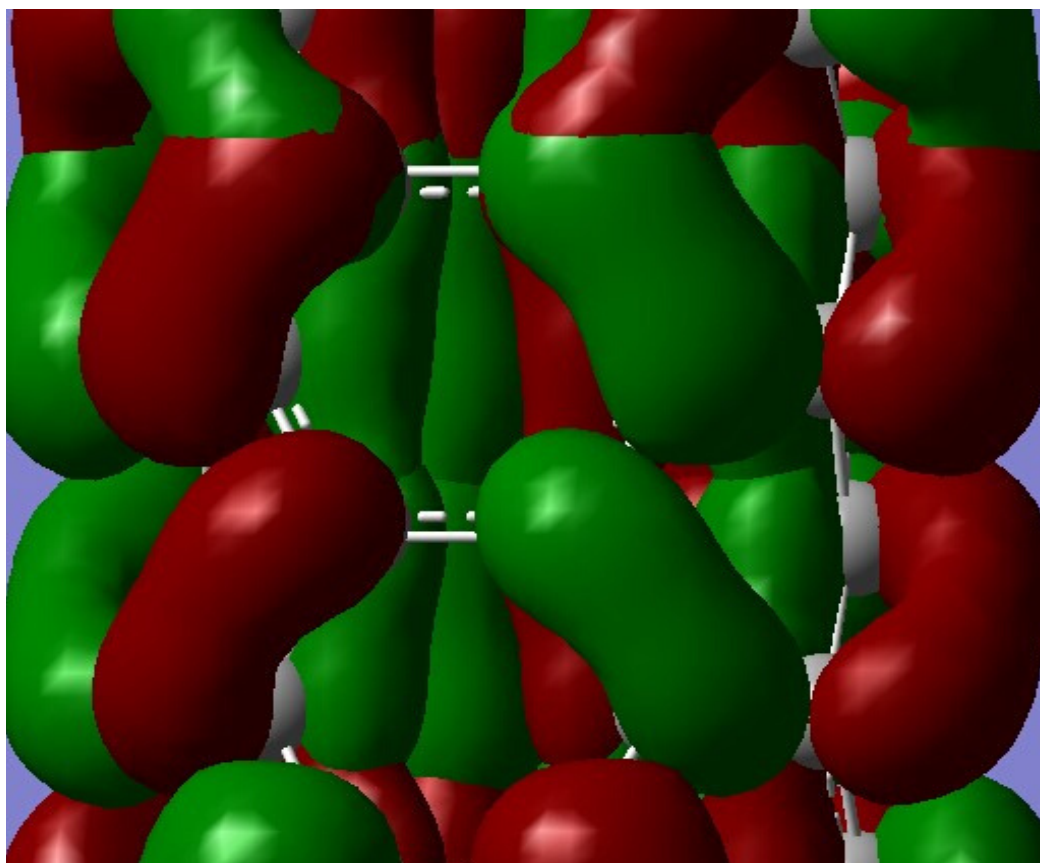


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# DFT study on detection of toxic gases

Research Article

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**Abstract:** Silicon Carbide nanocones have good mechanical properties and are used in detection of toxic gases. Most of toxic gases are colorless, odorless and tasteless. It is not easy to have timely alertness to their presence. Study of interaction of toxic gases CO, NO, etc. with silicon carbide nanocone tips might help develop detection and removal techniques for these toxic gases upto the precision of single molecule. A systematic study of SiC nanocones of disclination angle  $240^\circ$  with pentagonal tip geometry and CO and NO gas molecules using finite cluster approximation is presented. Following optimization with Density functional theory approach, B.E. per atom, HOMO-LUMO gap, bond length, electron transfer and orbital change were calculated. Changes in B.E. per atom, HOMO-LUMO gap, bond length, electron transfer and orbital etc. help in determination of interaction of a toxic gas with nanocone. Binding energy of SiC nanocones is increased with increasing size, HOMO-LUMO gap showed oscillatory pattern and Dipole moment is increased with increasing size. And when toxic gases approached SiC nanocone, binding energy of the interacting system decreased extremely. Other electronic properties are also changed for interacting system. All these comparison suggested that SiC nanocone can be a promising gas sensor.

