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Research Paper

Density Functional Theory Investigation for H_2-Silver Interactions

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Abstract: *Density functional theory has been carried out for H_2 molecule, Ag_n and Ag_nH_2 nanoclusters, (n=4, 5, 6, 7). Optimization plus frequency, B3LYP, 3-21G basis sets has been investigated at the ground state level. Point group symmetry determined for H_2 molecule, Ag_n and Ag_nH_2 nanoclusters. Binding energy has been computed for Ag_nH_2 nanoclusters, Ag_7H_2 nanocluster has lower binding energy (0.0329 eV) and this point out that Ag_7H_2 nanocluster is more binding than the other Ag_nH_2 nanoclusters . Hardness and Softness has been calculated for H_2 molecule, Ag_n and Ag_nH_2 nanoclusters. Hardness Softness Acid Base (HSAB principle) has been applied to know behaviour of H_2 molecule, Ag_n and Ag_nH_2 nanoclusters. Electronegativity and electrophilicity have been computed for H_2 molecule, Ag_n and Ag_nH_2 nanoclusters. Dipole moment has been evaluated for H_2 molecule, Ag_n and Ag_nH_2 nanoclusters. Also average polarizability has been calculated for H_2 molecule, Ag_n and Ag_nH_2 nanoclusters. Finally density of state (DOS) has been investigated for Ag_n and Ag_nH_2 nanoclusters, Ag_5 posses DOS raises as compared with other pure silver nanoclusters, but Ag_5H_2 has DOS rises as compared with all other nanoclusters. All calculations have been investigated by using Gaussian 09 software package.*

Keywords: DFT, B3LYP, HSAB, Binding energy, Symmetry.

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1. Introduction:

1.1. Density Functional Theory (DFT):

The quantum mechanics wave function contains all the informations about a given system [1]. For the case of a simple 2-D square potential or even a hydrogen atom, Schrodinger equation can be solved in order to get the wave function of the system. Then the allowed energy states of the system can be determined [2]. Evidently, some approximations must involved to render a solved problem albeit tricky. The simplest definition of DFT is a method which is used to obtain an approximate solution to Schrodinger equation of many body system [3]. DFT is represented by computational codes in Gaussian 09 program, and it is used in applications to investigate the structural, electronic and some physical properties to the molecules and materials, such as binding energies of the molecules in chemistry and band structures of solids in physics, also in other areas [4]. Thus DFT is one of the most popular methods of quantum mechanics [5]. DFT owes its versatility to the generality of its fundamental concepts and its flexibility and generality [6]. DFT is completely based on a rigorous conceptual structure. DFT aims to calculate the electronic ground state energy of a system of N electrons only through its density without prior knowledge of the wave function of the system [7].

1.2. Basis Sets:

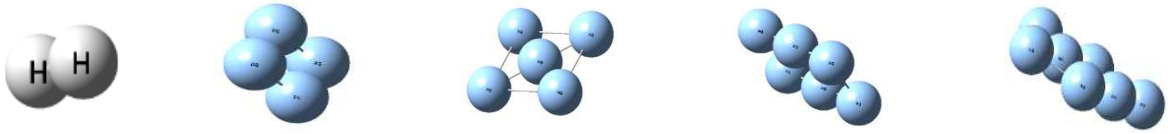
In general a basis sets are collections of vectors which spans a space in which a problem is solved [8]. In quantum chemistry the basis set usually refers to the sets of (non-orthogonal) one particle functions which is used to build molecular orbitals [9]. Molecular orbitals are built from atomic orbitals. The orbital has a one electron function. Atomic orbitals are represented by atom centered Gaussian in most quantum chemistry programs [10]. In physics the plane wave basis sets have been used. The basis set 3-21G refers to three Gaussian type orbitals for inner shell, two Gaussian type orbitals for inner valence, and one Gaussian type orbital for outer valence [11]. B3LYP means Becke three parameter Lee-Yang-Parr, and this method has been named Hyprid method to get the approximations of DFT [12].

