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Quantum chemical studies on cationic, anionic and neutral states of AgF nanostructures

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Abstract : The realistic nanocone, nanotube and nanosheet AgF nanostructures are optimized and simulated successfully with B3LYP/ LanL2DZ basis set. The structural stability of AgF nanostructures is studied for neutral, cationic and anionic states using binding energy and calculated energy. The dipole moment and point group of nanocone, nanotube and nanosheet AgF nanostructures are also reported. Utilizing HOMO – LUMO gap, electronic properties of AgF nanostructures can be studied. From the present work,the structural stability and electronic properties of neutral, cationic and anionic AgF nanostructures are explored which find its importance in superionic conductors and in photographic materials.

Keywords: silver fluoride; nanostructures; structural stability; binding energy; HOMO-LUMO.

Introduction

Silver halides have attracted the researchers owing to their vital role in technological applications. Silver halides can be used as solid electrolytes, photographic materials and in liquid semiconductors. The peculiar role is accredited to the small electronic structure of halides due to strong hybridization of *p* orbitals of halogens with *d* orbital of silver in the valence orbit.

Silver is rarely occurring element and it is comparatively harder than gold.Pure silver has high thermal and electrical conductivity among all other metals and it has low contact resistance.Moreover, it is malleable and ductile [1-3]due to these reasons silver is used in a wide range of applications. The investigation of silver halides isofkeen interest in the few decades owing to their significant application in superionic conductors and in photographic materials.The better understanding of physical and chemical properties of these systems needs a complete knowledge about the electronic structure of the corresponding halides.The most important silver halides such as silver fluoride (AgF), silver chloride (AgCl) and silver bromide (AgBr) exhibits in the form of face centered cubic rock salt NaCl structure. The electronic structure of alkali halides such as AgCl, AgF and AgBr are theoretically studied by non-self-consistent method [4-8].Ves et al [9] studied self-consistent method andobserved the band structure of silver and copper halides. Kunz et al [10] carried out Hartree-Fock self-consistent calculations for AgF, AgBr and AgCl in the fcc phase.Gordienko et al [11] calculated the charge density and band structure of silverhalide series using pseudopotentialsin density functional theory.

The motivation behind this work is to investigate the structural stability and electronic properties of AgF using density functional theory (DFT). To our knowledge, there are not muchwork available for AgF nanostructures.DFT method explores the structural stability and electronic properties of AgF nanostructures [12-15]. In this work, anionic, neutral and cationic states of AgF in three different nanostructures namely, nanocone, nanotube and nanosheet are optimized and reported.

Computational details

The realistic nanocone, nanotube and nanosheet of AgF are simulated and optimized successfullyusing Gaussian 09 package [16]. In this work, Becke's three-parameter hybrid functional in combination with Lee-Yang-Parr correlation functional (B3LYP), LanL2DZ basis set has been usedin DFT method. The atomic numbers of silver and fluorine are forty seven and nine respectively. The significant criteria for simulating AgF nanostructure is the selection of suitable basis set.The LanL2Dz basis set is a better choice among others which gives more accurate results with a pseudo potential approximationfor AgF nanostructures [17-19]. The HOMO-LUMO gap and density of states (DOS) spectrum of nanocone, nanotube and nanosheet for anionic, cationic and neutral AgF nanostructures are calculated through Gauss Sum 3.0 package [20]. While optimizing AgF nanostructures, the convergencein the order of 10^{-5} eV is achieved.

Results and discussion

The prime focus of the work is on binding energy (BE), HOMO-LUMO gap, calculated energy, point group, dipole moment and embedding energy (EE) of anionic, neutral and cationic state of AgF nanostructures in three forms namely nanocone, nanotube and nanosheet. Figure 1 (a), Figure 1 (b) and Figure 1 (c) represents AgF nanocone, AgF nanotube and AgF nanosheet respectively.In that order, all the three forms of AgF nanostructure have equal number of ten silver atoms and ten fluorine atoms to form nanocone, nanotube and nanosheet like structures.

