Chapter 1

Result and Discussion

1.1 General Consideration

This section includes result and discussion of the present work. We have carried out the first-principles calculations to study the stability of the Neutral and Singly charged cationic argon atom and its clusters (Ar_n and Ar_n⁺ upto a size of n = 7) in the different levels of approximations. The calculations have been carried out for the search of structures using Gaussian 03W set of program. The different basis sets used for the computation are 3-21G, 3-21G^{*}, 6-31G, 6-31G^{*}, 6-311G, 6-311G^{*}, 6-311++G(d,p) and 6-311++G(3df,3pd). The consistency of the result has been tested by their convergence with respect to the use of basis sets of increasing size and complexity. We have also used chem Craft and Gauss view molecular builder for structure formation and to build z-matrix and Multiwfn to analyse electrostatic Potential Surfaces.

1.2 Result and Discussion

In this present work, the first-principles calculations have been performed:

- to estimate the total ground state energy and the equilibrium geometry of the neutral argon atom (Ar) and its clusters (Ar_n) .
- to estimate the total ground state energy and the equilibrium geometry of the singly charged argon atom (Ar⁺) and its clusters (Ar⁺_n).
- to estimate the binding energy for (Ar_n) and (Ar_n^+) clusters.
- to analyse the Electro Static Potential (ESP) of Ar_n^+ using multiwfn (A Multifunctional Wave function Analyser).

We have estimated the Binding energy of the cluster of argon atom by using the following relation :

$$\delta E_{BE} = E_{cluster,(N-1)} + E_1 - E_{cluster,N} \tag{1.1}$$

where, $E_{cluster,N}$ represents the total energy of a cluster of N atoms including the reference atom, $E_{cluster,(N-1)}$ represents the total energy of a cluster of (N-1) atoms with the reference atom removed. E_1 is the energy of the reference atom. The above equation may be put in a simple form as : Binding Energy = Energy of complex - Energy of monomers

1.3 Total Ground State Energy of Argon Atom

1.3.1 Total Ground State Energy of Neutral Argon Atom (Ar)

We have estimated the ground state energy of Ar atom in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets 3-21G, 3-21G^{*}, 6- $31G, 6-31G^*, 6-311G, 6-311G^*, 6-311++G(d,p)$ and 6-311++G(3df,3pd). Polarization and diffuse functions are included for the detailed study of the argon atom. The Gaussian outputs of the ground state energy of Ar atom in the MP2, QCISD and DFT(M05-2X) levels of approximations has been presented in Appendix Table A.1 From the Table A.1, it is found that the ground state energy of Ar atom are basis set dependent. i.e., different values of energy corresponding the different basis sets and the energy of atom gets lowered as the size or complexity of the basis set increases. The energy estimated using the polarised basis set is lower than the corresponding energy estimated by using the unpolarised basis set. It is also seen that, among the MP2, QCISD and DFT(M05-2X) levels of approximations, the energy estimated in the DFT (M05-2X) level of approximation is lower than the corresponding energy estimated in the QCISD level of approximation and which in turn, is lower than the MP2 level of approximation i.e., $E_{MP2} > E_{OCISD} >$ $E_{DFT(M05-2X)}$ As the size or complexity of the basis set increases, the energy gets lowered. Here we have assumed that the basis sets 3-21G, 3-21G^{*}, 6-31G, 6-31G^{*}, 6-311G, $6-311G^*$, 6-311++G(d,p) and 6-311++G(3df,3pd) are in ascending order of size and complexity. The energy of the Ar atom in the MP2, QCISD and DFT(M05-2X) levels of approximations corresponding to the basis set 3-21G are -527.01155 a.u., -527.02975 a.u., -527.52690 a.u. respectively. As we move from the basis set 3-21G to the corresponding polarized basis set 3-21G^{*}, MP2, QCISD and DFT(M05-2X) values of energy is lowered by 0.2 a.u., 0.2 a.u., and 0.1 a.u. respectively. The energy estimated by using the basis set $6-31G^*$ is lower than the corresponding energy estimated by using the basis set 6-31G by 0.10 a.u., 0.11 a.u. and 0.004 a.u. in the MP2, QCISD and DFT(M05-2X) levels of approximations respectively, indicating the polarisation effect in lowering the energy of the system. It is also seen that inclusion of (3df)-type polarisation function to the basis set 6-311G, the values of energy gets lowered. The lowered values of energy in going from basis set 6-311G^{*} to 6-311G(3df,3pd) in MP2, QCISD and DFT(M05-2X) levels of approximations are 0.06 a.u., 0.06 a.u. and 0.00 a.u. respectively. From the Table A.1, it is also seen that the energy of Ar atom does not change in moving from the basis set 6-311G to the basis set 6-311G^{*} in the DFT(M05-2X) level of approximation. Furthermore, the lowest value of energy is estimated in the DFT(M05-2X) level of approximation using M05-2X functional in the basis set 6-311++G(3df,3pd) and that value of energy is -527.52690 a.u. The calculations show that DFT(M05-2X) level of approximation using new hybrid functional M05-2X gives more accurate and convergent result on the ground state energy of Ar atom. This basis set convergence of the above mentioned fact is shown in the figure 1.1. In the figure 1.1, $1 \rightarrow 3-21G$,





Figure 1.1: Variation of the total energy of Ar atom with increasing size and complexity of basis sets.

 $2 \rightarrow 3-21G^*$, $3 \rightarrow 6-31G$, $4 \rightarrow 6-31G^*$, $5 \rightarrow 6-311G$, $6 \rightarrow 6-311G^*$, $7 \rightarrow 6-311++G(d,p)$, $8 \rightarrow 6-311++G(3df,3pd)$ represent the corresponding basis sets on x-axis in ascending order of size and complexity. From the figure 1.1, it is seen that the ground state energy estimated for the different basis sets in the DFT(M05-2X) level of approximation is less than the corresponding MP2 and QCISD values.

1.3.2 Total Ground State Energy of Charged Argon Atom (Ar⁺)

We have estimated the ground state energy of Ar^+ atom in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets 3-21G, 3-21G^{*}, 6-31G, 6-31G^{*}, 6-311G^{*} and 6-311++G(3df,3pd). The Gaussian outputs of the

ground state energy of Ar^+ atom in the MP2, QCISD and DFT(M05-2X) levels of approximations has been presented in Appendix Table A.2. From the Table A.2, it is seen that the ground state energy of Ar^+ atom is also basis set dependent. We have studied the cationic argon atom (Ar^+) using the different basis sets and levels of approximations as done in the case of Ar atom. As the size or complexity of the basis set increases, the energy gets lowered. The energy estimated for the basis set 6-31G^{*} is lower than the corresponding energy estimated for the basis set 6-31G by 0.10 a.u., 0.11 a.u. and 0.00 a.u. in the MP2, QCISD and DFT(M05-2X) levels of approximations respectively, indicating the polarisation effect in lowering the energy of the system. It is also seen that, among the MP2, QCISD and DFT(M05-2X) levels of approximations, the energy estimated in the DFT(M05-2X) level of approximation is lower than the corresponding energy estimated in the QCISD level of approximation and which in turn, is lower than the MP2 level of approximation i.e., $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ The calculations show that DFT(M05-2X) level of approximation using new hybrid functional M05-2X gives more accurate and convergent result on the ground state energy of Ar⁺ atom. This basis set convergence of the above mentioned fact is shown in the figure 1.2.



Figure 1.2: Variation of total energy of Ar^+ atom with increasing size and complexity of basis sets.

In the figure 1.2, $1 \rightarrow 3\text{-}21\text{G}$, $2 \rightarrow 3\text{-}21\text{G}^*$, $3 \rightarrow 6\text{-}31\text{G}$, $4 \rightarrow 6\text{-}31\text{G}^*$, $5 \rightarrow 6\text{-}311\text{G}$, $6 \rightarrow 6\text{-}311\text{G}^*, 7 \rightarrow 6\text{-}311\text{+}+\text{G}(3\text{d}\text{f},3\text{p}\text{d})$ represent the corresponding basis sets on x-axis in ascending order of size and complexity. From the figure 1.2, it is seen that the ground state energy estimated for the different basis sets in the DFT(M05-2X) level of approximation is less than the corresponding MP2 and QCISD values.

1.3.3 Comparison between Ar and Ar⁺ atom

From the above discussion, it is found that

- The ground state energies of Ar and Ar⁺ are basis set dependent and basis set convergent.
- $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ holds good for both Ar and Ar⁺ atom.
- The ground state energy of Ar atom is minimum than that of Ar⁺ atom within the limit of basis sets and levels of approximations used.

1.4 The Ground State Energy, Binding Energy and Equilibrium Configuration of Argon Dimer.

1.4.1 The Ground State Energy, Binding Energy and Equilibrium Configuration of the Neutral Argon $Dimer(Ar_2)$

We have estimated the ground state energy and binding energy of Ar_2 dimer in the MP2, QCISD and DFT(M05-2X) levels of the approximations using the basis sets 3-21G, 3- $21G^*$, 6-31G, 6-31G^{*}, 6-311G, 6-311G^{*} and 6-311++G(3df, 3pd). The Gaussian outputs of the ground state energy of Ar_2 dimer in the MP2, QCISD and DFT(M05-2X) levels of approximations has been presented in Appendix Table A.3. From the Table A.3, it is seen that the ground state energy of Ar_2 dimer is basis set dependent. As the size and complexity of the basis set increases, the energy gets lowered. Furthermore, It is also seen that, among the MP2, QCISD and DFT(M05-2X) levels of approximations, the energy estimated in the DFT(M05-2X) level of approximation is lower than the corresponding energy estimated in the QCISD level of approximation and which in turn, is also lower than the MP2 level of approximation i.e., $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ From the Table A.3, it is seen that the ground state energy of Ar_2 dimer estimated for the polarised basis set is lower than the corresponding energy for the unpolarised basis set. The equilibrium configuration of Ar_2 dimer in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd) is shown in the fig 1.3. We have also estimated the bond distance of Ar_2 dimer in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis set mentioned in the present work. The bond distance for Ar_2 dimer in the MP2, QCISD and DFT(M05-2X) levels of approximations has been presented in Table 1.1. From the Table 1.1, it is seen that the MP2 values of the bond distance for Ar_2 dimer has large deviation (up to 29%) from the experimental value of 3.76A. This deviation may be due to the electron correlation effect and hence this effect needs to be considered to account the stability of Ar_2 dimer. Considering the MP2, QCISD and DFT(M05-2X) calculations for the equilibrium configuration of Ar_2 dimer,





Figure 1.3: Equilibrium configuration of Ar_2 dimer in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

	Bond distance (r) in \mathring{A}					
Basis Set	MP2	QCISD	DFT(M05-2X)	EXPT		
3-21G	4.10	4.10	3.5			
3-21G*	3.94	3.98	3.62			
6-31G	4.43	4.43	3.90	3.76^{a}		
6-31G*	4.18	4.21	3.89			
6-311G	4.84	4.81	3.94			
6-311G*	4.36	4.42	3.72			
6-311++G(3df,3pd)	3.78	3.90	3.94			

