



## Structural and electronic properties of nanoparticle: density functional study of small palladium clusters ( $Pd_n$ $n=1-6$ )

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DOI: <https://doi.org/10.33545/26646781.2020.v2.i1a.16>

### Abstract

Structure and relative stability of  $Pd_n$  clusters for  $n=1-6$  were investigated using density functional methods at the B3PW91 level of theory. The structures of the optimized Palladium clusters were investigated and the results are compared with the available experimental values. Stability of the clusters was determined from their relative energy values, binding energies, HOMO-LUMO gap and electronic properties. The binding energy per atom also increases with cluster size. The study revealed that  $Pd_4$  and  $Pd_6$  are relatively more stable than their neighboring clusters. The most stable isomer for all clusters under investigation is the triplet. The  $Pd_4$  and  $Pd_5$  showed different Pd-Pd bond lengths due to Jahn-Teller distortion. Stability function and atom addition energy change predict that  $Pd_4$ , and  $Pd_6$  are relatively more stable than their neighboring clusters. Electron affinity (EA), Ionization potential (IP) and electronegativity values suggest that larger clusters have stronger tendency to accept electrons, thereby supporting the relative stability of  $Pd_4$  and  $Pd_6$ . Finally, Collision diameter increases as the cluster size increases.

**Keywords:** palladium nano clusters, DFT, binding energy, collision diameter

### Introduction

Atomic or molecular clusters are those nanoparticles which are aggregates of identical or different atoms or molecules ranging from a few to many millions. They constitute a separate class of materials in between the bulk on one hand and the molecular state on the other. In nanoparticles the chemical, optical, electrical, physical, and magnetic properties can be significantly different from the respective bulk materials. For example, while bulk gold appears yellow in color, nanosized gold particles appear in red, or while bulk gold does not react with oxygen, gold clusters do. Thus, materials that are commonly chemically inert in bulk can become catalytically active [1, 5]. Palladium catalysts are being widely used to perform many important reactions, and their study has been increased in the last decades due to the current need to eliminate some contaminants coming from vehicle emissions [6]. Nano clusters such as clusters of transition metals of group 10 (Ni, Pd, Pt), offer unique physical and chemical behavior, with the possibility of fine-tuning size and structures [6, 7]. The high surface area to volume ratio significant change values in the electronic structures which are important features of the clusters and also it makes ultrafine dispersed d-metal clusters attractive for catalytic applications [6, 8]. Previous studies have pointed to the importance of palladium clusters during the adsorption of nitric oxide which transforms triple bonds to double bonds [9, 10]. Palladium has better magnetic, ionization energy and binding energies than the other metals in its group (Ni, Pt, Pd) and at different temperature the palladium structures exhibited high stability in comparison with rest of the group [7]. Theoretical calculations can help in determining the equilibrium geometries of these clusters and can complement the experimental studies [8, 9].

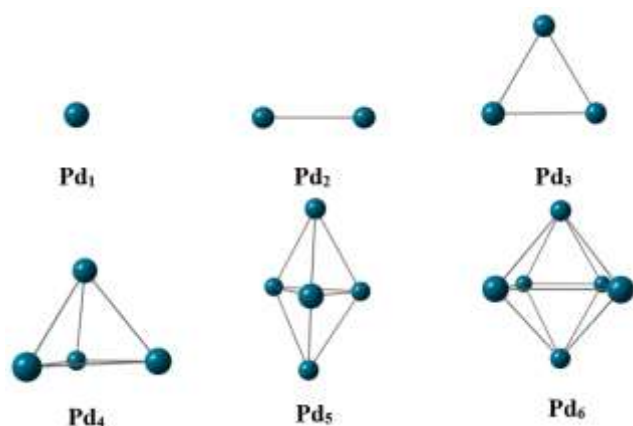
magnetic and the point group of the clusters [Ni, Pd, Pt] varies with the direction of the magnetization, which are even more pronounced for the 4d palladium metal [11]. Previous investigation showed that the most stable geometry of  $Pd_4$  is a regular tetrahedron with  $T_d$  symmetry [11, 12]. The aim of the present work is to model a system for palladium clusters and investigate some properties in particular, structural properties, binding energy, vertical; adiabatic ionization potential, collision diameter, volume and stretching frequency.

### Computational Details

The calculations were carried out using Gaussian 09 package [13]. The B3PW91 exchange and correlation functional [14, 15] were used with the SDD [16] valence basis set for all the calculations in this study Full geometry optimization with no symmetry restrictions were carried out in each case and stationary points were confirmed to be genuine minima by analytic calculation of their harmonic vibrational frequencies.

