most extensive theoretical investigation performed on the ground and low-lying states of the neutral  $Ni_8$ , cationic  $Ni_8^+$  and anionic  $Ni_8^-$  cluster.

## 2 Computational details

All calculations were performed using the density functional theory (DFT) deMon2k program [22]. The exchange-correlation potential was numerically integrated on an adaptive grid [23]. The grid accuracy was set to  $10^{-5}$  in all calculations. The Coulomb energy was calculated by the variational fitting procedure proposed by Dunlap, Connolly and Sabin [24, 25]. The structure optimizations were performed in the local density approximation (LDA) with the exchange-correlation functional of Vosko, Wilk and Nusair (VWN) [26]. DFT optimized double zeta plus valence polarization (DZVP) all-electron basis sets were employed [27]. The VWN same functional was used for the frequency analysis in order to be able to distinguish between stable structures and transition state structures. Since such calculations are insufficient for energetic considerations, single point energies were finally calculated using the same basis and auxiliary function set with the exchange-correlation functional proposed by Perdew and Wang (PW86) [28, 29]. This approach has already been proven reliable for other small TM clusters [4]. For the fitting of the density the auxiliary function set A2 were automatic generated. The way how the automatic generation of the auxil-

ary functions is performed will be presented somewhere else [30]. In order to localize different minima on the potential energy surface (PES) of the neutral, cationic and anionic nickel octamer, the structures of the three clusters have been optimized considering as starting points different initial geometries and multiplicities. To avoid spin contamination the calculations were performed with the restricted open shell Kohn–Sham (ROKS) method. A quasi-Newton method [31] with analytic energy gradients was used for the structure optimization. The convergence was based on the gradient and displacement vectors with a threshold of  $10^{-4}$  and  $10^{-3}$  a.u., respectively. For the vibrational analysis the second derivatives were calculated by numerical differentiation (two-point finite difference) of the analytic energy gradients using a displacement of 0.002 a.u. from the optimized geometry for all 3N coordinates. The harmonic frequencies were obtained by diagonalizing the mass-weighted Cartesian force constant matrix.

### 3 Results and Discussion

The optimized structure parameters, the relative energies and the spin multiplicity of the minima structures we found for the neutral nickel octamer are presented in Figure 1. The corresponding results obtained for the minima structures of the ions are presented in Figure 2 and 3, respectively. All optimized bond distances are given in Å.

In Figs. 1, 2 and 3 the relative energy values obtained with the VWN functional are given in round brackets, whereas the values obtained with the PW86 functional are given in square brackets.

For  $\text{Ni}_8$ ,  $\text{Ni}_8^+$  and  $\text{Ni}_8^-$  we investigated several initial structures as the bisdisphenoid, capped pentagonal bipyramid, cube, bi-capped tripyramidal prism, bi-capped octahedron, a square antiprism and a  $D_{2d}$  star structure. In all cases, the energy was minimized by optimization of the structural parameters and several spin multiplicities were considered. Some of the starting initial geometries during the optimization collapsed in some of other structures. For example, in our study we did not find any minima with cubic structure although the cubic topology was considered as initial guess in different multiplicities.

For the neutral  $\text{Ni}_8$  cluster the multiplicities 11, 9, 7, 5 and 3 were studied for all possible isomers. For the charged systems the multiplicity 10, 8, 6 and 4 were investigated.

For the neutral nickel octamer eight minima were found (Fig. 1). For  $\text{Ni}_8$ , the  $D_2$  bisdisphenoid structure in multiplicity 9 (structure a) was found as ground state. This structure has a twofold HOMO state full filled. This result is in agreement with both experimental data [32] and another theoretical study [19]. This isomer is followed by a  $C_{2v}$  bi-capped prism (structure b) with the same multiplicity at only 0.09 eV (Fig. 1). The next two found minima, a  $C_{2v}$  bi-capped prism (structure c) and a  $D_{2d}$  bisdisphenoid (structure d) structure, are in the sextet PES, at 0.19 and 0.27 eV above the ground state structure, respectively. Follows at higher energy a  $T_d$  bi-capped tripyramidal structure in multiplicity 9 (structure e) and three isomers in multiplicity 5 (structures f), g) and h) in Fig. 1). The minima structures in multiplicity 11 are not reported since these structures were found much higher in energy as respect the ones reported in Fig. 1.