1.3. Geometry Optimization:

Geometry optimization is an attempt to find a configuration for the minimum energy to the molecule [13]. Geometry optimization goals are to find the local minimum structure, the global minimum structure and the transition state structure [14]. Geometry optimization investigates the wave function and the energy at stationary geometry and then it searches on a lower energy [15]. Finally the force on each atom will equal to zero, in other words the force resultant equal to zero, and this means a stationary point is found [16]. In the geometry optimization procedure the optimized coordinates, the bond lengths, the bond angles and dihedral angles are investigated [17].

2. Molecular Structure:

The molecular structure for hydrogen molecule, pure silver nanoclusters and Ag_nH_2 nanoclusters has been investigated by using optimization plus frequency at the ground state level. B3LYP, 3-21G basis sets have been implemented for optimization procedure. Density functional theory has been applied to optimize hydrogen molecule, pure silver nanoclusters and Ag_nH_2 nanoclusters with Gaussian 09 software program.



H_2 Ag_4 Ag_5 Ag_6 Ag_7

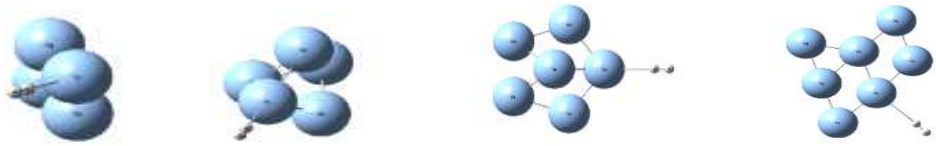


Figure 1: The molecular structure for H_2 Molecule, Ag_n and Ag_nH_2 nanoclusters

3. Calculations:

3.1. Point Group Symmetry:

Some geometrical figures look more symmetry than the others, For example the sphere is more symmetry than the cube because the sphere looks the same after rotation through any angle about the diameter [18]. The cube looks the same only if it is rotated through certain angles about specific axes, such as 90^o, 180^o, 270^o about an axis passing through the centers of any of its opposite faces, or by 120^o or 240^o about an axis passing through any of the opposite corners. Symmetry operations include rotations, reflections and inversions. There is corresponding symmetry element for each symmetry operation [19], which is point, line or plane with respect to which the symmetry operation is performed. Molecules symmetry can be classified with respect to the symmetry elements to the operations that leave at least one common point unchanged. Symmetry study is very important because it gives general conclusions about the molecule properties without calculations, for example, dipole moment, degenerate states [20].

Table 1: Point group symmetry for H_2 Molecule, Ag_n and Ag_nH_2 nanoclusters

System	Symmetry
H_2	$D_{\infty h}/C_1$
Ag_4	D_{2h}/C_1
Ag_5	D_{2h}/C_1
Ag_6	D_{2h}/C_1
Ag_7	C_s/C_1
Ag_4H_2	C_s/C_1
Ag_5H_2	C_1
Ag_6H_2	C_1
Ag_7H_2	C_s/C_1

3.2. Binding Energy:

The binding energy of a cluster estimates how strongly the atoms are bound to the cluster during its formation. The binding energy for a cluster X_nY_m is given by the equation [21]:

$$E_B = nE(X) + mE(Y) - E(X_nY_m) \quad \text{.....(1)}$$

E_B: Binding Energy

$E(X)$: Energy of the molecule X

$E(Y)$: Energy of the molecule Y

$E(X_nY_m)$: Energy of the molecule X_nY_m

n: Number of atoms for the molecule X

m: Number of atoms for the molecule Y.

Table 2: Binding energy for Ag_nH_2 nanoclusters

System	Binding Energy (eV)
Ag_4H_2	0.0616
Ag_5H_2	1.6262
Ag_6H_2	1.4897
Ag_7H_2	0.0329

3.3. Hardness Softness Acid Base (HSAB Principle):

Chemical hardness fundamentally determine the resistance toward the deformation or polarization of electron cloud of the atoms, ions or molecules [22]. Chemical hardness is one of the extremely useful conceptual constructs of chemistry and physics. Based on this concept, Lewis acids and bases are classified as hard and soft, and this principle is named Hardness Softness Acid Base (HSAB Principle), And this principle was put by Pearson [23].