### Results and discussion

The Justification of methodology employed in the present work was recognized by comparing the structural and electronic data of palladium clusters calculated at theoretical level with that obtained by experimental studies [17], Figure 1. And Table 1,2. The results show that for palladium atom, singlet state is the lowest energy state with 0.83 eV lower in energy than the triplet state. This value is in excellent agreement with the experimental value of 0.82eV [18] and superior to the previous theoretical values [19, 20].



**Fig 1:** The structures of the most stable palladium clusters.

The lowest energy structure of palladium dimer ( $\text{Pd}_2$ ) is a triplet state ( $^3\Sigma_u$ ) is with a symmetric point group of  $D_{\infty h}$  in agreement with other studies [17, 19, 20]. The singlet state ( $^1\Sigma_g$ ) is lies 0.41 eV higher in energy than the triplet state. The possible structures of the palladium dimer with different multiplicity are listed in Table 3. The bond length of this structure is found to be 2.497 Å, which better than the previous theoretical results of 2.53 Å and 2.559 Å obtained from reference [19, 20] since the experimental value is 2.48 Å [21]. Finally, the dissociation energy, electron affinity and stretching frequency of  $\text{Pd}_2$  are in excellent agreement with the experimental values.

**Table 1:** Vertical (VIP) and Adiabatic ionization potentials (ADIP), Binding energy (eV) Dipole moment D.M (Debye) for the most stable palladium clusters.

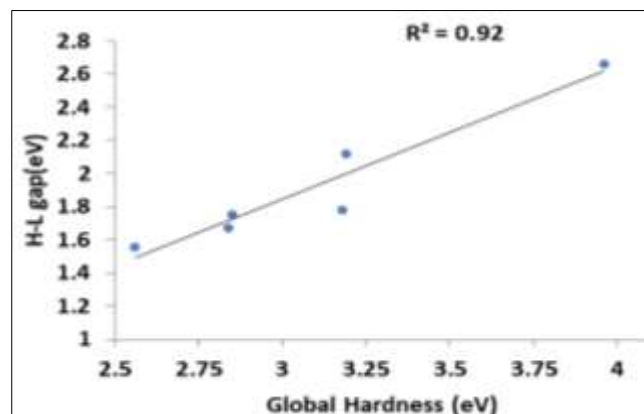
sys	VIP	ADIP with	VIP	AIP	Exp.	BE	D.M
$\text{Pd}_1$	8.62	8.62	8.6883	8.6883	$8.3365 \pm 0.0001$ $8.3369 \pm 0.0001$	0.00	0.00
$\text{Pd}_2$	7.91	7.86	7.6936	7.6280	$7.7 \pm 0.3$	0.46	0.00
$\text{Pd}_3$	7.67	7.66	7.5608	7.5734		0.84	0.00
$\text{Pd}_4$	6.77	6.77	6.8580	6.8492		1.28	0.049
$\text{Pd}_5$	7.28	7.25	6.6046	6.6006		1.35	0.048
$\text{Pd}_6$	6.85	6.83	6.3268	6.3289		1.46	0.00

**Table 2:** Vertical (VEA) and Adiabatic Electron affinity (ADEA), Global hardness, dissociation energy ( $D_0$ ) and HOMO-LUMO (H-L g) gap all in (eV) for the most stable palladium clusters.

Sys	VEA	ADEA	Exp.	Global hardness	$D_0$	H-L g
$\text{Pd}_1$	0.70	0.70	$0.5620 \pm 0.0050$ $0.5570 \pm 0.0080$	3.96	-	2.66
$\text{Pd}_2$	1.54	1.53	$1.6850 \pm 0.0080$ $1.30 \pm 0.15$	3.19	0.93	2.12
$\text{Pd}_3$	2.00	2.06	$1.35 \pm 0.10$ $1.50 \pm 0.10$	2.84	1.79	1.67
$\text{Pd}_4$	1.38	1.41	$1.35 \pm 0.10$	3.18	2.43	1.78
$\text{Pd}_5$	1.58	1.57	$1.45 \pm 0.10$	2.85	1.66	1.75
$\text{Pd}_6$	1.74	1.73	$1.65 \pm 0.10$	2.56	1.98	1.56