In the case of the cation  $\text{Ni}_8^+$ , eleven minima structures were found (Fig. 2). Similar to the neutral nickel octamer, for the cationic nickel octamer we found as ground state structure the  $D_2$  bisdisphenoid structure in higher multiplicity. The Ni-Ni bond distance of the two atoms which cap the square pyramid is about 0.06 Å shorter as respect the one on the neutral ground state structure. The cationic ground state is followed by five other isomers within an energy range of only 0.19 eV. A  $D_2$  bisdisphenoid structure on the octuplet PES (structure b), a  $C_{2v}$  bi-capped prism in multiplicity 10 and the same isomer in multiplicity 8 (structures c) and d), respectively), a  $D_2$  bisdisphenoid structure on the sextet PES (structure e) and a  $T_d$  bi-capped tripyramidal structure in multiplicity 8 (structure f). Other five isomers follow well separated in energy with respect the ground state structure (Fig. 2).

Nine minima structures were found for the anionic nickel octamer (Fig. 3). Different from the neutral and anionic case, the ground state structure of  $Ni_8^-$  is found as a  $T_d$  bi-capped tripyramidal structure on the octuplet PES structure a) ). It is followed at only 0.07 eV by a  $D_2$  bisdisphenoid (structure b) ) in the same multiplicity. Also this case, GGA corrections are crucial for the correct determination of the ground state structure. In fact, the LDA level of theory predicts the change of order of structure a) and b) (see Fig. 3). As Fig. 3 shows, all remaining seven minima found for the anionic nickel octamer are well separated in energy with respect the ground state structure. As we can see from Fig. 2, the order of the minima a) and b) is exchanged when the local approximation is used. Therefore, the GGA corrections are very important for the correct prediction of the global minimum and for the relative stability of isomers.

In order to characterize the calculated ground state structure of nickel octamer and its ions and to give clues for further desirable experimental investigations, the harmonic vibrational frequencies have been calculated. The calculated harmonic frequencies for all minima are listed in Table 1. All the presented structures have no imaginary frequency and therefore they are real minima on the PES (Table 1).

In Table 2 the calculated binding energy, adiabatic ionization potential and adiabatic electron affinity are listed. The binding energy per atom calculated with the VWN functional is 4.1 eV, whereas the PW86 functional gives a value of 3.38 eV (Table 2).

With the LDA level of theory the calculated adiabatic ionization potential and the adiabatic electron affinity are 6.78 eV and 2.29 eV, respectively. The GGA corrections give 6.72 and 2.37 eV, respectively. The experimental adiabatic ionization potential [33] is 6.13 eV, which is about 0.6 eV lower than our LDA and GGA values. We also calculated the adiabatic ionization potential considering the structures b) reported in Figs. 1 and 2. The obtained value with the PW86 gradient corrected functional is 6.48 eV, much closer to the experimental value. This result gives evidence that due to the very small energy difference between ground state and low-lying states the last ones could not be excluded in the calculation of properties like adiabatic ionization potential in small nickel clusters.

The calculated adiabatic electron affinity for is in good agreement with the experimental value of  $1.97 \pm 0.05$  eV [34].

## 4 Conclusions

In this work we have reported the LCGTO-DFT local and GGA first principle all-electron calculations for the structural and spectroscopic properties of neutral, cationic and anionic nickel octamer. Several topological structures in different PES were investigated for the neutral cluster as well as for the ionic systems. All found minima were characterized by vibrational analysis in order to guide future experiments, which we hope will be forthcoming. The inclusion of gradient corrections is very important because of the very small energy separation between different low-lying isomers. Binding energies, adiabatic ionization potential and adiabatic electron affinity have been reported. Due to the very small energy difference between ground state and low-lying states different isomers might be considered for the comparison of the calculated energy properties with the available experimental values. Experimental investigations which provide vibrational resolved photo-electron spectra for small nickel clusters are highly desirable in order to be able to give a final answer concerning the ground state structure of these systems.

## Acknowledgments

Financial support from the Conacyt projects 36037-E and 40393-F and computational support from the DGSCA-UNAM is gratefully acknowledged.