Soft Base: Donor atom is of high polarizibility, low electronegativity, easily oxided and associated with empty low-lying orbitals.

Hard Base: Donor atom is of low polarizability, high electronegativity easily oxided and associated with empty orbitals of high energy and hence inaccessible.

Soft Acid: The acceptor atom is of low positive charge, large size, and has several easily excited outer electrons, polarizable.

Hard Acid: Acceptor atom is of high positive charge, small size, and does not have easily excited outer electrons, not polarizable [24].

In DFT some chemical properties are identified as response functions of the electronic energy (E) with respect to number of electrons, chemical hardness is given by:

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v \quad \text{..... (2)}$$

Chemical hardness can be calculated directly from the relation [25]:

$$\eta = \frac{I.P - E.A}{2} \quad \text{.....(3)}$$

η: Hardness

$I.P$: Ionization potential

$E.A$: Electron affinity

Softness (σ) can be calculated from the equation:

$$\sigma = \frac{1}{2\eta} \quad \text{..... (4)}$$

And according to Koopman theorem

$$I.P = -E_{HOMO} \quad \text{..... (5)}$$
$$E.A = -E_{LUMO} \quad \text{..... (6)}$$

Table 3: E_{HOMO}, E_{LUMO}, Hardness and softness for H_2 molecule, Ag_n and Ag_nH_2 nanoclusters

system	E_{HOMO}(eV)	E_{LUMO}(eV)	Hardness	Softness
H_2	-11.6652	3.1822	7.4237	0.0674
Ag_4	-4.1044	-2.6312	0.7366	0.6788
Ag_5	-4.0478	-2.2222	0.9128	0.5478
Ag_6	-4.0573	-2.5207	0.7683	0.6508
Ag_7	-3.8293	-2.1221	0.8536	0.5858
Ag_4H_2	-4.0706	-2.6157	0.7275	0.6873
Ag_5H_2	-3.8483	-2.9017	0.4733	1.0564
Ag_6H_2	-4.6271	-2.2508	1.1881	0.4208
Ag_7H_2	-3.8309	-2.1012	0.8649	0.5781

3.4. Electronegativity and Electrophilicity:

Electronegativity stands for measure of the tendency of an atom to attract a bonding pair of electrons. It is given by the relation [26]:

$$X = \frac{I.P + E.A}{2} \quad \text{..... (7)}$$

An electrophile (literarly electron lover) is a reagent attracted to electrons. In general electrophilies are positively charged species that are attracted to an electron rich center, it participates in chemical reactions by accepting an electron pair in order to bond to a nucleophile. Electrophilicity has been calculated for H_2 molecule, Ag_n, Ag_nH_2 clusters by using the equation [27]:

$$\omega = \frac{X^2}{2\eta} \quad \text{..... (8)}$$

ω: Electrophilicity

X: Electronegativity

Table 4: Electronegativity and Electrophilicity for H_2 molecule, Ag_n, Ag_nH_2 nanoclusters

System	Electronegativity	Electrophilicity
H_2	4.2415	1.2117
Ag_4	3.3678	7.6991
Ag_5	3.1350	5.3838
Ag_6	3.2890	7.0402
Ag_7	2.9757	5.1868
Ag_4H_2	3.3432	7.6820

Ag_5H_2	3.3750	12.0327
Ag_6H_2	3.4389	4.9769
Ag_7H_2	2.9660	5.0859

3.5. Dipole Moment:

Dipole moment stands for the product of charge by displacement, Dipole moment change with change of any direction of displacement(r). It is given by the equation:

$$P = q * r \quad \text{..... (9)}$$

P: Dipole moment

q: Charge

r: Displacement.[28]

Table 5: Dipole moment for H_2 molecule, Ag_n, Ag_nH_2 nanoclusters

System	**Dipole Moment (Debye)**
H_2	0.0000
Ag_4	0.0000
Ag_5	0.0000
Ag_6	0.0000
Ag_7	0.1409
Ag_4H_2	0.3707
Ag_5H_2	0.7504
Ag_6H_2	0.5943
Ag_7H_2	0.1102