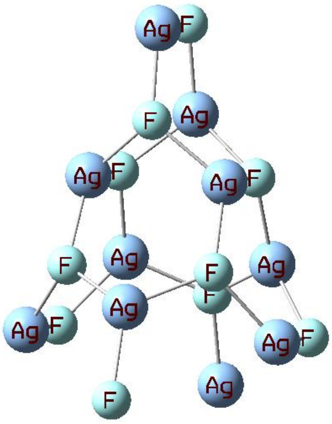


Figure.1(a) Structure of AgF nanocone

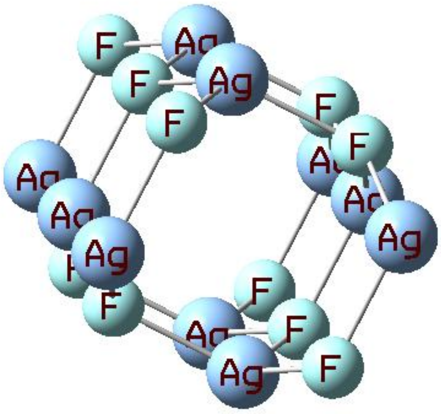


Figure.1(b) Structure of AgF nanotube

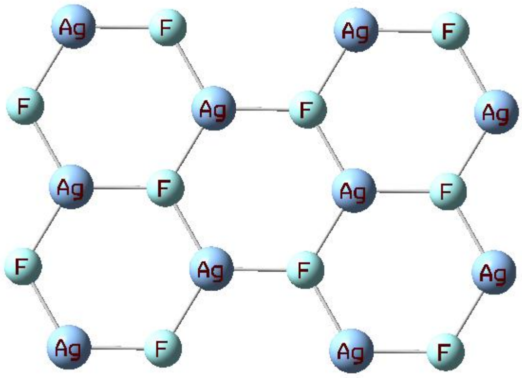


Figure.1(c) Structure of AgF nanosheet

Table.1 Calculated energy, point symmetry and dipole moment of AgF nanostructures

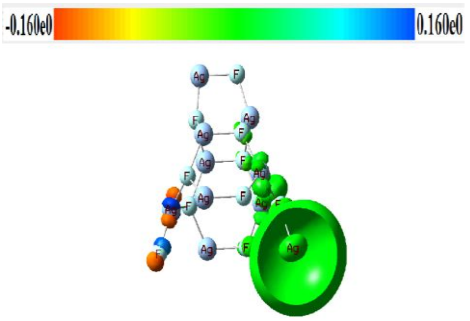
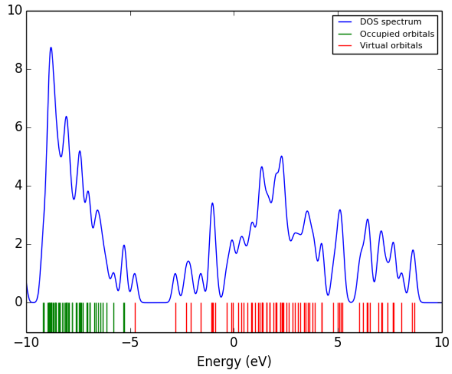
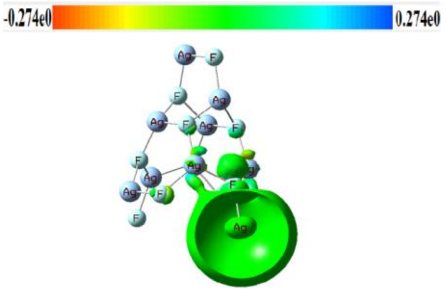
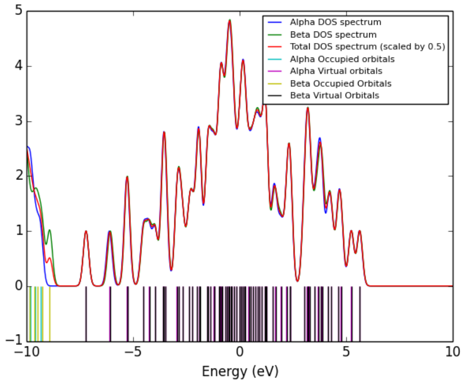
Nanostructures	Energy (Hartrees)	Dipole moment (Debye)	Point Group
AgF neutral nanocone	-2456.44	7.77	C_S
AgF cationic nanocone	-2456.18	3.73	C_S
AgF anionic nanocone	-2456.55	9.03	C_S
AgF neutral nanotube	-2456.49	0	C_{2H}
AgF cationic nanotube	-2456.21	0	C_{2H}
AgF anionic nanotube	-2456.55	0	C_{2H}
AgF neutral nanosheet	-2456.63	16.61	C_{2V}
AgF cationic nanosheet	-2456.37	4.26	C_{2V}
AgF anionic nanosheet	-2456.72	1.62	C_{2V}