Table 1: Vibrational frequencies [ $\text{cm}^{-1}$ ] of the neutral  $\text{Ni}_8$ , cationic  $\text{Ni}_8^+$  and anionic  $\text{Ni}_8^-$  cluster. The calculations were performed with the VWN/DZVP/GEN-A2 method. The cluster structures are given in Figure 1, 2 and 3.

$\text{Ni}_8$	Frequencies	$\text{Ni}_8^+$	Frequencies	$\text{Ni}_8^-$	Frequencies
a)	87, 118, 132, 141, 156, 169, 171, 177, 188, 193, 252, 252, 253, 262, 285, 288, 312, 320	a)	84, 115, 131, 133, 144, 171, 173, 176, 186, 191, 237, 245, 250, 259, 278, 313, 316, 319	a)	90, 95, 104, 118, 158, 162, 167, 171, 191, 195, 222, 229, 241, 257, 261, 304, 318, 337
b)	81, 94, 98, 120, 138, 163, 165, 178, 195, 199, 227, 235, 238, 257, 267, 311, 319, 338	b)	81, 106, 117, 125, 133, 149, 172, 176, 189, 195, 229, 245, 251, 260, 280, 317, 319, 329	b)	98, 109, 118, 127, 133, 155, 167, 170, 182, 187, 231, 244, 257, 258, 278, 307, 314, 320
c)	78, 93, 115, 119, 151, 163, 170, 171, 185, 206, 220, 221, 249, 266, 269, 305, 330, 344	c)	97, 99, 111, 122, 136, 147, 164, 175, 183, 188, 231, 256, 259, 269, 278, 302, 320, 327	c)	46, 64, 81, 119, 142, 151, 160, 167, 186, 207, 217, 235, 244, 246, 265, 297, 320, 344
d)	103, 105, 112, 113, 135, 146, 170, 172, 184, 185, 225, 245, 248, 272, 279, 313, 318, 327	d)	62, 85, 91, 115, 138, 159, 161, 178, 191, 204, 222, 222, 243, 248, 267, 306, 326, 337	d)	43, 59, 99, 117, 123, 144, 147, 181, 184, 200, 210, 237, 239, 245, 270, 307, 326, 344
e)	60, 65, 107, 132, 135, 151, 159, 185, 196, 210, 216, 235, 249, 262, 284, 308, 328, 347	e)	115, 119, 123, 128, 166, 174, 180, 191, 195, 213, 233, 247, 250, 267, 270, 311, 320, 341	e)	134, 194, 214, 220, 223, 231, 234, 249, 257, 261, 274, 294, 295, 311, 325, 344, 362, 366
f)	37, 61, 74, 100, 113, 118, 136, 161, 176, 195, 207, 221, 227, 273, 284, 323, 326, 340	f)	61, 66, 104, 126, 130, 153, 161, 184, 190, 193, 218, 220, 242, 250, 278, 316, 325, 347	f)	114, 117, 125, 125, 162, 165, 165, 181, 184, 193, 245, 245, 261, 266, 281, 281, 316, 323
g)	42, 93, 119, 135, 149, 152, 159, 172, 199, 218, 223, 242, 258, 290, 297, 339, 359, 373	g)	54, 71, 104, 132, 138, 157, 166, 177, 183, 204, 209, 225, 241, 253, 281, 311, 322, 343	g)	125, 131, 144, 156, 158, 170, 171, 190, 208, 222, 245, 247, 259, 266, 284, 299, 310, 345
h)	69, 72, 103, 118, 153, 162, 188, 204, 210, 228, 239, 264, 279, 291, 300, 313, 330, 337	h)	96, 104, 122, 129, 133, 149, 175, 182, 183, 192, 224, 250, 258, 278, 278, 312, 319, 325	h)	76, 86, 109, 116, 126, 130, 159, 161, 162, 196, 216, 240, 248, 267, 269, 292, 310, 313
		i)	20, 75, 91, 109, 118, 168, 179, 202, 208, 209, 221, 253, 261, 275, 287, 306, 317, 342	i)	103, 112, 119, 116, 126, 130, 159, 161, 162, 196, 216, 240, 248, 267, 269, 292, 310, 313
		l)	83, 90, 95, 102, 131, 134, 147, 169, 184, 206, 221, 234, 242, 257, 266, 311, 320, 333		
		m)	108, 131, 139, 142, 152, 157, 162, 175, 219, 224, 240, 251, 256, 265, 285, 311, 320, 359		

Table 2: Binding energy (eV), ionization potential (eV) and electron affinity (eV) for  $\text{Ni}_8$ . The calculations were performed with the VWN/DZVP/GEN-A2 and the PW86/DZVP/GEN-A2 methods. The PW86/DZVP/GEN-A2 values are in parenthesis.