Table 1.1: The MP2, QCISD and DFT (M052X) values of bond distance(r) for Ar_2 dimer obtained using different basis sets along with the experimental value.

it is seen that MP2 and QCISD values of bond distance (r) estimated with the basis set $6-311G^*$ are larger (nearly 16% and 18%) as compared to the corresponding DFT(M05-2X) values of bond distance estimated with the basis set $6-311G^*$. In this case the deviations are 0.60Å, 0.66Å and 0.04Å respectively from the experimental value 3.76Å. The value of bond distance estimated with the basis set $6-311G^*$ in the DFT(M05-2X) level of approximation is 3.72Å and is nearer to the experimental value 3.76Å. By using the equation (1.1), we have estimated the binding energy of Ar₂ dimer within the limit of our basis set mentioned in the present work. The result of the calculations has been presented in the Table 1.2. Table 1.2 shows that the binding energy estimated in the different levels of approximations are all positive. The experimental value of binding energy for Ar₂ dimer is about 0.242 kcal/mol at an equilibrium distance of 3.76Å. [?]. The values of binding energy for Ar_2 dimer in the MP2, QCISD and DFT(M05-2X) levels of approximations corresponding to the basis set 3-21G are 0.038 kcal/mol, 0.038 kcal/mol and 0.496 kcal/mol respectively. These values indicate the large deviation from the experimental value. There is no linear variation in the binding energy values in the different levels of approximations using the different basis sets. The large deviations are for MP2 and QCISD levels of approximations. The binding energy for Ar_2 dimer in the MP2, QCISD and DFT(M05-2X) levels of approximations corresponding to the basis set 6-311++G(3df,3pd) are 0.301 kcal/mol, 0.207 kcal/mol and 0.276 kcal/mol respectively.

	Bindir	ng energy (δE_{BE})	in kcal/mol
Basis Set	MP2	DFT(M05-2X)	EXPT
3-21G	0.038	0.490	
3-21G*	0.069	0.420	
6-31G	0.019	0.276	
6-31G*	0.063	0.276	0.242^{b}
6-311G	0.013	0.251	
6-311G*	0.031	0.238	
6-311++G(3df,3pd)	0.207	0.276	

Table 1.2: The binding energy for Ar_2 dimer in the MP2 and DFT(M05-2X) levels of approximations for the different basis sets

These values are nearer to the experimental value. The value of binding energy in the DFT(M05-2X) level of approximation using the basis 6-311G^{*} is 0.238 kcal/mol which is the nearest value to the experimental value 0.242 kcal/mol. The values of binding energy in the DFT(M05-2X) level of approximation using the basis sets 6-31G, 6-31G^{*} and 6-311++G(3df,3pd) are equal and is 0.276 kcal/mol. The Table 1.2 clearly shows that there is some polarisation effect in the different levels of approximations for the different basis sets. The above discussion clearly includes the basis set dependency of binding energy.

The Ground State Energy, Binding Energy and Equilibrium Configuration of the Charged Argon Dimer (Ar_2^+)

We have estimated the ground state energy and binding energy of Ar_2^+ dimer in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis sets 3-21G, 3-21G*, $6-31G, 6-31G^*, 6-311G, 6-311G^*$ and 6-311++G(3df, 3pd). The Gaussian outputs of the ground state energy for Ar_2^+ dimer in the MP2, QCISD and DFT(M05-2X) levels of approximations has been presented in Appendix Table A.4. From the Table A.4, it is seen that the ground state energy for Ar_2^+ dimer is basis set dependent. As the size and complexity of the basis set increases, the energy gets lowered. Furthermore, it is also seen that among the MP2, QCISD and DFT(M05-2X) levels of approximations, the energy estimated in the DFT(M05-2X) level of approximation is lower than the corresponding energy estimated in the QCISD level of approximation and which in turn, is also lower than the MP2 level of approximation i.e., $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$. From the Table A.4, it is seen that the ground state energy for Ar_2^+ dimer estimated for the polarised basis set is lower than the corresponding energy value for unpolarised basis set. The equilibrium configuration of Ar_2^+ dimer in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd) is shown in figure 1.4. We have also estimated the bond distance for Ar_2^+ dimer in the MP2, QCISD and DFT(M05-2X) levels



Figure 1.4: Equilibrium configuration of Ar_2^+ dimer in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd)

of approximations using the basis set mentioned in the present work. The bond distance for Ar_2^+ dimer in the MP2, QCISD and DFT(M05-2X) levels of approximations has been presented in the Table 1.3. c- Table 1.3 shows the variation of bond distances for Ar_2^+

Table 1.3: The MP2, QCISD and DFT(M05-2X) values of bond distance(r) for Ar_2^+ dimer obtained using the different basis sets along with the experimental value.

	Bond distance (r)in Å				
Basis Set	MP2	QCISD	DFT(M05-2X)	EXPT	
3-21G	2.60	2.60	2.58		
3-21G*	2.52	2.52	2.53		
6-31G	2.62	2.62	2.60	2.32^{c}	
6-31G*	2.52	2.52	2.52		
6-311G	2.61	2.62	2.59		
6-311G*	2.48	2.49	2.51		
6-311++G(3df,3pd)	2.42	2.51	2.46		

dimer in the different levels of approximations using the different basis sets mentioned in the present work. The experimental value of bond distance for Ar_2^+ dimer is 2.32Å. Table 1.3 shows equal bond distance value in the different levels of approximations. The largest value of bond distance(r) is found to be 2.62Å in the MP2 and QCISD levels of approximations using the basis sets 6-31G and 6-311G respectively. This deviation is about 13% to the experimental value 2.32Å. From the Table 1.3, it is seen that the values of bond distances for polarised basis sets are lower than that of unpolarised basis sets. This relates the properties of bond distance with the polarisation functions. Though the values of bond distances are close to the experimental value but still, they deviate from the experimental value. Inclusion of the diffuse functions to the basis set lowers the value of bond distance which is observed for the basis set 6-311++G(3df,3pd). By using the equation (1.1), we have estimated the binding energy for Ar_2^+ dimer within the limit of our basis sets mentioned in the present work. The results of the calculation has been presented in the Table 1.4 d- e- Table 1.4 shows that the binding energy estimated in the different levels of approximations are all positive value. Hence there is no negative values

	Bin	Binding energy (δE_{BE}) in kcal/				
Basis Set	MP2	QCISD	DFT(M05-2X)	EXPT		
3-21G	22.301	22.797	38.171			
3-21G*	26.010	24.303	37.855			
6-31G	19.032	20.074	33.734	30.318^d		
6-31G*	24.002	22.596	35.705	30.000^{e}		
6-311G	18.125	18.881	32.197			
6-311G*	23.757	22.038	34.601			
6-311++G(3df,3pd)	29.631	26.976	38.140]		

Table 1.4: The binding energy for Ar_2^+ dimer in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets

of binding energy and exists a strong bonding in Ar_2^+ dimer. The experimental value of binding energy for Ar_2^+ dimer is about 30.318 kcal/mol at an equilibrium distance of 2.32Å. citeOT. The values of binding energy for Ar_2^+ dimer in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis set 3-21G are 22.301 kcal/mol, 22.797 kcal/mol and 38.171 kcal/mol respectively. These values are far more than that of experimental value. The MP2 and QCISD levels values of binding energy for the basis set 6-311++G(3df,3pd) are 29.631 kcal/mol and 26.976 kcal/mol respectively which are nearer to the experimental value 30.318 kcal/mol. There is no linear variation in the binding energy values in the different levels of approximations using the different basis sets. The value of binding energy in the DFT(M05-2X) level of approximation using the basis set 6-311G is 32.197 kcal/mol which accounts the deviation of about 6% with the experimental value. Table 1.4 clearly shows the effect of polarisation function to the binding energy value in the different levels of approximations for the different basis sets. The above discussion clearly includes the basis set dependency of binding energy.

1.4.2 Electrostatic Potential

Table 1.5: Electrostatic potential of Ar_2^+ dimer in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

0	(/ 1 /
Location	ESP(max) kcal/mol	ESP(min) kcal/mol
8/10	153.815	134.660

The Table 1.5 shows the maximum and minimum values of the electric potential around the given structure. The position of maximum and minimum predicts the sites of the molecule at which they are most likely to react. The above figure 1.5 shows a static distribution of electronic charge around a rigid nuclear framework. Minimum 10



Figure 1.5: Molecular structure, surface minima and maxima of Ar_2^+ dimer in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

(134.660 kcal/mol) is global minimum on the surface arising from negatively charged argon atom. Maximum 8 (153.815 kcal/mol) is global maximum on the surface arising from the positively charged argon atom. Here, multiwfn shows 22 maxima and 43 minima around the molecular structure which are local minima and local maxima. These two position of maximum (8) and minimum (10) are the favourable sites for the reaction to another atom.

1.4.3 Comparison of Ar_2 and Ar_2^+ dimer.

From the above discussion, we found that

- The ground state energies of Ar_2 and Ar_2^+ are basis set dependent and basis set convergent.
- $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ holds good for both Ar₂ and Ar₂⁺ dimer.
- The ground state energy of Ar_2 dimer is minimum than that of Ar_2^+ dimer within the limit of the basis sets and levels of approximations used.
- The equilibrium bond distance for Ar_2 is 3.76Å whereas that for Ar_2^+ is 2.32Å.
- Ar_2^+ binding energy values are larger than Ar_2 binding energy values. Hence Ar_2^+ dimer is more stable than Ar_2 .

1.5 The Ground State Energy, Binding Energy and Equilibrium Configuration of Argon Trimer.

1.5.1 The Ground State Energy, Binding Energy and Equilibrium Configuration of the Neutral Argon Trimer (Ar₃)

We have estimated the ground state energy and binding energy of Ar_3 in the MP2, QCISD and DFT(M052X) levels of approximations using the basis sets 3-21G, $3-21G^*$, 6-31G, $6-31G^*$, 6-311G, $6-311G^*$ and 6-311++G(3df,3pd). The Gaussian outputs of the ground state energy for Ar_3 in the MP2, QCISD and DFT(M05-2X) levels of approximations have been presented in Appendix Table A.5 and Table A.7. The total ground state energy for Ar_3 estimated with the basis sets mentioned in the present work shows similar basis set dependence as the energy values for Ar_2 dimer. Furthermore, E_{MP2} $> E_{QCISD} > E_{DFT(M05-2X)}$ also holds. We have performed the frequency calculations to ensure that the optimized geometry is global minimum with all 3N-6 frequencies being real, N represents the number of atoms in a given cluster. We tested different isomeric structure for Ar_3 and obtained mainly two different structure, linear and triangular geometries with all frequencies being real. Both linear and triangular structures have nearly the same values of energy in the different levels of approximations using the different basis sets. For Ar_3 linear structure, in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis set 3-21G, the values of energy are -1573.14516 a.u., -1573.16091 a.u. and -1575.04085 a.u. respectively. For Ar₃ triangular structure (equilateral triangle), the values of energy in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis set 3-21G are -1573.14522 a.u., -1573.16091 a.u. and-1575.04166 a.u. respectively. Taking only two decimal places, the values of energy are exactly the same for both linear and triangular structures. The minimum value of energy corresponding to the DFT(M05-2X) level of approximation for the basis set 6-311++G(3df,3pd) is -1582.58157 a.u. for Ar₃ linear whereas it is -1582.58204 a.u. for Ar_3 triangular structure. This ensures that different isomers of Ar_3 exist, among them we have taken that clusters having minimum energy. For Ar₃, triangular structure has minimum value of energy for the basis set 6-311++G(3df,3pd) in the DFT(M05-2X) level of approximation. The equilibrium configuration of Ar_3 linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd) is shown in fig1.6. The

Ar3 Ar2 Ar1

Figure 1.6: Equilibrium configuration for Ar_3 linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

Table 1.6: The bond distances and bond angles for Ar_3 linear obtained in the MP2, QCISD and DFT(M05-2X) levels of approximations for the basis set 6-311++G(3df,3pd).