3.6. Polarizability:

Polarizability is the capability of a molecule to be polarized. Polarizabilities signify the dynamical response of a bound system to external fields and supply insight into a molecule's internal structure. The electronic polarizability is defined as the ratio of the induced dipole moment of an atom to the electric field that produce this dipole moment.

$$\alpha = \frac{P}{E} \quad \text{..... (10)}$$

α: represents the polarizability

P: represents the dipole moment

E: represents the electric field

The mean polarizability $< \alpha >$ is evaluated by using the equation:

$$< \alpha > = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \ldots\ldots\ldots (11)$$

Where $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$ are the eigen values of the polarizability tensor [29]

Table 6: Polarizability for H_2 molecule, Ag_n, Ag_nH_2 nanoclusters

System	α_{xx}	α_{yy}	α_{zz}	$<\alpha>$
H_2	0.000	0.000	0.000	0.000
Ag_4	134.150	181.659	357.437	224.415
Ag_5	167.477	375.880	419.384	320.913
Ag_6	180.163	527.941	368.195	358.766
Ag_7	447.959	583.671	199.004	410.211
Ag_4H_2	360.105	180.589	137.447	226.047
Ag_5H_2	364.409	286.555	195.531	282.165
Ag_6H_2	389.821	375.686	184.465	316.657
Ag_7H_2	454.642	589.639	198.752	414.344

3.7. Density of States (DOS):

Density of state stands for number of states per interval of energy at each energy level that are available to be occupied. Density of state can be computed for electrons, photons and phonons according to quantum mechanics. In general density of states influenced by the topological properties of the system [30].

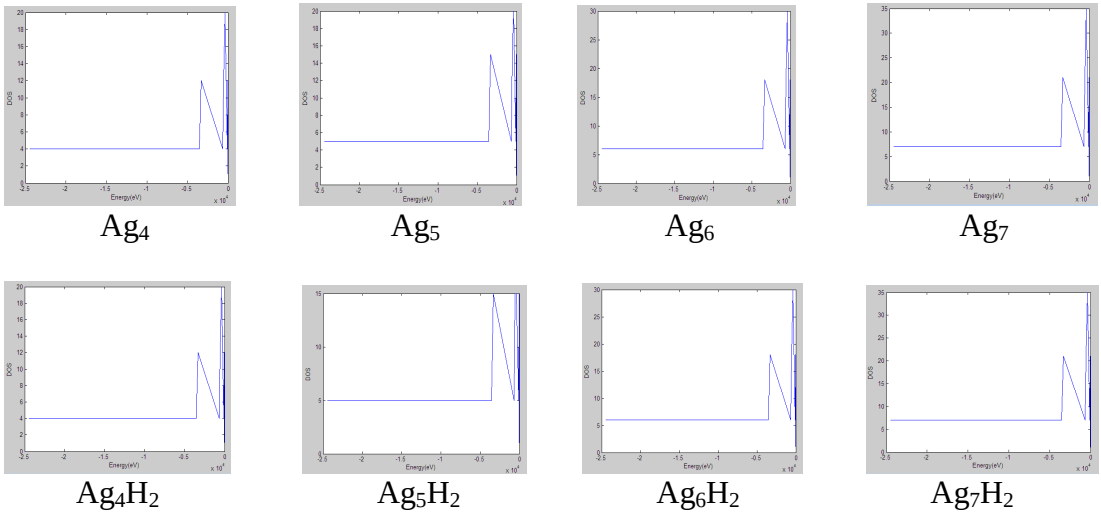


Figure 2: Density of states for Ag_n, Ag_nH_2 nanoclusters

4. Results and Discussion:

From table (1) it has been seen, H_2 molecule has $D_{\infty h}/C_1$ point group symmetry, H_2 molecule has D_{∞} symmetry because it is a linear molecule, the symbol *h* refers to that H_2 molecule posses horizontal mirror plane, in general all homonuclear diatomic molecules belong to the $D_{\infty h}$ group, and the operation C_1 means H_2 molecule rotates by 360^o because this operation represents C_n symmetry and in this kind of symmetry the rotation obtain through $\frac{360^o}{n}$ angle. thus, the rotation repeat the same molecule. The clusters Ag_4, Ag_5, Ag_6 nanoclusters have the symmetry D_{2h}/C_1, the symbol D_2 means these nanoclusters have two fold principal axis C_n and two fold axes perpendicular to C_n, the symbol *h* means these nanoclusters have horizontal mirror plane, and because of presence of these symmetry