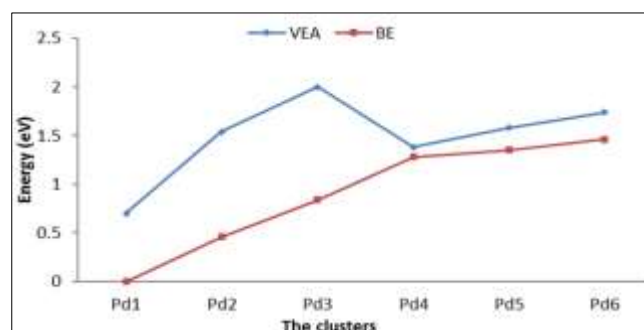
The ground state of  $\text{Pd}_3$  has a triangle structure in  $C_{2v}$  symmetry with ground state of  $^3B_1$ . The singlet  $\text{Pd}_3$  with  $^1A'$  is identical in energy with the above  $C_{2v}$  symmetry Table 3. The singlet  $D_{3h}$  with  $^1A_1$  state lies 0.20 eV higher in energy than the triplet state, and once more the singlet  $C_s$  with  $^1A'$  has the same energy as the singlet  $D_{3h}$ . The ground state of  $\text{Pd}_3$  has a triangle structure in  $C_{2v}$

symmetry with ground state of  $^3B_1$ , while the linear structure corresponds to a transition state. As for dimers, triplet states are located below the singlet states. The difference in energy with the singlet state is about 0.20 eV. Another two triplet are located with  $C_{2v}$  and  $D_{3h}$  symmetry which also above the minima by 0.01 and 0.08 eV respectively. These trends are also in good agreements with previous works [22, 24]. It should be noted that a series of similar structures relatively close in energy corresponding to different electronic states have been identified but we do not go into details of these different electronic states Table 3. The triplet  $D_{3h}$  state shifts to a distorted  $C_{2v}$  geometry (64.9° for the apex angle) due to a Jahn–Teller effect.



**Fig 3:** A linear relationship between the Global hardness for palladium clusters.

The electronic ground state is  $^3B_2$ , as confirmed previously [17]. This electronic asymmetry is reflected in structural parameters by introducing a bond length longer at the base (2.96 Å) than the sides of isosceles triangle (2.51 Å). The VIP of the trimer cluster is 7.67 eV which are comparable with the value of 7.56 eV reported previously [25]. Finally, the VEA of  $\text{Pd}_3$  cluster is calculated as 2.00 eV which identical with the value of 2.02 eV [26]. The lowest energy structure of  $\text{Pd}_4$  cluster is a triplet in  $C_s$  state. Above the ground state  $C_s$  there are two equal energy structures (0.75 eV) representing the  $^1A'$  and  $^1A$  electronic states Table 3. The VIP of the  $\text{Pd}_4$  of 7.16 eV Figure 2, is comparable with the published value of 6.86 eV [25]. The HOMO-LUMO gap results predicted that the  $\text{Pd}_4$  is the most stable cluster, this fact has been demonstrated previously [25].  $\text{Pd}_4$  possesses the highest value of bond dissociation energy (2.40 eV) in the clusters series of  $>\text{Pd}_2$  and also a high HOMO-LUMO gap of 1.78 eV.

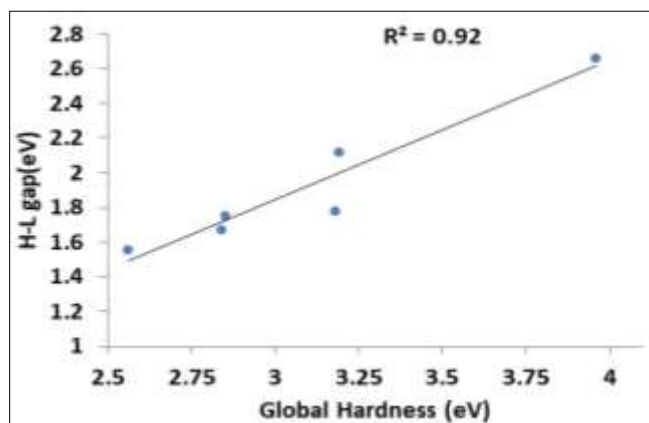


**Fig 2:** Binding energy and vertical electron affinity as a function of cluster size.

**Table 3:** The state, total energy (ET in Hz), Relative energy to the most stable isomer ( $\Delta E$  in eV), Bond length (B.L in Å) and the stretching frequency (Freq in  $\text{cm}^{-1}$ ) for palladium clusters.