**Keywords:** Carbon Nanocones • Toxic Gases • DFT • LANL2DZ

## 1. Introduction

Nanocones have been firstly identified as the closing caps of carbon nanotubes; however, they have been subsequently synthesized as free standing structure [1]. Nanocones can be very useful in applications as atomic forces microscopy and scanning tunneling microscopy probes. Nanocone arrays have exhibited enhanced absorption due to superior anti-reflection properties over a large range of wavelength and angles of incidence [2]. This also suggests the application of nanocones as promising nanostructure to enhance the solar cell energy conversion[3]. Carbon nanocones have been used to cap ultrafine gold needles. Such needles are widely used in scanning probe microscopy owing to their high chemical stability and electrical conductivity. But their tips are prone to mechanical wear due to the high plasticity of gold. Adding a thin carbon cap mechanically stabilizes the tip without sacrificing its other properties. Arrays of gold nanocones have been fabricated by the nanotransfer printing (nTP) method and utilized those nanocones for field emission. Nanocones of different materials such as carbon, silicon

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carbide, graphene, aluminium nitride, etc. show extreme sensitivity to some gaseous molecules. Thus there is great application of nanocones as gas sensors. It is expected that Silicon Carbide nanocone could be a promising gas sensor for detecting the toxic gases like formaldehyde, carbonmonoxide, hydrogen cyanide, etc. Theoretical studies have shown that Silicon Carbide nanocones have better reactivity than carbon nanocones due to their polar nature [4]. SiC nanocones has good mechanical properties including high temperature strength, thermal shock resistance, low density, oxidation resistance, low thermal expansion and high thermal conductivity.

The electronic properties of nanocones depends on disclination angles, size of the nanocone clusters and the structure of edge of the nanocones [5]. The disclination angles of nanocones can be noticed as a result of the removal of a segment from a flat sheet. Various computational and experimental works have examined the possibilities and stabilities of nanocones of different materials. Carbon nanocones were observed by the first time in 1992 as caps at the ends of the nanotubes just after the discovery of nanotubes and also as free standing structures two years latter. Since that time, similar structures with B and N instead of C atoms have been proposed and also experimentally observed [6].

## 2. Methodology

There are two approaches of modeling a nanocones. One is cutting out a sector of different angles from the graphitic sheet and then wrapping it seamlessly. Another approach is introducing a number of pentagonal defects in the hexagonal graphitic sheet. At first smallest nanocones of certain disclination angles are constructed and nanocones are grown by attaching silicon or carbon atoms in order to construct nanocones of desired size. The open ends of all the nanocones are passivated by hydrogen atoms to avoid instability of the edges of the nanocones due to the unsaturated bonds. The open nanocone can be modeled as a wrapped graphene-like sheet. To have strain-free, seamless wrapping, a sector has to be cut out of the sheet. That sector should have an angle of  $n \times 60^\circ$ , where  $n=1-5$  and thus, the resulting cone angle has only certain discrete values  $\theta = 2\sin^{-1} (1-n/6) = 19, 39, 60, 84, 113$  degrees. A nanotube is a nanocone with a cone angle of  $0^\circ$ . When a section of  $60^\circ$  is cut out and cone sheet is wrapped to form a nanocone of cone angle  $113^\circ$ , the cone has one pentagon at its apex. The pentagonal defect in the structure leads to the construction of either carbon-rich or silicon-rich nanocones. Similarly, if the cutout sector is  $120^\circ$ , the nanocone has a rhomboic defect at its apex. Because of this even-numbered ring at the apex, the number of silicon atoms and carbon atoms are equal. This scheme of constructing nanocones leads to a problem in the cases of nanocones of disclination angles of  $240^\circ$  and  $300^\circ$ . The defects at the apices of nanocones of disclination angles  $240^\circ$  and  $300^\circ$  are a dimer and a single atom, respectively. Such apices mightnot be energetically favourable due to unavoidable dangling bonds at the apices of the nanocones. Therefore the nanocones with disclination angle  $240^\circ$  and  $300^\circ$  are modeled in such a way that they have only pentagonal defects at their apices. The disclination of nanocone structure corresponds to the presence of a given number of pentagonal defects at or around nanocone apices. When a pentagonal defect is introduced in a two dimensional