elements it is necessary to have two vertical planes at angles $\frac{360^o}{2n}$ to one another, also these nanoclusters rotate by 360° because the operation C_1. The nanoclusters Ag_7, Ag_4H_2, Ag_7H_2 have C_s/C_1 point group symmetry, the symbol C_s refers to that these nanoclusters consists of two elements, identity and mirror plane, also these nanoclusters rotate by 360° because the operation C_1. The nanoclusters Ag_5H_2, Ag_6H_2 have the symmetry C_1 and this means these nanoclusters rotate through 360° which is equivalent to the identity, this results is in good agreement with the reference [31].

Table (2) represents the binding energy for Ag_nH_2 nanoclusters, it has been showed that the binding energy affected randomly by the size of the nanocluster, this means the binding energy influence randomly with the number of atoms for the nanocluster, for example, one can note from this table Ag_7H_2 has lower binding energy(0.0329 eV) and this point out that Ag_7H_2 nanocluster is more binding than the other Ag_nH_2 nanoclusters because this cluster loses less energy to enter binding state , but Ag_5H_2 cluster has higher binding energy(1.6262 eV) and this refers to that nanocluster is less binding than the other Ag_nH_2 nanoclusters because this cluster loses more energy than other Ag_nH_2 nanoclusters to enter binding state. Binding energy is very important property because it keeps existence of the system. the difference in values of binding energy because of the entanglement, and this results are in general agreement with modern physics science[32].

Table (3) stands for E_{HOMO} , E_{LUMO}, Hardness and softness for H_2 molecule, Ag_n, Ag_nH_2 nanoclusters, H_2 molecule has ($E_{HOMO} = -0.42871\ eV$) and this means H_2 easily release the electrons for unoccupied orbitals as compared with Ag_n Ag_nH_2 nanoclusters, so H_2 molecule is higher reactivity than Ag_n nanoclusters according to HOMO Energies, for example HOMO energy for Ag_4 nanocluster equal to(-0.15084*eV*), thus the HOMO energy for H_2 is greater than HOMO energy for Ag_4 nanocluster, also it is clearly from the same table H_2 is higher HOMO energy than all Ag_n nanoclusters, thus H_2 stands for acceptor, but silver nanoclusters represents donors. It has been appear from this table hydrogen molecule has higher hardness than all pure silver nanoclusters, thus hydrogen molecule represents hard acid as compared with all slilver nanoclusters(silver nanoclusters stands for soft bases). For example, Ag_4 nanocluster has higher softness than H_2 molecule, thus Ag_4 nanocluster has been considered soft base as compared with H_2 molecule (H_2 molecule represents hard acid). Also one can see from this table Ag_4 nanocluster has greater softness than Ag_5, Ag_6, Ag_7 nanoclusters and this principle has been used in reference [33].

Table (4) gives the values of electronegativity and electrophilicity for H_2, Ag_n, Ag_nH_2 nanoclusters, the electronegativity of silver nanoclusters is smaller than the electronegativity of H_2 molecule, thus the silver atom adsorbed on hydrogen atoms, so hydrogen molecule has been considered acceptor and silver nanoclusters stand for donors, and this result confirm the results in table(3), also the atomic size of hydrogen is less than the atomic size of silver, thus silver will adsorbs on hydrogen because the electronegativity increase as the atomic size decrease. Also in this table, it has been observed that Ag_4 nanocluster has higher electrophilicity than the other silver nanoclusters because electrophilicity increase as the elctronegativity increase, also it has been showed in this table that Ag_7 has lower electrophilicity than the other silver nanoclusters because the electrophilicity decrease as the electronegativity decrease, this results agree with basics of physical chemistry [34].