	Level of	Distance (d) in Å		Bond Angle(θ^0)
Basis set	approximation	Ar1-Ar2	Ar2-Ar3	Ar1-Ar2-Ar3
	DFT	3.95	3.95	178.9^{0}
6-31++G(3df,3pd)	MP2	3.80	3.80	170.7^{0}
	QCISD	2.92	2.92	179.4°

bond distances and bond angles for Ar_3 linear in MP2, QCISD and DFT(M05-2X) levels of approximations has been presented in the table 1.6. The equilibrium configuration of Ar_3 triangular structure in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd) is shown in fig 1.5.1.







Figure 1.7: Equilibrium configuration of Ar_3 triangular structure in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

The MP2, QCISD and DFT(M05-2X) values of the bond distances and bond angles for Ar₃ triangular structure obtained using the basis set 6-311++G(3df,3pd) is presented in the Table 1.7 From the Table 1.7, it is seen that the bond distances for Ar₃ linear structure in the DFT(M05-2X) level of approximation for the basis set 6-311++G(3df,3pd)are larger than the corresponding MP2 and QCISD values. But for Ar₃ triangular structure, the values of the bond distances in the DFT(M05-2X) level of approximation for the basis set 6-311++G(3df,3pd) are smaller than the corresponding MP2 and QCISD values. The optimized Ar₃ linear structure is not exactly linear whereas the optimized

Table 1.7: The bond distances and bond angles for Ar_3 triangular structure obtained in the MP2, QCISD and DFT(M05-2X) levels of approximations for the basis set 6-311++G(3df,3pd).

	Level of	Dis	Distance (d) in \mathring{A}		Bond Angle(θ^0)
Basis set	approximation	Ar1-Ar2	Ar2-Ar3	Ar1-Ar3	Ar1-Ar2-Ar3
	DFT	3.73	3.73	3.73	60.0^{0}
6-311++G(3df,3pd)	MP2	3.79	3.79	3.79	60.0^{0}
	QCISD	3.79	3.79	3.79	60.0^{0}

Table 1.8: The binding energy for Ar_3 linear in the MP2 and DFT(M05-2X) levels of approximations for the different basis sets

	Binding	$g energy(\delta E_{BE})$ in kcal/mol
Basis Set	MP2	DFT(M05-2X)
3-21G	0.038	0.552
3-21G*	0.0816	0.427
6-31G	0.0314	0.264
6-31G*	0.0628	0.276
6-311G	0.006	0.251
6-311G*	0.069	0.301
6-311++G(3df,3pd)	0.301	0.270

Ar₃ triangular structure forms an equilateral triangle. Hence the value of bond angle for Ar₃ triangular structure is 60.0° . The large variation in the bond distances and the bond angles is seen for Ar₃ linear structure whereas there is least variation in bond distances for Ar₃ triangular structure and no variation in bond angles. This prefers triangular structure is more stable than the linear one. Further, We have estimated the binding energy for Ar₃ linear using the relation **??** which is presented in the Table1.8. We have also estimated the binding energy value for Ar₃ triangular structure which is presented in the Table 1.9

From the Table 1.8 and Table 1.9, it is seen that all the binding energy values are positive. The binding energy values in the DFT(M05-2X) level of approximation are greater than the corresponding MP2 values. It ensures that there is strong binding between the atoms of Ar₃. The values of binding energy for Ar₃ triangular in the DFT(M05-2X) level using the basis set 3-21G is 1.060 kcal/mol whereas the corresponding MP2 value is 0.075 kcal/mol. For Ar₃ linear, the corresponding DFT(M05-2X) and MP2 binding energy values for the basis set 3-21G are 0.552 kcal/mol and 0.038 kcal/mol respectively. This mentioned the fact that triangular structure is more stable than the linear one.

	Binding energy (δE_{BE}) in kcal/mol			
Basis Set	MP2	DFT(M05-2X)		
3-21G	0.075	1.060		
3-21G*	0.169	0.853		
6-31G	0.149	0.558		
6-31G*	0.119	0.584		
6-311G	0.0125	0.521		
6-311G*	0.069	0.577		
6-311++G(3df,3pd)	0.615	0.565		

Table 1.9: The binding energy for Ar_3 triangular in the MP2 and DFT(M05-2X) levels of approximations for the different basis sets

1.5.2 The Ground State Energy, Binding Energy and Equilibrium Configuration of the Charged Argon Trimer (Ar_3^+)

We have estimated the ground state energy and equilibrium configuration of Ar_3^+ in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis sets 3- $21G, 3-21G^*, 6-31G, 6-31G^*, 6-311G, 6-311G^* and 6-311++G(3df, 3pd)$. The Gaussian outputs of the total ground state energy for Ar_3^+ are presented in Appendix in Table A.6 and Table A.8. The total energy of Ar_3^+ trimer estimated with the basis sets mentioned above shows similar basis set dependence as the energy values of Ar_3 trimer. Furthermore, $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ holds good. We have performed the frequency calculations to ensure that the optimized geometry is global minimum with all 3N-6 frequencies being real. We tested different isomeric structure for Ar_3^+ and finally got linear and triangular geometries with all frequencies being real. This ensures that different isomers of Ar_3^+ exist, among them we have taken that clusters having minimum energy. For Ar_3^+ , linear structure has minimum value of energy. Both linear and triangular structures of Ar_3^+ have nearly the same values of energy in the different levels of approximations using the different basis sets as found in the case of Ar_3 trimer. For Ar_3^+ linear in the MP2, QCISD and DFT(M05-2X) levels of approximations for the basis set 3-21G, the values of energy are -1572.62621 a.u., -1572.64357 a.u. and -1574.53443 a.u. respectively. For Ar⁺₃ triangular, the values of energy in the MP2, QCISD and DFT(M05-2X) levels of approximations for the basis set 3-21G are -1572.62147 a.u., -1572.63716 a.u. and -1574.51751 a.u. respectively. The minimum value of energy corresponding to DFT(M05-2X) level of approximation for the basis set 6-311++G(3df,3pd) is -1582.07528 a.u. for Ar_3^+ linear whereas it is -1582.06454 a.u. for Ar_3^+ triangular. The equilibrium configuration for Ar_3^+ linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd) is shown in the fig ??. The MP2, QCISD and DFT(M05-2X) values of the bond distances and bond angles for Ar_3^+ linear obtained using the basis set 6-311++G(3df,3pd) is presented in the Ta-



Figure 1.8: Equilibrium configuration for Ar_3^+ linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

ble 1.10. The equilibrium configuration of Ar_3^+ triangular in the DFT(M05-2X) level of

Table 1.10: The bond distances and bond angles for Ar_3^+ linear obtained in the MP2, QCISD and DFT(M05-2X) levels of approximations for the basis set 6-311++G(3df,3pd).

	Level of	Distance (d) in Å		Bond Angle(θ^0)
Basis set	approximation	Ar1-Ar2	Ar2-Ar3	Ar1-Ar2-Ar3
	DFT(M05-2X)	2.63	2.63	178.6^{0}
6-311++G(3df,3pd)	MP2	2.46	2.46	178.6^{0}
	QCISD	2.63	2.63	178.3^{0}

approximation obtained using the basis set 6-311++G(3df,3pd) is shown in the fig 1.9. The MP2, QCISD and DFT(M05-2X) values of the bond distances for Ar_3^+ triangular obtained for the basis set 6-311++G(3df,3pd) is presented in the Table 1.11. The MP2,

Table 1.11: The bond distances for Ar_3^+ triangular obtained in the MP2, QCISD and DFT(M05-2X) levels of approximations for the basis set 6-311++G(3df,3pd).

	Level of	Distance (d) in Å		n Å
Basis set	approximation	Ar1-Ar2	Ar2-Ar3	Ar1-Ar2
	DFT(M05-2X)	3.59	3.59	2.46
6-311++G(3df,3pd)	MP2	3.56	3.56	2.42
	QCISD	3.95	3.95	2.49

QCISD and DFT(M05-2X) values of the bond angles for Ar_3^+ triangular obtained using the basis set 6-311++G(3df,3pd) is presented in the Table refchtriba. From the Table 1.10, it is seen that the bond distance for Ar_3^+ linear is 2.63Å in the DFT(M05-2X) level of approximation for the basis set 6-311++G(3df,3pd) whereas the corresponding MP2 value of the bond distance is 2.46Å for the basis set 6-311++G(3df,3pd). The variation in the bond angles for Ar_3^+ linear shows that the optimized geometry is not linear. From the Table 1.11, it is seen that the bond distances for Ar1Ar2= Ar2Ar3 are equal and the corresponding MP2, QCISD and DFT(M05-2X) values of bond distances are 3.56Å, 3.95Å and 3.59Å respectively. These values show that the optimized geometry for Ar_3^+ is an isosceles triangle. Comparing the geometry, the bond distances for triangular are



Figure 1.9: Equilibrium configuration for Ar_3^+ triangular in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

	Level of	Bond angles in θ		
Basis set	approximation	Ar1-Ar2-Ar3	Ar2-Ar3-Ar1	Ar3-Ar1-ar2
	MP2	39.8	70.1	70.1
6-311++G(3df,3pd)	QCISD	36.8	71.6	71.6
	DFT(M05-2X)	40.0	70.0	70.0

Table 1.12: The MP2, QCISD and DFT(M05-2X) values of the bond angles for Ar_3^+ triangular obtained using the basis set 6-311++G(3df,3pd)

larger than the linear. We have also estimated the binding energy for Ar_3^+ linear using the same relation 1.1, which is presented in the Table 1.13. We have also estimated

	Binding energy $(\delta \mathbf{E}_{BE})$ in kcal/mol			
Basis Set	MP2	QCISD	DFT(M05-2X)	EXPT
3-21G	3.219	4.273	10.737	
3-21G*	3.640	4.323	10.837	4.890^{a}
6-31G	1.286	2.742	10.197	5.060^{b}
6-31G*	2.246	3.125	9.682	4.150^{c}
6-311G	0.853	2.203	9.362	5.000^{d}
6-311G*	01.650	2.234	8.597	
6-311++G(3df,3pd)	3.495	1.864	8.484	

Table 1.13: The binding energy for Ar_3^+ linear in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets

he binding energy for A:	$\frac{1}{3}$ triangular	which is presented	in the	Table 1.14.	The total
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Table 1.14: The binding energy for Ar_3^+ triangular in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets

	Binding energy (δE_{BE}) in kcal/mol				
Basis Set	MP2	QCISD	DFT(M05-2X)	EXPT	
3-21G	0.245	0.251	0.126		
3-21G*	-261.669	0.621	1.525	a	
6-31G	10.169	0.182	0.835	b	
6-31G*	438.292	0.514	1.199	c	
6-311G	0.100	0.100	0.609	d	
6-311G*	0.414	0.389	0.784		
6-311++G(3df,3pd)	1.851	1.167	1.744		

binding energy values along with different experimental values are tabulated in Table 1.13 and Table 1.14 for Ar_3^+ linear and triangular structures respectively. The binding energy values for Ar_3^+ linear are larger than the corresponding Ar_3^+ triangular values. We have estimated the binding energy values in the MP2, QCISD and DFT(M05-2X) levels of approximations, among them DFT(M05-2X) values of binding energy are larger. All the binding energy values for Ar_3^+ linear structure are positive indicating the fact that there exist strong binding. However there is negative value of binding energy for Ar_3^+ triangular in the MP2 level for the basis set 3-21G* indicating the fact that there exists no binding at all. From the above estimation we can conclude that Ar_3^+ linear is more stable than Ar_3^+ triangular.