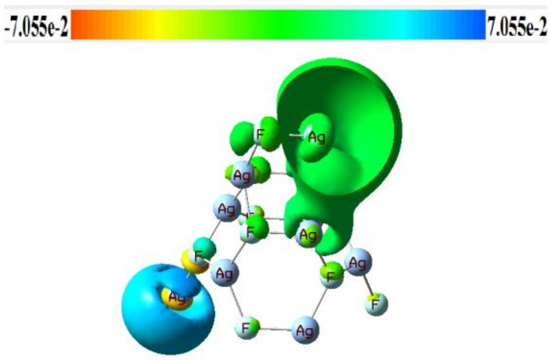
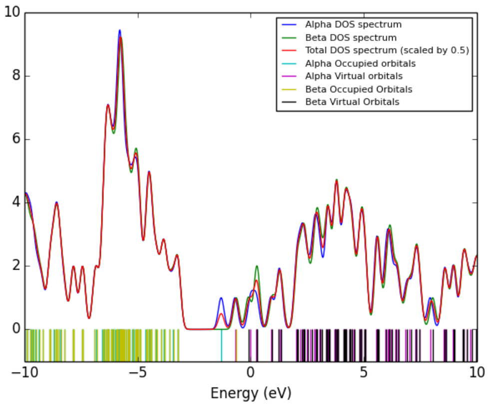
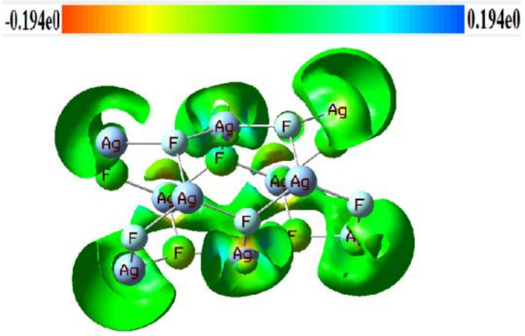
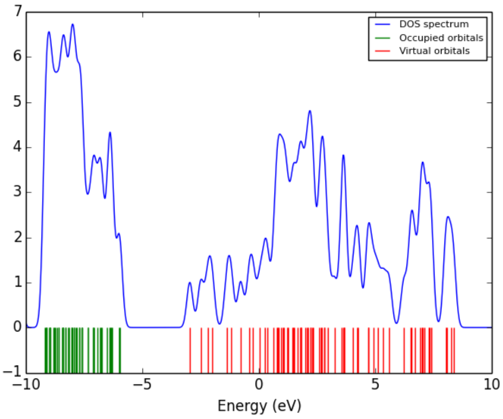
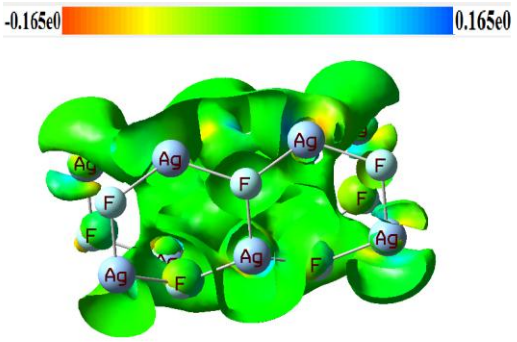
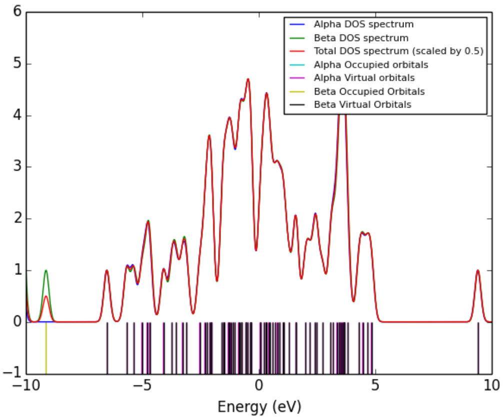
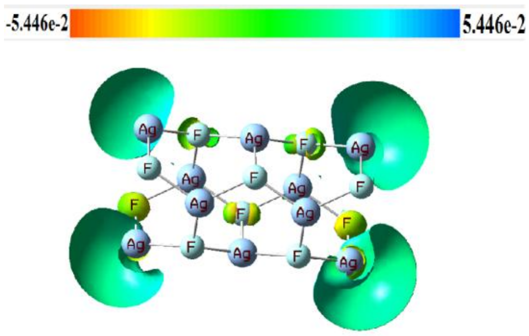
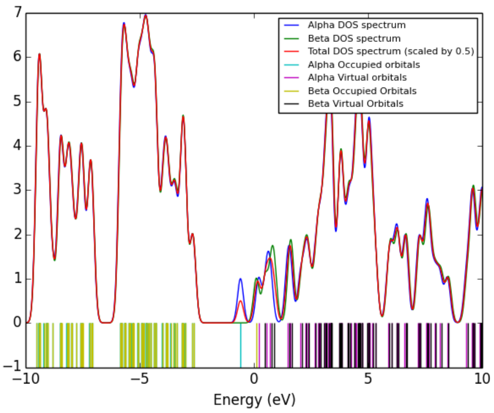
The structural stability of AgF nanostructures can be described by calculated energy. Table 1 represents point group, dipole moment and calculated energy of AgF nanostructure for all the three categories of neutral, cationic and anionic states. The calculated energy of AgF nanostructures is found to be around -2456 Hartrees.There is not much variation in stability of AgF nanostructure.Comparing AgF neutral nanostructure with anionic state, the stability of AgF anionic nanostructures slightly increases.Moreover, the cationic state of AgF nanostrucutres shows less stability. Dipole moment gives clear information about the arrangement of charges in AgF nanostructures.The charge distribution is not uniform in the case of nanocone and nanosheet. Since, different trends are observed in neutral, cationic and anionic AgF nanocone and nanosheet structures. In contrast, the charge distribution is perfectly uniform in the case of AgF nanotube which is found to be zero Debye.For AgF nanocone, nanotube and nanosheet the point symmetry is observed to be C_S, C_{2H} and C_{2V}respectively.