Pd <sub>N</sub>	State	E <sub>t</sub>	$\Delta E$	B.L	Freq.
Pd <sub>2</sub>					
Singlet D <sub>∞h</sub>	<sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	-255.8544	0.41	2.73979	133
Triplet D <sub>∞h</sub>	<sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	-255.8696	0.00	2.49787	210
Quintet D <sub>∞h</sub>	<sup>5</sup> Σ <sub>u</sub> <sup>-</sup>	-255.7757	2.55	2.46599	202
Pd <sub>3</sub>					
Singlet D <sub>3h</sub>	<sup>1</sup> A <sub>1</sub> '	-383.8398	0.20	2.480	157-260
Triplet C <sub>2v</sub>	<sup>3</sup> B <sub>1</sub>	-383.8473	0.00	2.459-2.573	116-242
Triplet C <sub>s</sub>	<sup>3</sup> A <sup>-</sup>	-383.8473	0.00	2.459-2.573	117-243
Triplet C <sub>2v</sub>	<sup>3</sup> B <sub>2</sub>	-383.8471	0.01	2.510-2.964	122-210
Triplet D <sub>3h</sub>	<sup>3</sup> A <sub>2</sub>	-383.8442	0.08	2.531-2.543	149-236
Pd <sub>4</sub>					
Singlet C <sub>s</sub>	<sup>1</sup> A <sup>-</sup>	-511.8324	0.75	2.544	78-245
Singlet Td	<sup>1</sup> A	-511.8324	0.75	2.545	77-246
Triplet C <sub>s</sub>	<sup>3</sup> A <sup>-</sup>	-511.8600	0.00	2.565-2.665	80-244
Pd <sub>5</sub>					
Triplet C <sub>2v</sub>	<sup>3</sup> B <sub>2</sub>	-639.8391	0.00	2.573-2.657	67-236
Triplet C <sub>1</sub>	<sup>3</sup> A	-639.8391	0.00	2.573-2.657	67-236
Singlet C <sub>2v</sub>	<sup>1</sup> A <sub>1</sub>	-639.8151	0.65	2.557-2.595-2.684	45-238
Singlet D <sub>3h</sub>	<sup>1</sup> A	-639.8151	0.65	2.608-2.630-2.646	32-237
Pd <sub>6</sub>					
Triplet O <sub>h</sub>	<sup>3</sup> B <sub>2g</sub>	-767.8297	-	2.595-2.698	77-223

The global hardness and dipole of Pd<sub>4</sub> are higher than the other clusters. Although binding energy values of Pd<sub>5</sub>, Pd<sub>6</sub> are higher than that of Pd<sub>4</sub>, their AIP and VIP values are lower. The Pd<sub>4</sub> cluster has higher HOMO-LUMO gap, bond dissociation energies, and global hardness. There is a linear relationship between HOMO-LUMO gap and the global hardness Figure 3.

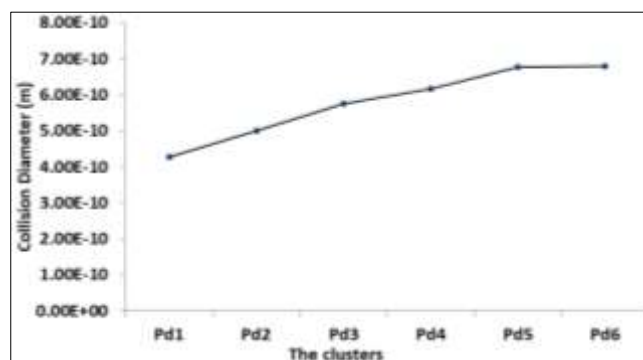
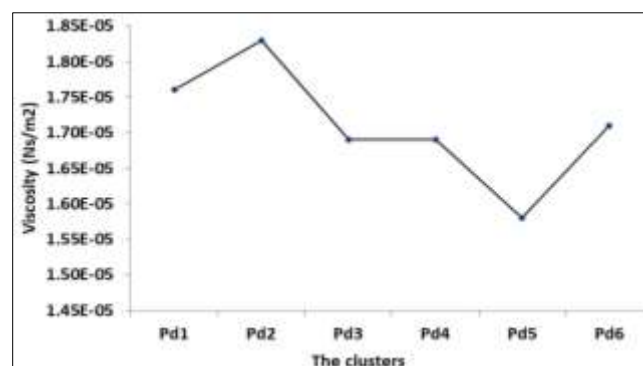
**Fig 3:** A linear relationship between the Global hardness for palladium clusters.