Figure 1.10: Molecular structure, surface minima and maxima of Ar_3^+ linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

Table 1.15: Electrostatic potential of Ar_3^+ linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

0		/ 1 /
Location	ESP(max) kcal/mol	ESP(min) kcal/mol
27/32	133.606	105.313

1.5.3 Electrostatic Potential

The Table 1.15 shows the maximum and minimum values of the electric potential around the given structure. The position of maximum and minimum predicts the sites of the molecule at which they are most likely to react. In the above figure 1.10, Minimum 32 (105.313 kcal/mol) is global minimum on the surface arising from negatively charged argon atom. Maximum 27 (133.606 kcal/mol) is global maximum on the surface arising from the positively charged argon atom. Here, multiwfn shows 47 maxima and 41 minima around the molecular structure which are local minima and local maxima. These two position of maximum (27) and minimum (32) are the favourable sites for the reaction to another atom. The Table 1.16 shows the maximum and minimum values of the electric



Figure 1.11: Molecular structure, surface minima and maxima for Ar_3^+ triangular in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

Table 1.16: Electrostatic potential of Ar_3^+ triangular in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

0		
Location	ESP(max) kcal/mol	ESP(min) kcal/mol
10/6	151.797	70.877

potential around the given structure. The position of maximum and minimum predicts the sites of the molecule at which they are most likely to react. In the above figure 1.11, Minimum 6 (70.877 kcal/mol) is global minimum on the surface arising from negatively charged argon atom. Maximum 10 (151.797 kcal/mol) is global maximum on the surface arising from the positively charged argon atom. Here, multiwfn shows 11 maxima and 12 minima around the molecular structure which are local minima and local maxima. These two position of maximum (10) and minimum (6) are the favourable sites for the reaction to another atom.

1.5.4 Comparison between Ar_3 and Ar_3^+ trimer

From the above discussion, it is found that

- The ground state energies of Ar_3 and Ar_3^+ are basis set dependent and basis set convergent.
- $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ holds good for both Ar₃ and Ar₃⁺ trimer.
- The maximum value of binding energy for Ar_3 linear is estimated to be 0.552 kcal/mol for the basis set 3-21G in the DFT(M05-2x) level of approximation whereas the maximum value of binding energy for Ar_3^+ linear is estimated to be 10.837 kcal/mol for the basis set 3-21G^{*} in the DFT(M05-2x) level of approximation.
- The maximum value of binding energy for Ar_3 triangular is estimated to be 1.060 kcal/mol for the basis set 3-21G in the DFT(M05-2x) level of approximation whereas the maximum value of binding energy for Ar_3^+ triangular is estimated to be 1.744 kcal/mol for the basis set 6-311++G(3df,3pd) in the DFT(M05-2x) level of approximation.
- The binding energy values of Ar_3^+ are larger than the binding energy values of Ar_3 and hence Ar_3^+ structure is more stable.

1.6 The Ground State Energy, Binding Energy and Equilibrium Configuration of Argon Tetramer.

1.6.1 The Ground State Energy, Binding Energy and Equilibrium Configuration of Neutral Argon Tetramer (Ar₄)

We have estimated the ground state energy and binding energy of Ar₄ tetramer in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis sets 3-21G, 3-21G^{*}, 6-31G, 6-31G^{*}, 6-311G, 6-311G^{*} and 6-311++G(3df,3pd). The Gaussian outputs of the ground state energy for Ar₄ is presented in Appendix in Table A.9. The Table A.9 shows the basis set dependence of the ground state energy of Ar₄ tetramer. In moving

from top to bottom for the different basis sets, the energy gets lowered. The values of energy estimated in the MP2 and QCISD levels of approximations for the different basis sets are almost equal however the values of energy estimated in the DFT(M05-2X) level of approximation for the different basis sets are lower than the MP2 and QCISD values. It is also seen that the values of energy for the unpolarised basis sets are lower than the corresponding values of energy for the corresponding polarized basis sets. The values of energy in the MP2, QCISD and DFT(M05-2X) levels of approximations for the basis set 6-311G are -2107.41024 a.u., -2107.43107 a.u. and -2110.10793 a.u. respectively. But the values of energy in the same levels of approximations mentioned for the basis set $6-311G^*$ are -2107.81612 a.u., -2107.86367 a.u. and -2110.10806 a.u. respectively. The values of energy gets lowered with the inclusion of the diffuse functions which is obtained for the basis set 6-311++G(3df,3pd). The above discussion also maintains the fact that the ground state energy of Ar_4 is basis set convergent. From the Table A.9, it is clearly seen that $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ holds. The equilibrium configuration of Ar₄ in the DFT(M05-2X) level of approximation corresponding to the basis set 6-311++G(3df,3pd)is shown in the fig 1.12. From the figure 1.12, it is seen that the optimized geometry



Figure 1.12: Equilibrium configuration of Ar_4 tetramer in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(3df,3pd).

of Ar_4 is tetrahedron geometry. We have estimated the bond distances, bond angles and dihedral angles for Ar_4 tetrahedron using the basis sets 6-311++G(3df,3pd) and $6-311G^*$ in the MP2 and QCISD levels of approximations which is presented in the Table 1.17. The values of the bond distances for the basis set 6-311++G(3df,3pd) in the MP2

Table 1.17: The bond distances, bond angles and dihedral angles for Ar_4 tetrahedron obtained in the MP2 and QCISD levels of approximations for the basis sets 6-311++G(3df,3pd) and 6- $311G^*$.

	Level of	Distance (d) in Å	Bond Angle(θ^0)	Dihedral angle(θ^0)
Basis set	approximation	Ari-Arj	Ari-Arj-Ark	(Ar4Ar1Ar2Ar3)
6-311++G(3df,3pd)	MP2	3.78	60.0	70.6
	QCISD	4.11	60.0	70.7
6-311G*	MP2	4.36	60.0	70.5
	QCISD	4.42	60.0	70.6

and QCISD levels of approximations are 3.78Å and 4.11Å respectively. The bond angle for this structure in the MP2 and QCISD levels of approximations using the basis set 6-311++G(3df,3pd) is 60.0° . The corresponding dihedral angles for the same basis set in the same levels of approximations are $(Ar4Ar2Ar3Ar1) = 70.4^{\circ}$ and 70.7° respectively. From the Table 1.17, it is seen that the bond distance for Ar₄ tetrahedron in the MP2 level of approximation is smaller than the corresponding value obtained in the QCISD level of approximation. The variation may be due to electron correlation. The variation in the bond distance is least for the basis set $6-311G^*$ within MP2 and QCISD levels by an amount of 0.06Å. Hence from the Table 1.17, it is seen that three atoms occupy the vertices of an equilateral triangle in a plane with the fourth atom lying in the different plane making a dihedral (Ar4Ar1Ar2Ar3) of 70.5° . We have estimated the total energy value of argon atom (Ar), its trimer (Ar₃) and tetramer (Ar₄), which in turn made easy to estimate the binding energy (δE_{BE}) of Ar₄ using the relation 1.1. The Table 1.18 shows the MP2, QCISD and DFT(M05-2X) values of binding energy of Ar₄ using the different basis sets. From the Table 1.18, it is clearly seen that the MP2 value of

	Binding energy (δE_{BE}) in kcal/mol			
Basis Set	MP2	QCISD	DFT(M05-2X)	EXPT
3-21G	0.100	0.100	1.569	
3-21G*	0.264	0.238	1.070	
6-31G	-0.0677	0.056	0.991	
6-31G*	0.182	0.151	1.010	
6-311G	0.025	0.025	0.916	
6-311G*	0.100	4.852	0.954	
6-311++G(3df,3pd)	0.960	0.590	0.998	

Table 1.18: The binding energy for Ar_4 tetrahedron in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets

binding energy for Ar_4 for the basis set 6-31G is negative. The QCISD value of binding

energy estimated for the basis set 6-311G is far less than the corresponding QCISD value of binding energy for the basis set 6-311G^{*}. This includes the polarisation effect on binding energy. The binding energy values in the different levels of approximations for the different basis sets are different. This analysis maintains the fact that the basis set dependence of the binding energy values of Ar_4 and is similar to the Ar_2 and Ar_3 . The maximum value of binding energy is estimated in the MP2 level with the basis set 6-311G^{*} which is 4.852 kcal/mol.