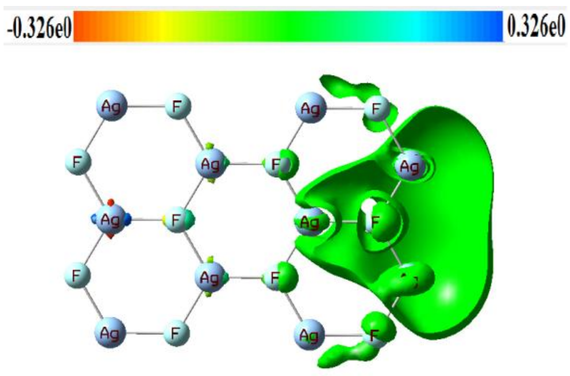
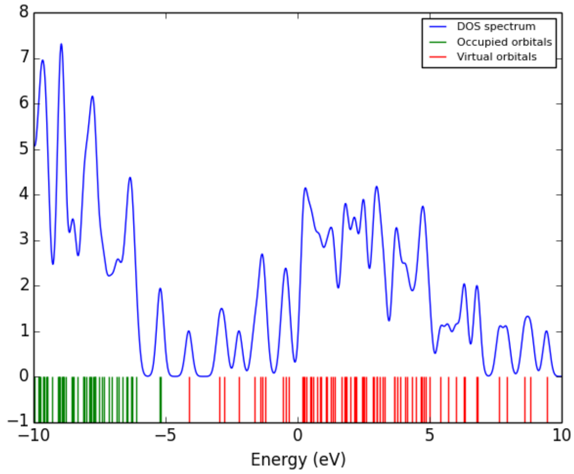
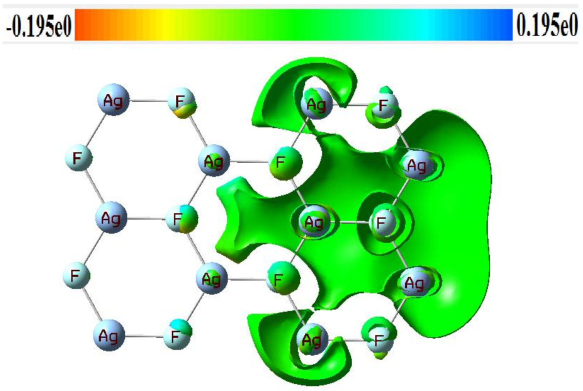
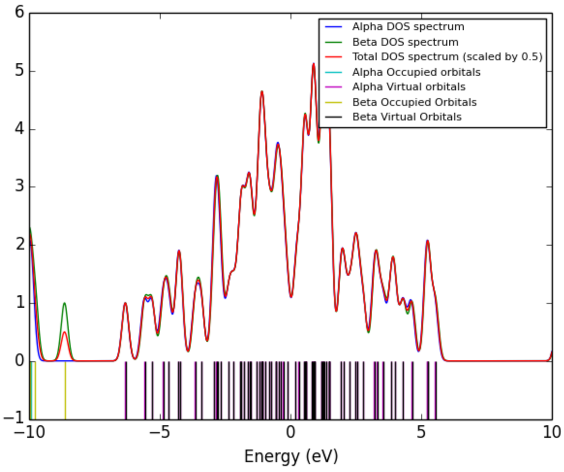
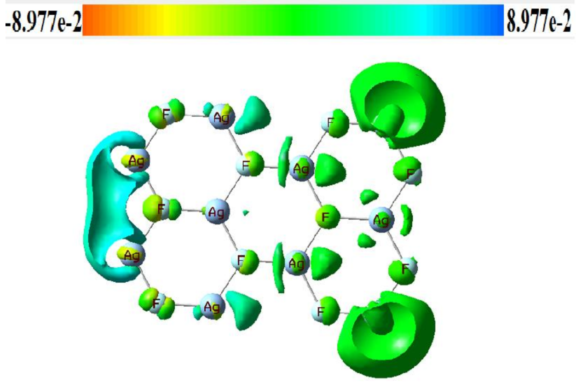
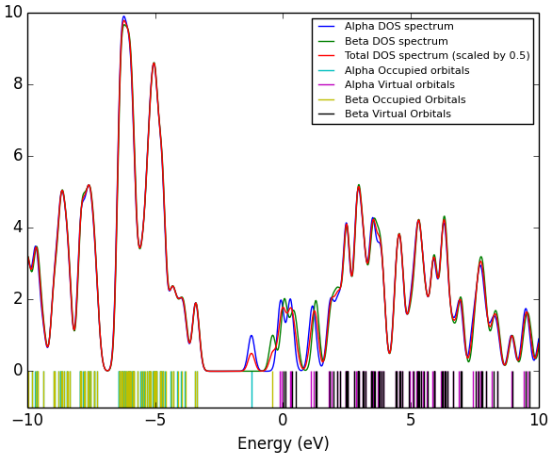
HOMO-LUMO gap of AgFnanostructures