These values support Pd<sub>4</sub> as a magic cluster, and enhanced stability are hallmarks of magic clusters. Therefore, we can accept Pd<sub>4</sub> as the electronically most stable cluster or a magic-number cluster among the clusters under study. The lowest energy structure of Pd<sub>5</sub> cluster is a triplet <sup>3</sup>B<sub>2</sub> in C<sub>2v</sub> symmetry with trigonal bipyramid structure. This triplet <sup>3</sup>B<sub>2</sub> shifts to a distorted geometry ((65.48°) for the apex angle of the middle triangle) due to a Jahn–Teller effect and the original D<sub>3h</sub> is ruined [27]. This distortion is evident since the dipole moment has value of 0.048 D instead of zero. Identical triplet <sup>3</sup>A with equal energy and C<sub>1</sub> symmetry is identified. Two identical energies singlet

with C<sub>2v</sub> and D<sub>3h</sub> are located at 0.65 eV above the ground state (<sup>3</sup>B<sub>2</sub>). The VEA of Pd<sub>5</sub> is noted at 1.38 eV which in excellent agreement with the experimental value of 1.35±0.1 eV [9, 11]. The binding energy is higher than those of lower clusters, and the Pd<sub>4</sub> cluster showed lower dissociation energy in comparison with Pd<sub>3</sub>, Pd<sub>4</sub> and Pd<sub>6</sub>. The Pd<sub>6</sub> cluster showed only one stable structure as a triplet <sup>3</sup>B<sub>2g</sub> state in octahedral symmetry. The value of VEA (1.74 eV) of Pd<sub>6</sub> is in agreement with experimental value of 1.65±0.1 eV. The Pd<sub>6</sub> cluster showed high dissociation energy (1.98 eV) actually the second in the series after Pd<sub>4</sub>. The collision diameter of the palladium cluster is increase as the cluster size increases Figure 4, the collision diameter is defined as the distance between the centers of two colliding molecules when at their closest point of approach, the basic relationship between the mean free path and the average velocity is used to calculate the viscosity of the gaseous palladium clusters are given in Figure 5, Table 4. The viscosity of a gas can be thought of as a measure of its resistance to flow. Gas viscosity is only weakly dependent on pressure near atmospheric pressure. The volume of the palladium clusters is calculated using volume keyword in Gaussian package.

**Table 4:** The collision diameter C.D; mean free path I (in meter), mass (g/mol) viscosity (Nsm<sup>-2</sup>) and volume (m<sup>3</sup>/mol) for the most stable isomer.

Sys.	C.D.	I	M	V'	Vis	Vol.
Pd1	4.28E-10	5.06E-08	0.1064	244.20	1.76E-05	2.37E-05
Pd2	4.99E-10	3.72E-08	0.2118	172.68	1.83E-05	5.63E-05
Pd3	5.74E-10	2.81E-08	0.3177	140.99	1.69E-05	7.7E-05
Pd4	6.17E-10	2.44E-08	0.4236	122.10	1.69E-05	9.61E-05
Pd5	6.76E-10	2.03E-08	0.5295	109.21	1.58E-05	8.6E-05
Pd6	6.79E-10	2.01E-08	0.6354	99.69	1.71E-05	9.42E-05

**Fig 4:** The collision diameter as a function of cluster size.**Fig 5:** The viscosity as a function of cluster size.

## Conclusion

The study investigated the properties included binding energy, chemical hardness, electronegativity, polarity, electron affinity and ionization potential of the palladium clusters. The study declares that Pd<sub>4</sub> as the electronically most stable among the clusters under study. Chemical reactivity parameters such as EA, IP and electronegativity suggest that larger clusters have stronger tendency to accept electrons. The trend of reactivity parameters mimics the result of the change in energy upon the addition of atom and stability function. All the Palladium clusters are found to be magnetic. The calculation showed that the binding energies increase whereas the bond energies decrease with the cluster size. Chemical hardness is also seen to decrease with cluster size, which suggests that large clusters are more prone to changes in their electronic structure. The results suggest that global hardness is the highest of Pd<sub>4</sub> and directly proportional to H-L gap (eV). Magnetic energy differences have been found to be small, such that there is an appreciable probability of finding excited magnetic isomers even at ambient temperatures. Chemical parameters such as EA, EN suggest that larger clusters have stronger tendency to accept electrons. The binding energy and dissociation energy increase with the cluster size, while the dissociation energy decreases for Pd<sub>5</sub>, possibly due to the geometrical shape and the Jahn-Teller effects.

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