BE	BE per atom	Adiabatic IP	Adiabatic EA
32.8 (27.06)	4.1 (3.38)	6.78 (6.72)	2.29 (2.37)

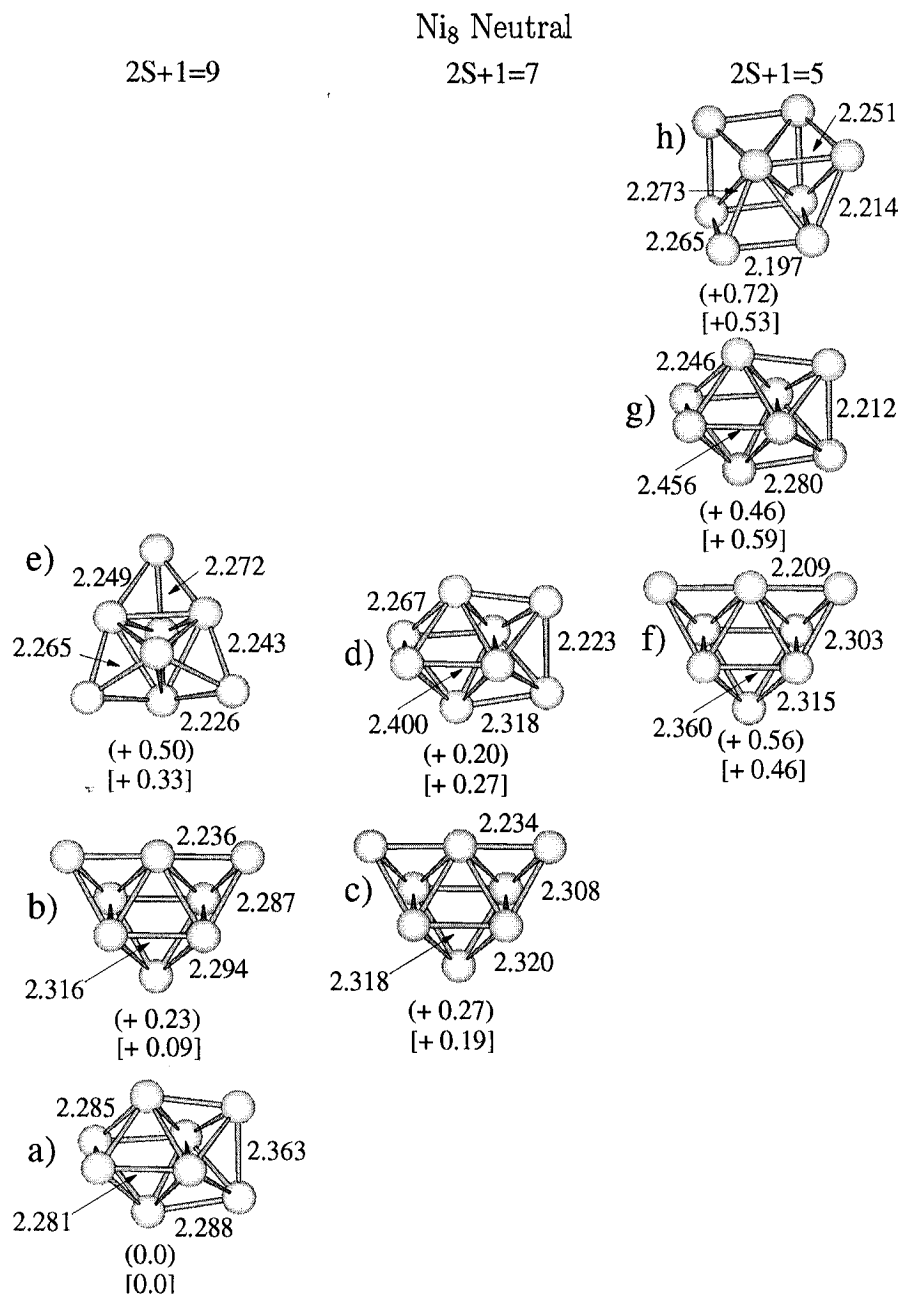


Figure 1: Ground state and excited state structures of  $Ni_8$  cluster. The calculations were performed with the VWN/DZVP/GEN-A2 method. The relative energy is given in eV. VWN values are in round brackets and PW86 values are in square brackets. Bond lengths are given in Å.