The electronic properties of neutral, cationic and anionic AgF nanostructures can be described by lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [21,22].The alpha gap arises due to spin up electron in AgF nanostructures and beta gap arisesdue to spin down electron in AgF nanostructures. The alpha HOMO-LUMO gap of neutral, cationic and anionic AgF nanocone are 0.49, 2.14 and 0.61 eV respectively. In that order, the alpha energy gap value for AgF nanotube is 3.01, 3.67 and 0.8 eV. The corresponding alpha gap value for neutral, cationic and anionic AgFnanosheet are 1.04, 3.58 and 1.12 eV. The beta gap mainly arises due to spin down electron especially in cationic and anionic states of AgF nanostructures.From the energy gap it is inferred that AgFnanostructures exhibits semiconducting nature.The HOMO-LUMO gap variations is due to electronic configuration of Ag atom *([Kr]* $4d^{10}$ $5s^{1}$*)* and F atom *([He]* $2s^{2}$ $2p^{5}$*)*.The neutral and anionic AgF nanostructuresshows narrow band gap value which may have higher conductivity.The narrow band gap results in easy transition of electrons from HOMO level to LUMO level in neutral and anionic AgF nanostructures. In contrast, wide band gap is observed for cationic AgF nanostructures. It infers that the more energy is required to move electrons from the valence band to the conduction band.Moderate HOMO-LUMO gap values are observed for anionic state of AgF nanostructures as shown in Table 2.Table 2 represents the density of states (DOS) and visualization of the HOMO - LUMO gap along with electron density.The conductivity of AgF nanostructures mainly depends on the concentration of electron in the conduction band. As a result, DOS spectrum clearly reveals that the density of charges is low in occupied orbital than virtual orbital owing to the orbital overlapping of Ag atoms and F atoms in the nanostructure. The geometry of AgF nanostructure is also one of the reasons for more density of chargesin virtual orbital than occupied orbital. Visualization of electron density also proves that the band gap of AgF nanostructure decreases in a neutral state of nanocone and nanosheetAgF nanostrcutres owing to the high value of electron density recorded. In contrast, the neutral state of AgF nanotube has a low value of electron density, which implies that the energy gap gets widened due to the geometry of the nanotube structure.Interestingly, the band gap of AgF nanostructure becomes narrow in the case of anionic state even for low electron density. Consequently, the gap between the valence band and conduction band get widened even at a high electron densityin the case of cationic state. Thus, the conductivity of AgF nanostructure can be described only after observing the electron density, HOMO – LUMO gap and geometry of the structures.