1.6.2 The Ground State Energy, Binding Energy and Equilibrium Configuration of Charged Argon Tetramer (Ar_4^+)

We have estimated the ground state energy and binding energy of Ar_4^+ tetramer in the MP2 and QCISD levels of approximations using the basis sets 3-21G, 3-21G^{*}, 6- $31G, 6-31G^*, 6-311G, 6-311G^*, 6-311++G(d,p)$ and 6-311++G(3df,3pd). The Gaussian outputs of the ground state energy for Ar_4^+ is presented in Appendix in Table A.10. The Table A.10 shows the basis set dependence of the ground state energy of Ar_4^+ tetramer. In moving from top to bottom for the different basis sets, the energy gets lowered. The values of energy estimated in the MP2 and QCISD levels of approximations for the different basis sets are almost equal. The values of energy in the MP2 and QCISD levels of approximations for the basis set 6-311G are -2106.88135 a.u. and -2106.89605 a.u. respectively. But the values of energy in the same levels of approximations estimated for the basis set $6-311G^*$ are -2107.29085 a.u. and -2107.33918 a.u. respectively. The values of energy gets lowered with the inclusion of the diffuse functions which is obtained for the basis set 6-311++G(3df,3pd). The above discussion also maintains the fact that the ground state energy of Ar_4^+ is basis set convergent. From the Table A.10, it is clearly seen that $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ holds. The equilibrium configuration of Ar_4^+ in the QCISD level of approximation corresponding to the basis set 6-311++G(3df,3pd)is shown in fig 1.13. From the figure 1.13, it is seen that the optimized geometry of Ar_4 is tetrahedron. We have estimated the bond distances, bond angles and dihedral angles for Ar_4 tetrahedron using the different basis sets. The values of bond distances for the basis set 6-311++G(3df,3pd) in the MP2 and QCISD levels of approximations are 3.78Å and 4.11Å respectively. The bond angles for this structure in the MP2 and QCISD levels of approximations using the basis set 6-311++G(3df,3pd) is 60.0° . The corresponding dihedral angles for the same basis set in the same levels of approximations are $(Ar4Ar2Ar3Ar1) = 70.4^{\circ}$ and 70.7° respectively. We have estimated the total energy values of argon atom (Ar), Ar_3^+ trimer and Ar_4^+ tetramer, which made easy to estimate the binding energy (δE_{BE}) of Ar⁺₄ using the relation 1.1. The Table 1.19 shows the MP2 values of binding energy of Ar_4^+ using the different basis sets. From the Table 1.19, it is seen that the maximum value of binding energy is estimated for the basis set $3-21G^*$ and is 263.056 kcal/mol. There is negative value of binding energy in the MP2 level of



Figure 1.13: Equilibrium configuration of Ar_4^+ tetramer in the QCISD level of approximation obtained using the basis set 6-311++G(3df,3pd)

	Binding energy (δE_{BE}) in kcal/mol	
Basis Set	MP2	EXPT
3-21G	0.270	
3-21G*	263.056	
6-31G	0.188	1.670^{a}
6-31G*	-437.144	
6-311G	0.094	
6-311G*	0.045	
6-311++G(3df,3pd)	2.127	

Table 1.19: The binding energy for Ar_4^+ tetrahedron in the MP2 level of approximation for the different basis sets

approximation for the basis set 6-31G^{*} and is -437.144 kcal/mol which is the indication of no binding. The experimental value of binding energy is 1.670 (1.670 \pm 0.200) kcal/mol. But our estimated values of binding energy for the different basis sets are smaller than this experimental value. We tested different isomeric structures for Ar₄⁺ and we got only this structure with all real frequencies. For Ar₄⁺, DFT(M05-2X) did not work properly.

1.6.3 Electrostatic Potential



Figure 1.14: Molecular structure, surface minima and maxima of Ar_4^+ in the MP2 level of approximation obtained using the basis set 6-311++G(d,p).

Table 1.20: Electrostatic potential of Ar_4^+ tetramer in the MP2 level of approximation obtained using the basis set 6-311++G(d,p).

Location	ESP(max) kcal/mol	ESP(min) kcal/mol
9/1	159.287	63.580

The Table 1.20 shows the maximum and minimum values of the electric potential around the given structure. The position of maximum and minimum predicts the sites of the molecule at which they are most likely to react. In the above figure 1.14, Minimum 1 (63.580 kcal/mol) is global minimum on the surface arising from negatively charged argon atom. Maximum 9 (159.287 kcal/mol) is global maximum on the surface arising from the positively charged argon atom. Here, multiwfn shows 10 maxima and 17 minima

around the molecular structure which are local minima and local maxima. These two position of maximum (9) and minimum (1) are the favourable sites for the reaction to another atom.

1.6.4 Comparison between Ar_4 and Ar_4^+ tetramer

From the above discussion, it is found that

- The ground state energies of Ar_4 and Ar_4^+ are basis set dependent and basis set convergent.
- $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ holds good for both Ar₄ and Ar⁺₄ tetramer.
- The ground state energy of Ar_4 tetramer is minimum than that of Ar_4^+ tetramer within the limit of basis sets and levels of approximations used.
- The optimized geometries of Ar_4 and Ar_4^+ are tetrahedron.

1.7 The Ground State Energy, Binding Energy and Equilibrium Configuration of Argon Pentamer

1.7.1 The Ground State Energy, Binding Energy and Equilibrium Configuration of Neutral Argon Pentamer (Ar₅)

We have estimated the ground state energy and binding energy of Ar_5 in the MP2, QCISD and DFT(M05-2X) levels of approximations. Here we have used the basis sets 3-21G, $3-21G^*$, 6-31G, $6-31G^*$, 6-311G, $6-311G^*$ and 6-311++G(d,p). The Gaussian outputs of the ground state energy of Ar₅ structures have been presented in Appendix in the Table A.11 and Table A.13. It is seen from the Table A.11 that the ground state energy values for Ar_5 linear in the MP2, QCISD and DFT(M05-2X) levels of approximations with the choice of basis set 3-21G are found to be -2621.90864 a.u., -2621.93479 a.u. and -2625.06865 a.u. respectively whereas the corresponding values for Ar₅ pyramidal are found to be -2621.90875 a.u., -2621.93494 a.u. and -2625.07039 a.u. respectively. Table A.11 and Table A.13 also indicate that the ground state energy values estimated in the given levels of approximations gets lowered with increasing the size and complexity of the basis sets. Furthermore, it is also seen that the values of total energy for Ar_5 estimated in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis sets considered in the present work show the basis set convergence in increasing the size and complexity. The equilibrium configuration of Ar_5 linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(d,p) is shown in the fig 1.15 We have estimated the equilibrium bond distances R(Ar1Ar2) = R(Ar4Ar5)



Figure 1.15: Equilibrium configuration of Ar_5 linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(d,p).

= 4.08 Å and R(Ar2Ar3)= R(Ar3Ar4)= 4.03Å for Ar₅ linear in the MP2 and QCISD levels of approximations using the basis set 6-311++G(d,p) whereas the corresponding value of bond distance is 3.94Å in the DFT(M05-2X) level of approximation using the basis set 6-311++G(d,p). This type of variation in the bond distance is also computed for solid carbon[?]. We tested different isomeric structure for Ar₅ and obtained mainly two different structure, linear and pyramidal as shown in the figure 1.15 and figure ?? respectively. The equilibrium configuration of the pyramidal structure of Ar₅ in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(d,p) is shown in the figure ??. The base of the above figure ?? is a rectangle with side (Ar1Ar4)=



Figure 1.16: The equilibrium configuration of Ar_5 pyramidal structure in the DFT(M05-2X) level of approximation using the basis set 6-311++G(d,p).

(Ar3Ar4) = 3.93Å and (Ar1Ar2) = (Ar4Ar3) = 6.44Å. The Ar5 atom is in equidistance (3.81Å) from all base atoms. This ensures that different isomers for Ar₅ exist, among them we have taken that clusters having minimum energy. For Ar₅, pyramidal structure has minimum value of energy for the basis set 6-311++G(d,p) in the DFT(M05-2X) level of approximation. We have also estimated the binding energy values of Ar₅ pyramidal structure in the MP2 and QCISD levels of approximations for the different basis sets which are shown in the Ttable From the Table ??, it is seen that some of the binding energy values are negative. This means there is no binding at all. The MP2 value of binding energy for the basis set 6-311++G(d,p) is negative. The QCISD values of binding energy are more negative than MP2 values. This may indicates that QCISD level of approximation calculation is not appropriate for Ar₅.

	Binding energy (δE_{BE}) in kcal/mol			
Basis Set	MP2	QCISD	EXPT	
3-21G	0.006	0.031		
3-21G*	0.006	0.075		
6-31G	0.006	-0.226		
6-31G*	0.006	0.000		
6-311G	0.000	-0.477		
6-311G*	0.006	-0.10668		
6-311++G(d,p)	-158.258	158.721		

Table 1.21: The binding energy for Ar_5 pyramidal in the MP2 and QCISD levels of approximations for the different basis sets

1.7.2 The Ground State Energy, Binding Energy and Equilibrium Configuration of Charged Argon Pentamer (Ar_5^+)

We have estimated the ground state energy and binding energy of Ar_5^+ in the MP2, QCISD and DFT(M05-2X) levels of approximations. Here we have used the basis sets 3-21G, $3-21G^*$, 6-31G, $6-31G^*$, 6-311G, $6-311G^*$ and 6-311++G(d,p). The Gaussian outputs of the ground state energy for Ar_5^+ structures are presented in Appendix in the Table A.12 and Table A.14. It is seen from the Table A.12 that the ground state energy values for Ar_5^+ linear in the MP2, QCISD and DFT(M05-2X) levels of approximations with the choice of the basis set 3-21G are found to be -2621.39143 a.u., -2621.41725 a.u. and -2624.57443 a.u. respectively whereas the corresponding values for Ar_5^+ parallelogram are found to be -2621.39017 a.u., -2621.41792 a.u. and -2624.56434 a.u. respectively. Table A.12 and Table A.14 also indicate that the ground state energy values estimated in the given levels of approximations gets lowered with increasing the size and complexity of the basis sets. Furthermore, it is also seen that the values of total energy for Ar_5^+ estimated in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis sets considered in the present work show the basis set convergence in increasing the size and complexity. The equilibrium configuration of Ar_5^+ linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(d,p) is shown in the fig 1.17 We have also estimated the equilibrium bond distances R(Ar1Ar2)



Figure 1.17: The equilibrium configuration of Ar_5^+ linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(d,p).

= R (Ar4Ar5) = 3.05 Å and R(Ar2Ar3)= R(Ar3Ar4)= 2.84Å for Ar_5⁺ linear in the DFT(M05-2X) level of approximation using the basis set 6-311++G(d,p) whereas the corresponding values of bond distances in the MP2 and QCISD levels of approximations using the basis set 6-311++G(d,p) are different than what we had expected to be as in the case of Ar₅ linear. The corresponding MP2 values of bond distances are (Ar1Ar2)= 3.92 Å, (Ar2Ar3)= 3.02 Å, (Ar3Ar4)= 2.54 Å and (Ar4Ar5)= 3.05 Å respectively. We tested different isomeric structure for Ar_5⁺ and obtained mainly two different structure, linear and parallelogram as shown in the figure 1.17 and figure ??. The equilibrium configuration of Ar_5⁺ parallelogram in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(d,p) is shown in the figure 1.18. The above figure 1.18 shows the parallelogram structure of Ar_5⁺ having bond distances



Figure 1.18: The equilibrium configuration of Ar_5^+ parallelogram DFT(M05-2X) level of approximation using the basis set 6-311++G(d,p).