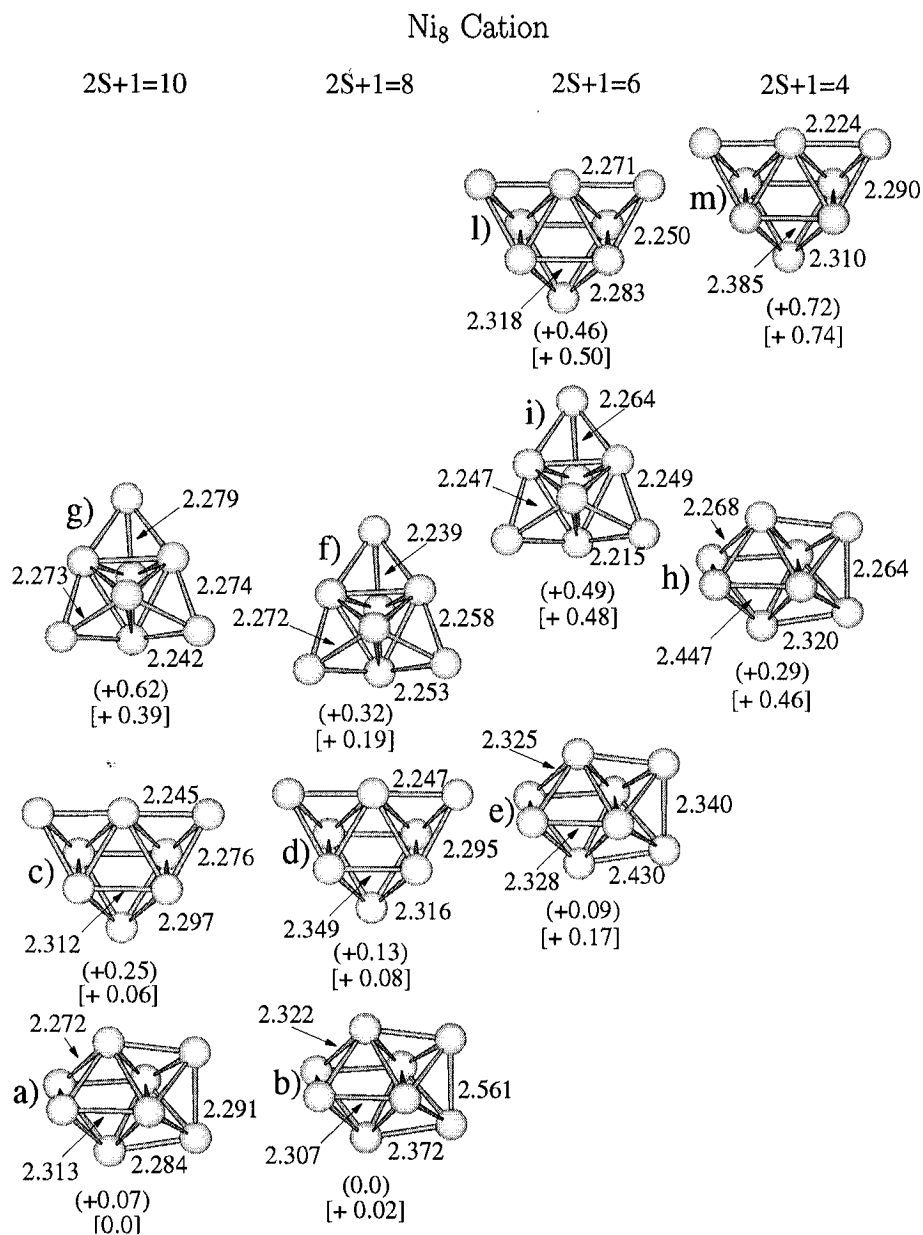


Figure 2: Ground state and excited state structures of  $\text{Ni}_8^+$  cluster. The calculations were performed with the VWN/DZVP/GEN-A2 method. The relative energy is given in eV. VWN values are in round brackets and PW86 values are in square brackets. Bond lengths are given in Å.