Table. 2 Density of states and HOMO-LUMO gap with electron density of AgF nanostructures

Nano Structures	**Visualization of Electron density**	**E_g (eV)**	**HOMO, LUMO and DOS Spectrum**
AgF neutral nanocone		0.49	
AgF cationic nanocone		2.14	

AgF anionic nanocone		0.61	
AgF neutral nanotube		3.01	
AgF cationic nanotube		3.67	
AgF anionic nanotube		0.8	

AgF neutral nanosheet		1.04	
AgF cationic nanosheet		3.58	
AgF anionic nanosheet		1.12	

Binding energy and Embedding energy of AgF nanostructures

The binding energy (BE) of AgF nanostructures can be described by equation (1)

BE= [(n *E(Ag) +n * E(F) – n * E(AgF)] /n ------------ (1)

where E(Ag), E(F) and E(AgF) are the energies of Ag atom, F atom and AgF nanostructures respectively, and 'n' refer the number of atoms in AgF nanostructures. Binding energy is one the most significant key factor to analyzethe structural stability of AgF nanostructures [23-25].The BE of AgF nanostructures is found to be in the range of 18.0 – 18.79 eV. Thus, the high value of AgF binding energy implies that the AgF nanostructures are more stable.

Embedded energy (EE) gives the clear insights to embed foreign atoms in AgF nanostructures. EE can be calculatedby the equation (2).

EE= [(n * E(Ag) + n * E(F) – n * E(AgF)] --------------- (2)

The embedding energy of AgF nanostructures is found to have high value in the range of 361 – 375 eV.The high value of EE infers that to embed impurities in AgF nanostructures is difficultand the structuresare also stable. Figure 2 depicts both embedding energy and binding energy of AgF nanostructures. Almost same trends have been observed for both EE and BE as shown in Figure 2.

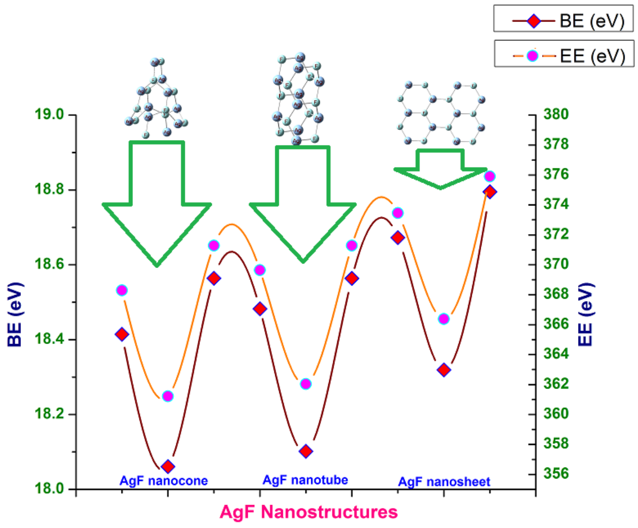


Figure. 2 BE and EE of AgF nanostructures

Conclusion

DFT method is utilized to study neutral, anionic and cationic AgF nanocone, nanotube and nanosheet. AgF nanostructures are optimized using B3LYP /LanL2DZ basis set. The electronic properties of AgF nanostructures are discussed in terms of HOMO-LUMO gap and density of states spectrum.The structural stability of all the three states, namely neutral, cationic and anionic AgF nanostructures are discussed using binding energy and calculated energy. Point group and dipole moment ofnanotube, nanocone and nanosheet AgF nanostructures are also reported.The present work gives the insights to the tailor AgF nanostructures with increased stability and electronic properties.

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