(Ar1Ar5) = (Ar5Ar3) = 2.70 Å, (Ar4Ar5) = (Ar5Ar2) = 3.72 Å, (Ar4Ar1) = (Ar3Ar2) =3.78 Å, (Ar1Ar2) = (Ar4Ar3) = 5.30 Å respectively. The bond angles (Ar3Ar2Ar1) = $(Ar3Ar4Ar1) = 70.88^{\circ}$ and $(Ar2Ar1Ar4) = (Ar4Ar3Ar1) = 107.50^{\circ}$ respectively. This ensures that different isomers for Ar_5^+ exist, among them we have taken that clusters having minimum energy. For Ar_5^+ , linear structure has minimum value of energy for the basis set 6-311++G(d,p) in the DFT(M05-2X) level of approximation. We have also estimated the binding energy values of Ar_5^+ for both isomers in the MP2 and QCISD levels of approximations for the different basis sets which are shown in the Table 1.22 and Table 1.23. The binding energy for Ar_5^+ parallelogram in the MP2 and QCISD levels of approximations for the different basis sets is presented in the Table 1.23. For Ar_5^+ linear, binding energy values along with the experimental values is presented in the Table 1.22. The maximum value of binding energy is estimated for the basis set 6-311G in the QCISD level which is 5.146 kcal/mol. This value is large (in deviation of about 27%) to the experimental binding energy value 4.036 kcal/mol. The binding energy values estimated for the basis set 6-311++G(d,p) in the MP2 and QCISD levels of approximations are 1.732 kcal/mol and 1.933 kcal/mol respectively which are nearer

	Binding energy (δE_{BE}) in kcal/mol			
Basis Set	MP2	QCISD	EXPT	
3-21G	3.872	4.154		
3-21G*	4.361	3.960		
6-31G	1.669	2.460	4.036^{a}	
6-31G*	2.755	3.972	1.620^{b}	
6-311G	1.305	5.146		
6-311G*	2.196	3.382		
6-311++G(d,p)	1.732	1.933		

Table 1.22: The binding energy for Ar_5^+ linear in the MP2 and QCISD levels of approximations for the different basis sets

Table 1.23: The binding energy for Ar_5^+ parallelogram in the MP2 and QCISD levels of approximations for the different basis sets

	Binding energy (δE_{BE}) in kcal/mol			
Basis Set	MP2	QCISD	EXPT	
3-21G	3.081	4.574		
3-21G*	3.307	3.922		
6-31G	1.199	3.320	a	
6-31G*	1.995	3.765	b	
6-311G	0.841	4.047		
6-311G*	1.581	2.893		
6-311++G(d,p)	1.688	1.977		

to the experimental value $1.620 (1.620 \pm 0.200)$ kcal/mol and are less in deviation (about 7% and 19% respectively) to the experimental value. For Ar₅⁺ parallelogram, the binding energy values along with the experimental values are presented in the Table 1.23. The maximum value of binding energy is estimated for the basis set 3-21G in the QCISD level of approximation which is 4.154 kcal/mol and nearer to the experimental value 4.036 kcal/mol. The MP2 values of binding energy are nearer to the experimental value 1.620 kcal/mol.

1.7.3 Electrostatic Potential



Figure 1.19: Molecular structure, surface minima and maxima of Ar_5^+ linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(d,p).

Table 1.24: Electrostatic potential of Ar_5^+ linear in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(d,p).

	× *	/ - /
Location	ESP(max) kcal/mol	ESP(min) kcal/mol
31/13	114.428	65.226

The Table 1.24 shows the maximum and minimum values of the electric potential around the given structure. The position of maximum and minimum predicts the sites of the molecule at which they are most likely to react. In the above figure 1.19, Minimum 13 (65.226 kcal/mol) is global minimum on the surface arising from negatively charged

argon atom. Maximum 31 (114.428 kcal/mol) is global maximum on the surface arising from the positively charged argon atom. Here, multiwfn shows 54 maxima and 22 minima around the molecular structure which are local minima and local maxima. These two position of maximum (31) and minimum (13) are the favourable sites for the reaction to another atom.



Figure 1.20: Molecular structure, surface minima and maxima of Ar_5^+ parallelogram in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(d,p).

Table 1.25: Electrostatic potential of Ar_5^+ parallelogram in the DFT(M05-2X) level of approximation obtained using the basis set 6-311++G(d,p).

Location	ESP(max) kcal/mol	ESP(min) kcal/mol
2/24	134.541	60.542

The Table 1.25 shows the maximum and minimum values of the electric potential around the given structure. The position of maximum and minimum predicts the sites of the molecule at which they are most likely to react. In the above figure 1.20, Minimum 24 (60.542 kcal/mol) is global minimum on the surface arising from negatively charged argon atom. Maximum 2 (134.541 kcal/mol) is global maximum on the surface arising from the surface arising from the positively charged argon atom. Here, multiwfn shows 10 maxima and 24 minima around the molecular structure which are local minima and local maxima. These two position of maximum (2) and minimum (24) are the favourable sites for the reaction to another atom.

1.7.4 Comparison between Ar_5 and Ar_5^+ clusters

From the above discussion, it is found that

- The ground state energies of Ar_5 and Ar_5^+ are basis set dependent and basis set convergent.
- $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ holds good for both Ar₅ and Ar₅⁺ clusters.
- The ground state energy of Ar_5 is minimum than the Ar_5^+ within the limit of basis sets and levels of approximations used.
- The binding energy values of Ar₅⁺ are all positive whereas there are some negative values of binding energy for Ar₅.

1.8 The Ground State Energy, Binding Energy and Equilibrium Configuration of Argon Hexamer

1.8.1 The Ground State Energy, Binding Energy and Equilibrium Configuration of Neutral Argon Hexamer (Ar₆)

We have estimated the ground state energy and binding energy of Ar_6 in the MP2, QCISD and DFT(M05-2X) levels of approximations. Here we have used the basis sets 3-21G, 3-21G^{*}, 6-31G, 6-31G^{*}, 6-311G and 6-311G^{*}. The Gaussian outputs of the ground state energy of Ar_6 has been presented in Appendix in the Table A.15. It is seen from the Table A.15 that the ground state energy values for Ar_6 in the MP2, QCISD and DFT(M05-2X) levels of approximations with the choice of basis set 3-21G are found to be -3146.29075 a.u., -3146.32213 a.u. and -3150.08921 a.u. respectively. Table A.15 also indicates that the ground state energy values obtained in the given levels of approximations gets lowered with increasing the size and complexity of the basis sets. Furthermore, it is also seen that the values of the total energy for Ar_6 estimated in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis sets considered in the present work shows the basis set convergence in increasing the size and complexity. The equilibrium configuration of Ar_6 in the DFT(M05-2X) level of approximation obtained using the basis set $6-311G^*$ is shown in the figure 1.8.1 The equilibrium configuration of Ar₆ in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G* shows that hexamer of Ar_6 is bipyramidal structure. Four atoms form the square on the base plane and two atom occupy exactly the above position as shown in the figure 1.8.1. The equilibrium bond distance between any two adjacent argon atom is 3.80Å. The interior angle of base plane is 90.0° . The value of dihedral (Ar1Ar2Ar3Ar4) is 180.0° whereas $(Ar1Ar2Ar3Ar5) = 90.0^{\circ}$ and $(Ar4Ar2Ar1Ar6) = 54.74^{\circ}$. We have also estimated the



Figure 1.21: The equilibrium configuration of the Ar_6 bipyramidal in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G^{*}. The equilibrium bond distance is 3.80Å.

binding energy values of Ar_6 bipyramidal in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets which is presented in the Table From

Table 1.26: The binding energy for Ar_6 bipyramidal in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets

	Binding energy (δE_{BE}) in kcal/mol			
Basis Set	MP2	QCISD	DFT(M05-2X)	
3-21G	0.201	0.176	3.614	
3-21G*	0.552	0.408	3.075	
6-31G	0.941	0.333	1.575	
6-31G*	0.370	0.314	1.744	
6-311G	0.044	0.515	2.058	
6-311G*	0.213	0.282	2.134	

the Table 1.26, the maximum value of binding energy is estimated in the DFT(M05-2X) level of approximation for the basis set 3-21G and is 3.614 kcal/mol. The values of binding energy estimated for the different basis sets in the MP2 and QCISD levels of approximations are very smaller than the values of binding energy estimated in the DFT(M05-2X) level of approximation. These values of binding energy estimated in the DFT(M05-2X) level of approximation show that DFT level with M05-2X functional is

appropriate for the estimation of binding energy values for argon clusters. The more the value of binding energy, the more stable the structure is and is estimated for the DFT(M05-2X) level.

1.8.2 The Ground State Energy, Binding Energy and Equilibrium Configuration of Charged Argon Hexamer (Ar_6^+)

We have estimated the ground state energy and binding energy of Ar_6^+ in the MP2, QCISD and DFT(M05-2X) levels of approximations. Here we have used the basis sets 3-21G, 3-21G^{*}, 6-31G, 6-31G^{*}, 6-311G and 6-311G^{*}. The Gaussian outputs of the ground state energy of Ar_6^+ has been presented in Appendix in the Table A.16. It is seen from the Table A.16 that the ground state energy values for Ar_6^+ in the MP2, QCISD and DFT(M05-2X) levels of approximations with the choice of basis set 3-21G are found to be -3145.77354 a.u., -3145.80608 a.u. and -3149.58605 a.u. respectively. Table A.16 also indicates that the ground state energy values estimated in the given levels of approximations gets lowered with increasing the size and complexity of the basis sets. Furthermore, it is also seen that the values of total energy for Ar_6^+ estimated in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis sets considered in the present work show the basis set convergence in increasing the size and complexity of the basis sets. The equilibrium configuration of Ar_6^+ in the DFT(M05-2X) level of approximation of Ar_6^+ in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G^{*} is shown in the figure ?? From the figure 1.22, we have estimated the bond distances and bond angles for Ar_6^+



Figure 1.22: The equilibrium configuration of Ar_6^+ in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G^{*}

cluster atoms. The bond distances (Ar1Ar3) = (Ar5Ar6) = 3.99Å, (Ar2Ar3) = (Ar4Ar6) = 2.90Å and bond angles $(Ar1Ar2Ar3) = (Ar5Ar4Ar6) = 74.12^{\circ}$ respectively. The dihedral angle $(Ar3Ar1Ar2Ar4) = 180^{\circ}$. We have also estimated the binding energy values for Ar_6^+ in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets which is presented in the Table From the Table 1.27, it is seen that the maximum value of binding energy is estimated in the DFT(M05-2X) level of approximation for

	Binding energy (δE_{BE}) in kcal/mol			
Basis Set	MP2	QCISD	DFT(M05-2X)	EXPT
3-21G	1.060	0.784	5.428	
3-21G*	1.857	1.067	4.493	
6-31G	0.690	0.477	4.393	2.762^{a}
6-31G*	1.481	0.935	3.790	1.620^{b}
6-311G	0.596	2.541	4.211	
6-311G*	1.192	1.010	3.514	

Table 1.27: The binding energy for Ar_6^+ in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets

the basis set 3-21G and is 5.428 kcal/mol. This value is very large as compared to the experimental value 2.762 kcal/mol and very very far than the experimental value 1.620 kcal/mol. The values of binding energy estimated in the MP2 and QCISD levels of approximations are very nearer to the experimental value 1.620 kcal/mol. The above Table 1.27 shows that the DFT(M05-2X) values of binding energy are very high and hence this method is practicable for the study of binding energy for Ar_6^+ .