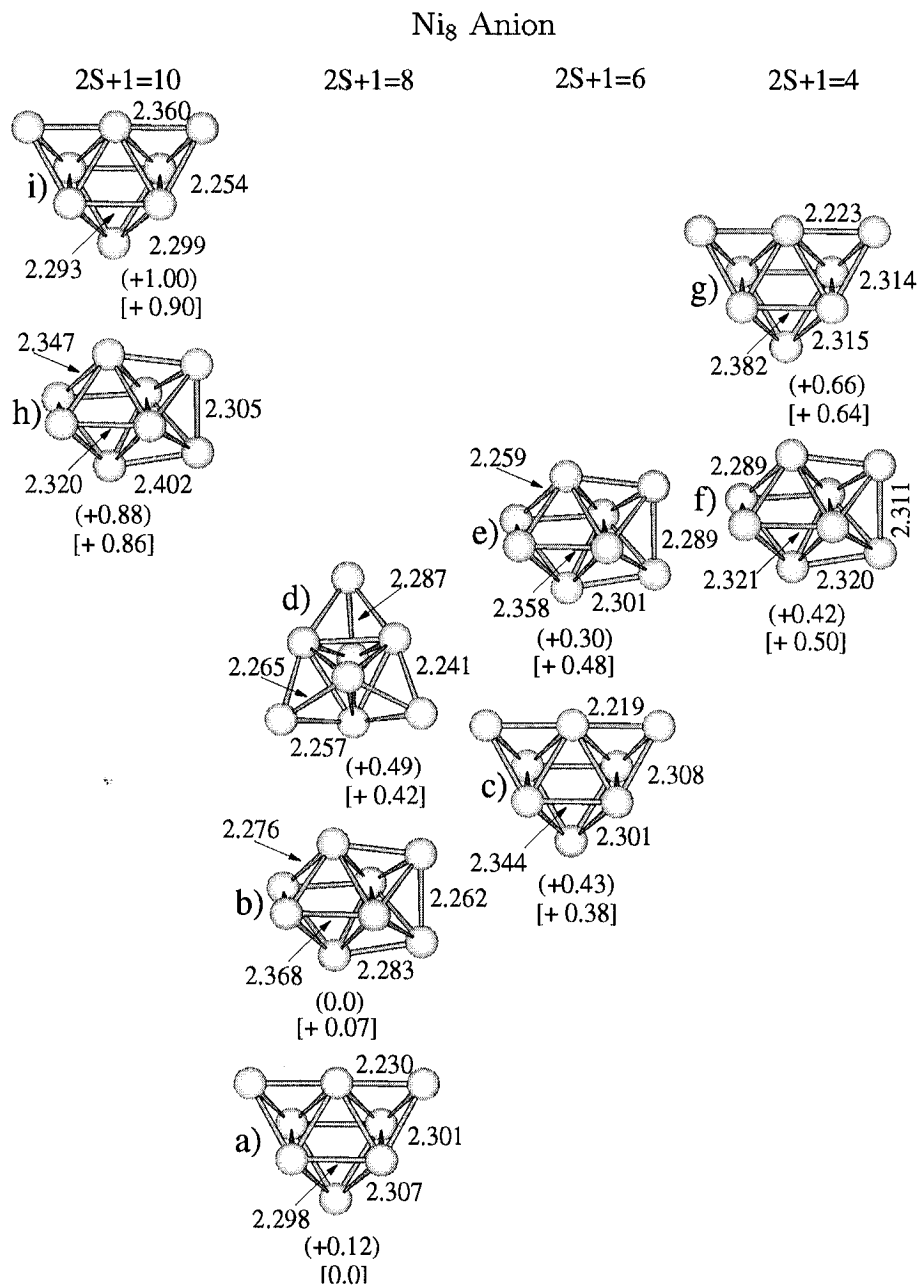


Figure 3: Ground state and excited state structures of  $Ni_8^-$  cluster. The calculations were performed with the VWN/DZVP/GEN-A2 method. The relative energy is given in eV. VWN values are in round brackets and PW86 values are in square brackets. Bond lengths are given in Å.