Table (5) stands for the dipole moment for H_2 molecule, Ag_n and Ag_nH_2 nanoclusters, H_2 molecule, Ag_4, Ag_5, Ag_6 nanoclusters have no dipole moment, Ag_7 nanocluster has small dipole moment because all of these are homonuclear, and these nanoclusters have no dipole moment changes during the rotation, this means the rotational spectrum does not appear, and these nanoclusters have no interact with the electromagnetic radiation. It has been seen Ag_5H_2 has dipole moment (0.7504 Debye) because this nanocluster is hetronuclear, so this cluster has a rotation and the dipole moment

interact with the electric field of the electromagnetic radiation, this results are in general agreement with the spectra science [35].

Table (6) represents the polarizability for H_2 molecule, Ag_n and Ag_nH_2 nanoclusters, it has been appeared that the polarizability more influenced by the number of atoms, for example, the average polarizability of Ag_4 nanocluster equal to (224.415 a.u), but A_7 nanocluster has the polarizability (410.211 a.u), and this explain the highest reactivity for Ag_7 nanocluster as compared with Ag_4 nanocluster, because the highest reactivity results from the highest polarizability. It has been showed that Ag_7H_2 nanocluster has the polarizability (414.344 a.u) and this value of polarizability is greater than the polarizability for all other nanoclusters because Ag_7H_2 nanocluster has the largest number of atoms as compared with the other nanoclusters, so Ag_7H_2 nanocluster has the highest reactivity among all these nanoclusters. Generally the polarizability increase as the the size occupied with electrons increase. It is very important to know that the polarizability gives information about the molecular structure, this consequences are in general agreement with [36].

Figure (2) stands for the density of states for Ag_n, Ag_nH_2 nanoclusters, it has been resulted many states to be occupied at the high density of state in any certain energy level. If density of state for undistributed system is zero, it is likely local density of state is not zero (LDOS is not zero) because of existence local potential at that position, LDOS results from local vibrations which results from in the origin of the system, in general it has been appear that LDOS has a value until when DOS is not found and this means the local potential causes the LDOS, it has been known when DOS equal to zero, there is no energy level available to be occupied. DOS influenced by the energy of electron, DOS increase as the electron energy increase, and many states become to be available occupied, another factors affect on density of state, and this factors are topological properties. It is very important in solid state physics to study density of state, because this gives the number of states which is to be occupied. One can observe clearly from this figure density of state become rise in Ag_5 and Ag_5H_2 nanoclusters, and this means there are many orbitals that available to be occupied, Ag_5H_2 has more states than Ag_5 nanocluster, this results is in good agreement with solid state physics [37].

Conclusion:

Hydrogen molecule has $D_{\infty h}/C_1$ symmetry, The nanoclusters Ag_4, Ag_5, Ag_6 have the symmetry D_{2h}/C_1, the nanoclusters Ag_7, Ag_4H_2, Ag_7H_2 posses C_s/C_1 point group symmetry, and Ag_5H_2, Ag_6H_2 have the symmetry C_1. It has been found that Ag_7H_2 nanocluster has the higher binding energy (0.0329eV) among Ag_nH_2 nanoclusters, so this nanocluster loses less energy to enter binding state, but Ag_5H_2 posses the lower binding energy (1.6262eV) among Ag_nH_2 nanoclusters. Hydrogen molecule release electrons to the unoccupied orbitals, H_2 stands for the acceptor, Ag_n nanoclusters represents the donors. Silver atoms adsorped on hydrogen, thus H_2 is higher electronegativity than silver. The nanocluster Ag_4 has higher value electrophilicity than other silver nanoclusters,but the nanocluster Ag_7 has lower electrophilicity value than other silver nanoclusters. Ag_nH_2 nanoclusters have dipole moment interact with the electromagnetic rays. The nanocluster Ag_7 is greater polarizability (410.211a.u) than other silver nanoclusters, so this nanocluster is more reactivity than other silver nanoclusters. There is many unoccupied states that available to be occupied, the topological properties affect on density of state.

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