1.8.3 Electrostatic Potential



Figure 1.23: Molecular structure, surface minima and maxima of Ar_6^+ in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G^{*}.

Table 1.28: Electrostatic potential of Ar_6^+ in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G^{*}.

Location	ESP(max) kcal/mol	ESP(min) kcal/mol
7/3	126.539	56.089

The Table 1.28 shows the maximum and minimum values of the electric potential around the given structure. The position of maximum and minimum predicts the sites of the molecule at which they are most likely to react. In the above figure 1.23, Minimum 3 (56.089 kcal/mol) is global minimum on the surface arising from negatively charged argon atom. Maximum 7 (126.539 kcal/mol) is global maximum on the surface arising from the surface arising from the positively charged argon atom. Here, multiwfn shows 14 maxima and 7 minima around the molecular structure which are local minima and local maxima. These two position of maximum (7) and minimum (3) are the favourable sites for the reaction to another atom.

1.8.4 Comparison between Ar_6 and Ar_6^+ clusters

From the above discussion, it is found that

- The ground state energies of Ar_6 and Ar_6^+ are basis set dependent and basis set convergent.
- $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ holds good for both Ar₆ and Ar₆⁺ clusters.
- The ground state energy of Ar_6 is minimum than that of Ar_6^+ within the limit of basis sets and levels of approximations used.
- The maximum value of binding energy for Ar_6^+ is estimated to be 5.428 kcal/mol in the DFT(M05-2X) level for the basis set 3-21G whereas the maximum value of binding energy for Ar_6 is estimated to be 3.614 kcal/mol in the DFT(M05-2X) level for the basis set 3-21G.

1.9 The Ground State Energy, Binding Energy and Equilibrium Configuration of Argon Heptamer

1.9.1 The Ground State Energy, Binding Energy and Equilibrium Configuration of Neutral Argon Heptamer (Ar₇)

We have estimated the ground state energy and binding energy of Ar_7 in the MP2, QCISD and DFT(M05-2X) levels of approximations. Here we have used the basis sets

3-21G, 3-21G^{*}, 6-31G, 6-31G^{*}, 6-311G and 6-311G^{*}. The Gaussian outputs of the ground state energy of Ar_7 heptamer has been presented in Appendix in the Table A.17. It is seen from the Table A.17 that the ground state energy values for Ar_7 in the MP2, QCISD and DFT(M05-2X) levels of approximations with the choice of basis set 3-21G are found to be -3670.67258 a.u., -3670.70920 a.u. and -3675.10429 a.u. respectively. Table A.17 also indicates that the ground state energy values estimated in the given level of approximation gets lowered with increasing the size and complexity of the basis sets. Furthermore, it is also seen that the values of the total energy for Ar_7 estimated in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis sets considered in the present work show the basis set convergence in increasing the size and complexity. The equilibrium configuration of Ar_7 in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G^{*} is shown in the figure 1.24 We have



Figure 1.24: The equilibrium configuration of Ar_7 in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G^{*}

also estimated the binding energy values of Ar_7 in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets which are shown in Table

From the Table 1.29, it is seen that the maximum value of binding energy is estimated for the basis set 6-31G in the DFT(M05-2X) level of approximation and is 1.293 kcal/mol. The MP2 and QCISD values of binding energy are smaller compared to the DFT(M05-2X) values of binding energy.

1.9.2 The Ground State Energy, Binding Energy and Equilibrium Configuration of Charged Argon Heptamer (Ar_7^+)

We have estimated the ground state energy and binding energy of Ar_7^+ in the MP2, QCISD and DFT(M05-2X) levels of approximations. We have used the basis sets 3-

	Binding energy (δE_{BE}) in kcal/mol			
Basis Set	MP2	QCISD	DFT(M05-2X)	
3-21G	0.094	0.100	1.268	
3-21G*	0.257	0.220	1.092	
6-31G	0.044	0.052	1.293	
6-31G*	0.176	0.144	1.217	
6-311G	0.019	0.025	0.671	
6-311G*	0.100	0.075	0.722	

Table 1.29: The binding energy for Ar_7 structure in the MP2, QCISD and DFT(M05-2X) levels of approximations for the different basis sets

21G, 3-21G^{*}, 6-31G, 6-31G^{*} and 6-311G . The Gaussian outputs of the ground state energy of Ar_7^+ heptamer has been presented in Appendix in the Table A.18. It is seen from the Table A.18 that the ground state energy values for Ar_7^+ in the MP2, QCISD and DFT(M05-2X) levels of approximations with the choice of basis set 3-21G are found to be -3670.15429 a.u., -3670.19256 a.u. and -3674.59657 a.u. respectively. Table A.18 also indicates that the ground state energy values estimated in the given levels of approximations gets lowered with increasing the size and complexity of the basis sets. Furthermore, it is also seen that the values of total energy for Ar_7^+ estimated in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis sets considered in the present work shows the basis set convergence in increasing the size and complexity of the basis sets. The equilibrium configuration of Ar_7^+ in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G is shown in the figure 1.25 The above figure 1.25



Figure 1.25: The equilibrium configuration of Ar_7^+ in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G

shows the equilibrium configuration of Ar_7^+ in the DFT(M05-2X) level of approxima-

tion. We tested the different isomeric structures for Ar_7^+ and obtained this structure with all real frequencies. We tried to estimate the binding energy values but there are all negative values. So we discarded the estimated values. The possibilities are either an inaccuracy of the levels of approximations we have used or due to geometry. Hence we left this estimation of binding energy for the future work.

1.9.3 Electrostatic Potential



Figure 1.26: Molecular structure, surface minima and maxima of Ar_7^+ in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G.

Table 1.30: Electrostatic potential of Ar_7^+ in the DFT(M05-2X) level of approximation obtained using the basis set 6-311G.

Location	ESP(max) kcal/mol	ESP(min) kcal/mol
8/1	134.745	57.896

The Table 1.30 shows the maximum and minimum values of the electric potential around the given structure. The position of maximum and minimum predicts the sites of the molecule at which they are most likely to react. In the above figure 1.26, Minimum 1 (57.896 kcal/mol) is global minimum on the surface arising from negatively charged argon atom. Maximum 8 (134.745 kcal/mol) is global maximum on the surface arising from the surface arising from the positively charged argon atom. Here, multiwfn shows 13 maxima and 12 minima

around the molecular structure which are local minima and local maxima. These two position of maximum (8) and minimum (1) are the favourable sites for the reaction to another atom.

1.9.4 Comparison between Ar_7 and Ar_7^+ clusters

From the above discussion, it is found that

- The ground state energies of Ar_7 and Ar_7^+ are basis set dependent and basis set convergent.
- $E_{MP2} > E_{QCISD} > E_{DFT(M05-2X)}$ holds good for both Ar₇ and Ar₇⁺ clusters.
- The ground state energy for Ar₇ is minimum than the Ar₇⁺ within the limit of basis sets and levels of approximations used.

1.10 Conclusion and Remarks

In this section, we present the main findings of our work. We have performed the first principles calculations to estimate the total ground state energy of Ar_n and Ar_n^+ (n = 2,...7) cluster in the MP2, QCISD and DFT(M05-2X) levels of approximations using the basis sets 3-21G, 3-21G^{*}, 6-31G, 6-31G^{*}, 6-311G, 6-311G^{*}, 6-311++G(d,p) and 6-311++G(3df,3pd) using Gaussian 03 set of programs. We have also used ChemCraft molecular builder to analyse the geometry and corresponding Z-matrices. The MP2, QCISD and DFT(M05-2X) calculations have also been carried out to estimate the binding energy values of Ar_n and Ar_n^+ cluster using the basis sets mentioned above.

1.10.1 Finding on the total ground state energy of Ar_n and Ar_n^+

We have estimated the ground state energy of Ar_n and Ar_n^+ clusters using the basis sets mentioned in our present work. The ground state energy of Ar_n and Ar_n^+ are basis set dependent and basis set convergence. In moving from top to bottom for different basis sets in the different levels of approximations, the ground state energy gets lowered. We have assumed that the basis set of the higher flexibility would give a better result and which is in good agreement with our present work. The total ground state energy values obtained in the DFT level of approximation using new hybrid functional M05-2X gives better result. The ground state energy for Ar atom in the DFT(M05-2X) level of approximation for the basis set 6-311++G(3df,3pd) is -527.52690 a.u. whereas the corresponding value of the total ground state energy for Ar⁺ atom in the same basis set and same level of approximation is -526.94718 a.u.. For Ar₂, the total ground state energy in the DFT(M05-2X) level of approximation for the basis set 6-311++G(3df,3pd) is -1055.05424 a.u. The corresponding energy for Ar_2 in the MP2 and QCISD levels of approximations for the same basis set are -1054.02358 a.u. and -1054.05983 a.u. respectively. This concludes that DFT(M05-2X) level calculations are better with the minimum values of the total ground state energy. The same holds good for all the cluster size. We have plotted the total ground state energy versus basis sets in increasing size and complexity for Ar and Ar⁺ in the figure 1.1 and figure 1.2 respectively. The variation of the total ground state energy per argon atom with increasing no. of Ar atom in the DFT(M05-2X) level of approximation using the basis set 6-311G is shown in figure



Figure 1.27: The variation of the total ground state energy per argon atom with increasing no. of Ar atom (Ar_n) in the DFT(M05-2X)/6-311G level of approximation

The variation of the total ground state energy per argon atom with increasing no. of Ar^+ atom in the DFT(M05-2X) level of approximation using the basis set 6-311G is shown in figure

1.10.2 Finding on the binding energy of Ar_n and Ar_n^+

We have estimated the values of binding energy for Ar_n and Ar_n^+ (n= 2,...7) cluster in the different levels of approximations using the different basis sets mentioned in our present work. The first-principles calculations have been carried out to estimate the binding energy of Ar_n and Ar_n^+ cluster. Due to the limitation of our computational resources and accuracy of the software, we could not use all possible basis sets and have to compromise to 6-311G as the highest and complex basis set for Ar_7^+ cluster. We have performed MP2, QCISD and DFT(M05-2X) levels of calculations to estimate the binding energy for the different cluster. We have not used any sophisticated techniques to estimate the binding energy of Ar_n and Ar_n^+ cluster. We have estimated the binding energy values by considering the relation 1.1. We have focused on DFT level of calculation



Figure 1.28: The variation of the total ground state energy per argon atom with increasing no. of Ar^+ atom (Ar_n^+) in the MP2/6-311G level of approximation



Figure 1.29: The variation of the total ground state energy per argon atom with increasing no. of Ar^+ atom (Ar_n^+) in the QCISD/6-311G level of approximation

with new hybrid functional M05-2X for the different basis sets mentioned in our present work. We have compared the estimated values of binding energy with the experimental values and comparative study has been made. For Ar_2^+ dimer, the maximum value of binding energy is estimated in the DFT(M05-2X) level of approximation for the basis set 3-21G and is 0.490 kcal/mol. The experimental value is 0.242 kcal/mol[?]. For Ar_2^+ dimer, the maximum value of binding energy is estimated in the DFT(M05-2X) level of approximation for the basis set 3-21G and is 38.171 kcal/mol. The experimental values are 30.318 kcal/mol and 30.000 kcal/mol[?] respectively. Further we have estimated the binding energy values for Ar_3^+ , Ar_4^+ , Ar_5^+ and Ar_6^+ in the different levels of approximations for the different basis sets. The binding energy values are plotted with increasing no. of argon atom in the different levels of approximations for the different basis sets.