## References

- [1] M.D. Morse, Clusters of Transition–Metal Atoms, *Chemical Reviews*, **86** 1049–1109(1986).
- [2] J.A. Alonso, Electronic and Atomic Structure, and Magnetism of Transition–Metal Clusters, *Chemical Reviews* **100** 637–677(2000).
- [3] V. Bonacic-Koutecky, L. Cespiva, P. Fantucci, J. Koutecky, Effective core potential-configuration interaction study of electronic structure and geometry of small neutral and cationic  $\text{Ag}_n$  clusters: Predictions and interpretation of measured properties, *Journal of Chemical Physics* **98** 7981–7994(1993)
- [4] K. Jug, B. Zimmermann, P. Calaminici, A. M. Köster, Structure and Stability of Small Copper Clusters  $\text{Cu}_n$  ( $n \leq 10$ ), *Journal of Chemical Physics* **116**, 4497–(2002)
- [5] P. Calaminici, A.M. Köster, N. Russo, P.N. Roy, T. Carrington Jr., D.R. Salahub,  $V_3$ : Structure and Vibrations from Density Functional Theory, Franck-Condon Factors and the PFI-ZEKE Spectrum, *Journal of Chemical Physics* **114**, 4036–4044(2001)
- [6] J. Jellinek and I.L. Garzon, Structural and Dynamic Properties of Transition-Metal Clusters, *Zeitschrift für Physik. D, Atoms, molecules and clusters* **20** 239–242(1991).
- [7] E.K. Parks, K.P. Kerns and S.J. Riley, The structure of  $\text{Ni}_{46}$ ,  $\text{Ni}_{47}$ , and  $\text{Ni}_{48}$ , *Journal of Chemical Physics* **114** 2228–2236(2001).
- [8] M.B. Knickelbein, Nickel clusters: The influence of adsorbates on magnetic moments, *Journal of Chemical Physics* **116** 9703–9711(2002).
- [9] F. Liu, R. Liyanage and P.B. Armentrout, Guided ion beam studies of the reaction of  $\text{Ni}_n^{(+)}$  ( $n = 2-16$ ) with  $\text{D}_2$ : Nickel cluster-deuteride bond energies *Journal of Chemical Physics* **117** 132–141(2002).
- [10] F.A. Reuse and S.N. Khanna, Photoabsorption spectrum of small  $\text{Ni}_n$  ( $n=2-6, 13$ ) clusters, *The European Physical Journal D - Atomic, Molecular and Optical Physics* **6** 77–81(1999).
- [11] T.L. Wetzel and DePristo, Structures and energetics of  $\text{Ni}_{24}\text{Ni}_{55}$  clusters, *Journal of Chemical Physics* **105** 572–580(1996).
- [12] F. Ruetter and C. Gonzalez, The importance of global minimization and adequate theoretical tools for cluster optimization: the  $\text{Ni}_6$  cluster case, *Chemical Physics Letters* **359** 428–433(2002).
- [13] S.N. Khanna and P. Jena, Magnetic moment and photo-detachment spectroscopy of  $\text{Ni}_5$  clusters, *Chemical Physics Letters* **336** 467–472(2001).
- [14] S.N. Khanna, M.R. Beltran and P. Jena, Relationship between photoelectron spectroscopy and the magnetic moment of  $\text{Ni}_7$  cluster, *Physical Review B* **64** 235419–235422(2001).
- [15] G.M. Pastor, R. Hirsch and B. Muhlshlegel, Magnetism and structure of small clusters: An exact treatment of electron correlations, *Physical Review B* **53** 10382–10396(1996).
- [16] M. Castro, C. Jamorski and D.R. Salahub, Structure, bonding, and magnetism of small  $\text{Fe}_n$ ,  $\text{Co}_n$ , and  $\text{Ni}_n$  clusters,  $n \leq 5$ , *Chemical Physics Letters* **271** 133–142(1997).
- [17] G.A. Cisneros, M. Castro and D.R. Salahub, DFT study of the structural and electronic properties of small  $\text{Ni}_n$  ( $n=2-4$ ) clusters, *International Journal of Quantum Chemistry* **75** 847–861(1999).

- [18] G.L. Estiu and M.C. Zerner, Structural, electronic, and magnetic properties of small Ni clusters *Journal of Physical Chemistry* **100** 16874-16880(1996).
- [19] N. Desmarais, C. Jamorski, F.A. Reuse and S.N. Khanna, Atomic arrangements in  $Ni_7$  and  $Ni_8$  clusters, *Chemical Physics Letters* **294** 480-486 (1998).
- [20] Z. Xie, Q.-M. Ma, Y. Liu, Y.-C. Li, First-principle study of the stability and Jahn-Teller distortion of nickel clusters, *Physics Letters A* **342** 459-467(2005).
- [21] M.C. Michelini, R. Pis Diez, A.H. Jubert, Density Functional Study of Small  $Ni_n$  Clusters, with  $n=2-6, 8$ , using the Generalized Gradient Approximation, *International Journal of Quantum Chemistry* **85** 22-33(2001).
- [22] A.M. Köster, P. Calaminici, R. Flores-Moreno, G. Geudtner, A. Goursot, T. Heine, F. Janetzko, S. Patchkovskii, J.U. Reveles, A. Vela and D.R. Salahub, deMon2k, The deMon developers (2004)
- [23] A.M. Köster, R. Flores-Moreno and J.U. Reveles, Efficient and reliable numerical integration of exchange-correlation energies and potentials, *Journal of Chemical Physics* **121** 681-690(2004).
- [24] B.I. Dunlap, J.W.D. Connolly and J.R. Sabin, On first-row diatomic molecules and local density models, *Journal of Chemical Physics* **71** 4993-4999(1979).
- [25] W. Mintmire and B.I. Dunlap, Fitting the Coulomb potential variationally in linear-combination-of-atomic-orbitals density-functional calculations, *Physical Review A* **25** 88-95(1982).
- [26] S.H. Vosko, L. Wilk and M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis, *Canadian Journal of Physics* **58** 1200-1211(1980).
- [27] N. Godbout, D.R. Salahub, J. Andzelm and E. Wimmer, Optimization of Gaussian-Type Basis-Sets for Local Spin-Density Functional Calculations .1. Boron Through Neon, Optimization Technique and Validation *Canadian Journal of Physics* **70** 560-571(1992)
- [28] J.P. Perdew and Y. Wang, Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation, *Physical Review B* **33**, 8800-8802(1986); Erratum: *Physical Review B* **40** 3399(1989).
- [29] J.P. Perdew, Density-functional approximation for the correlation energy of the inhomogeneous electron gas, *Physical Review B* **33**, 8822-8824(1986); Erratum: *Physical Review B* **34** 7406(1986).
- [30] P. Calaminici, R. Flores-Moreno, A.M. Köster, A Density Functional Study of Structures and Vibrations of  $Ta_3O$  and  $Ta_3O^-$ , *Computing Letters*, submitted
- [31] J.U. Reveles and A.M. Köster, Geometry Optimization in Density Functional Methods, *Journal of Computational Chemistry* **25** 1109-1116(2004).
- [32] H. Basch, M.D. Newton, J.W. Moskowitz, The electronic structure of small nickel atom clusters, *Journal of Chemical Physics* **73** 4492-4510(1980).
- [33] M.B. Knickelbein, S. Yang, S.J. Riley, Near-threshold photoionization of nickel clusters: Ionization potentials for  $Ni_3$  to  $Ni_{90}$ , *Journal of Chemical Physics* **93** 94-104(1990).

- [34] S.-R. Liu, H.-J. Zhai and L.-S. Wang, Evolution of the electronic properties of small  $\text{Ni}_n^-$  ( $n=1-100$ ) clusters by photoelectron spectroscopy, *Journal of Chemical Physics* **117** 9758-9765(2002).