Figure 1.30: Variation of the binding energy per argon atom with increasing no. of argon atom (Ar_n) in the MP2/3-21G level of approximation.



Figure 1.31: Variation of the binding energy per argon atom with increasing no. of argon atom (Ar_n^+) in the MP2/3-21G level of approximation.



Figure 1.32: Variation of the binding energy per argon atom with increasing no. of argon atom (Ar_n) in the MP2/6-31G^{*} level of approximation.



Figure 1.33: Variation of the binding energy per argon atom with increasing no. of argon atom (Ar_n^+) in the MP2/3-21G level of approximation with the experimental values.

Appendix A

Gaussian Outputs

	Level of approximation			
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)	
3-21G	-524.38168	-524.38691	-525.01306	
3-21G*	-524.58835	-524.60059	-525.13408	
6-31G	-526.8062	-526.81112	-527.48509	
6-31G*	-526.91105	-526.92308	-527.48985	
6-311G	-526.85254	-526.85775	-527.52631	
6-311G*	-526.95395	-526.96585	-527.52631	
6-311++G(3df,3pd)	-527.01155	-527.02975	-527.5269	

Table A.1: Total Ground state energy of Ar atom

Table A.2: Total Ground state energy of Ar⁺ atom

	Level of approximation			
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)	
3-21G	-523.82218	-523.82661	-524.43036	
3-21G*	-524.02276	-524.03999	-524.553054	
6-31G	-526.24848	-526.25228	-526.90267	
6-31G*	-526.34711	-526.36398	-526.90868	
6-311G	-526.29453	-526.29922	-526.94341	
6-311G*	-526.38977	-526.40685	-526.94509	
6-311++G(3df,3pd	-526.43511	-526.46006	-526.94718	

	Level of approximation			
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)	
3-21G	-1048.76342	-1048.77388	-1050.02691	
3-21G*	-1049.17681	-1049.20131	-1050.26883	
6-31G	-1053.61243	-1053.6228	-1054.97062	
6-31G*	-1053.82220	-1053.84624	-1054.98014	
6-311G	-1053.70510	-1053.71551	-1055.05302	
6-311G*	-1053.90795	-1053.93175	-1055.05300	
6-311++G(3df,3pd	-1054.02358	-1054.05983	-1055.054240	

Table A.3: Total Ground state energy of Ar_2 Dimer

Table A.4: Total Ground state energy of Ar_2^+ Dimer

	Level of approximation			
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)	
3-21G	-1048.23941	-1048.24985	-1049.50245	
3-21G*	-1048.65256	-1048.67931	-1049.74746	
6-31G	-1053.08501	-1053.09539	-1054.44153	
6-31G*	-1053.29641	-1053.32307	-1054.45544	
6-311G	-1053.17596	-1053.18706	-1054.52103	
6-311G*	-1053.38158	-1053.40782	-1054.52654	
6-311++G(3df,3pd	-1053.49388	-1053.53280	-1054.53486	

Table A.5: Total Ground state energy of Ar₃ linear

	Level of approximation			
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)	
3-21G	-1573.14516	-1573.16091	-1575.04085	
3-21G*	-1573.76529	-1573.80215	-1575.40359	
6-31G	-1580.41868	-1580.43343	-1582.45613	
6-31G*	-1580.73335	-1580.76941	-1582.47044	
6-311G	-1580.55765	-1580.57327	-1582.57973	
6-311G*	-1580.86201	-1580.89765	-1582.57979	
6-311++G(3df,3pd	-1581.03561	-1581.08109	-1582.58157	

	Level of approximation		
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)
3-21G	-1572.62621	-1572.64357	-1574.53443
3-21G*	-1573.24671	-1573.28679	-1574.89881
6-31G	-1579.89326	-1579.91086	-1581.94286
6-31G*	-1580.21104	-1580.25113	-1581.96071
6-311G	-1580.02986	-1580.04832	-1582.06224
6-311G*	-1580.33816	-1580.37723	-1582.06655
6-311++G(3df,3pd	-1580.51100	-1580.56552	-1582.07528

Table A.6: Total ground state energy of Ar_3^+ linear

Table A.7: Total ground state energy of Ar₃ triangular

	Level of approximation		
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)
3-21G	-1573.14522	-1573.16091	-1575.04166
3-21G*	-1573.76543	-1573.80215	-1575.40427
6-31G	-1580.41868	-1580.43345	-1582.45660
$6-31G^{*}$	-1580.73344	-1580.76948	-1582.47092
6-311G	-1580.55766	-1580.57328	-1582.58016
6-311G*	-1580.86201	-1580.89769	-1582.58023
6-311++G(3df,3pd	-1581.03611	-1581.09021	-1582.58204

Table A.8: Total Ground state energy of Ar_3^+ triangular

	Level of approximation			
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)	
3-21G	-1572.62147	-1572.63716	-1574.51751	
3-21G*	-1572.82391	-1573.28089	-1574.88397	
6-31G	-1579.89148	-1579.90680	-1581.92794	
6-31G*	-1580.20833	-1580.24697	-1581.94719	
6-311G	-1580.02866	-1580.04497	-1582.04831	
6-311G*	-1580.33619	-1580.37429	-1582.05430	
6-311++G(3df,3pd	-1580.50838	-1580.56441	-1582.06454	

	Level of approximation		
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)
3-21G	-2097.52706	-2097.54798	-2100.05722
3-21G*	-2098.35420	-2098.40312	-2100.54055
6-31G	-2107.22496	-2107.24466	-2109.94327
6-31G*	-2107.64478	-2107.69280	-2109.96238
6-311G	-2107.41024	-2107.43107	-2110.10793
6-311G*	-2107.81612	-2107.86367	-2110.10806
6-311++G(3df,3pd	-2108.04919	-2108.12090	-2110.11053

Table A.9: Total Ground state energy of Ar_4 tetramer

Table A.10: Total Ground state energy of Ar_4^+ tetramer

	Level of approximation	
Basis Set	MP2 (a.u)	QCISD(a.u)
3-21G	-2097.00358	-2097.02372
3-21G*	-2097.83147	-2097.88257
6-31G	-2106.69798	-2106.71652
6-31G*	-2107.12034	-2107.16907
6-311G	-2106.88135	-2106.89605
6-311G*	-2107.29085	-2107.33918
6-311++G(3df,3pd)	-2107.52332	-2106.7161

Table A.11: Total Ground state energy of Ar_5 linear

	Level of approximation		
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)
3-21G	-2621.90864	-2621.93479	-2625.06865
3-21G*	-2622.94225	-2623.00346	-2625.67307
6-31G	-2634.03112	-2634.05553	-2637.42715
6-31G*	-2634.55565	-2634.61569	-2637.45098
6-311G	-2634.26276	-2634.28838	-2637.63315
6-311G*	-2634.76996	-2634.82933	-2637.63317
6-311++G(d,p	-2634.77452	-2634.83468	-2637.63617

	Level of approximation		
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)
3-21G	-2621.39143	-2621.41725	-2624.57443
3-21G*	-2622.42677	-2622.48947	-2625.17870
6-31G	-2633.50684	-2633.53156	-2636.92419
6-31G*	-2634.03578	-2634.09848	-2636.95024
6-311G	-2633.73597	-2633.76200	-2637.12533
6-311G*	-2634.24830	-2634.31042	-2637.12808
6-311++G(d,p)	-2634.25347	-2634.31626	-2637.13014

Table A.12: Total Ground state energy of Ar_5^+ linear

Table A.13: Total Ground state energy of Ar_5 pyramidal

	Level of approximation		
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)
3-21G	-2621.90875	-2621.93494	-2625.07039
3-21G*	-2622.94256	-2623.00383	-2625.67465
6-31G	-2634.03117	-2634.05542	-2637.42823
6-31G*	-2634.55584	-2634.61588	-2637.45209
6-311G	-2634.26278	-2634.28806	-2637.63418
6-311G*	-2634.77008	-2634.82935	-2637.63426
6-311++G(d,p	-2634.77534	-2634.83542	-2637.63721

Table A.14: Total Ground state energy of Ar_5^+ parallelogram

	Level of approximation		
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)
3-21G	-2621.39017	-2621.41792	-2624.56434
3-21G*	-2622.42509	-2622.48941	-2625.17090
6-31G	-2633.50609	-2633.53309	-2636.91529
6-31G*	-2634.03457	-2634.09814	-2636.94323
6-311G	-2633.73523	-2633.	-2637.11657
6-311G*	-2634.24732	-2634.31964	-2637.12141
6-311++G(d,p)	-2634.25340	-2634.31633	-2637.12465

	Level of approximation			
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)	
3-21G	-3146.29075	-3146.32213	-3150.08921	
3-21G*	-3147.53179	-3147.60507	-3150.81363	
6-31G	-3160.83752	-3160.86707	-3164.91583	
6-31G*	-3161.46748	-3161.53946	-3164.94472	
6-311G	-3161.1539	-3161.14663	-3165.16377	
6-311G*	-3161.72437	-3161.79565	-3165.16397	

Table A.15: Total Ground state energy of Ar_6 hexamer

Table A.16: Total Ground state energy of Ar_6^+ hexamer

	Level of approximation		
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)
3-21G	-3145.77354	-3145.80608	-3149.58605
3-21G*	-3147.01640	-3147.09170	-3150.31214
6-31G	-3160.31339	-3160.34497	-3164.40738
6-31G*	-3160.94798	-3161.02272	-3164.43912
6-311G	-3160.58872	-3160.62205	-3164.64959
6-311G*	-3161.20317	-3161.27710	-3164.65332

Table A.17: Total Ground state energy of Ar_7 heptamer

	Level of approximation		
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)
3-21G	-3670.67258	-3670.70920	-3675.10429
3-21G*	-3672.12055	-3672.20601	-3675.94945
6-31G	-3687.64379	-3687.67827	-3692.40298
6-31G*	-3688.37881	-3688.46277	-3692.43651
6-311G	-3687.96796	-3688.00442	-3692.69115
6-311G*	-3688.67848	-3688.76162	-3692.69143

Table A.18: Total Ground state energy of Ar_7^+ heptamer

	Level of approximation		
Basis Set	MP2 (a.u)	QCISD(a.u)	DFT(M05-2X)(a.u)
3-21G	-3670.15429	-3670.19256	-3674.59657
3-21G*	-3671.60388	-3671.69261	-3675.44491
6-31G	-3687.11900	-3687.15586	-3691.88933
6-31G*	-3687.85838	-3687.94582	-3691.92754
6-311G	-3687.44058	-3687.47902	-3692.17232