graphitic sheet, a disclination angle of  $60^\circ$  is produced. In general, if  $n(n=1-5)$  pentagon replace the hexagonal rings in a graphitic sheet; a nanocone of disclination angle  $n \times 60^\circ$  is formed.

Thus nanocones of disclination angle  $240^\circ$  are constructed with pentagonal defects only because of the problem with unavoidable dangling bonds at the apices of the nanocones.

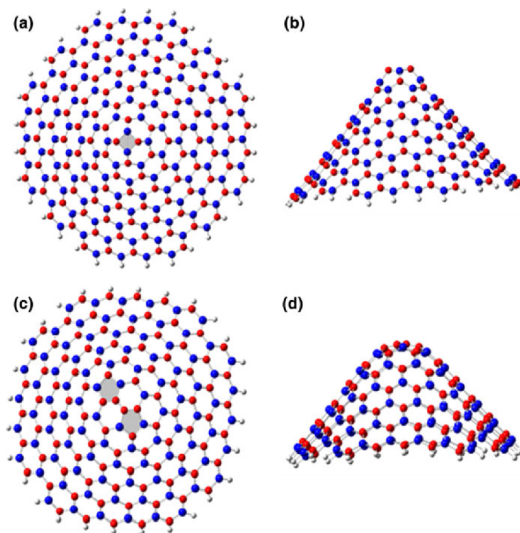


Figure 1. (a) Top view of nanocone with rhombohedral tip, (b) Side view of nanocone, (c) Top view of nanocone with two pentagonal defects at the tip, and (d) Side view of the nanocone [7].

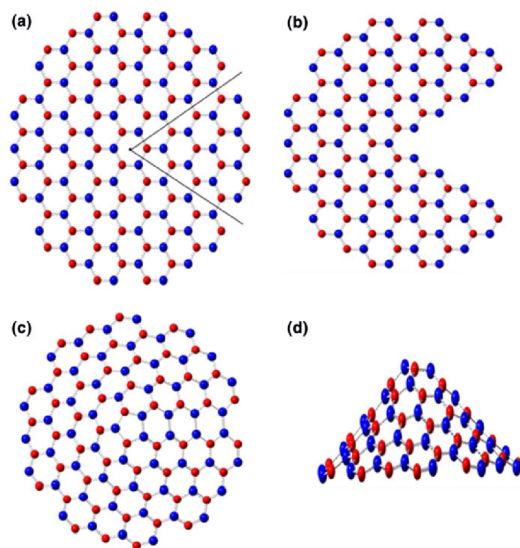


Figure 2. (a) Modeling of a SiC nanocone by cutting a section of a two-dimensional graphene-like sheet and wrapping the cone sheet, (b) Forming a nanocone, (c) Top view, and (d) Side view. Red and blue atoms represent carbon and silicon atoms, respectively [7].

### 3. Results and Discussion

The input geometries of SiC nanocones with  $240^\circ$  disclination angle and pentagonal tip structure containing equal number of carbon and silicon were optimized in 3-21G\* standard basis set. Later we adopted LANL2DZ standard basis set for the calculation regarding interaction of toxic gases with SiC nanocone because of high computational cost of 3-21G\* basis set within our approach. Various studies were performed using LANL2DZ basis set and it is quite reliable for the study of structures made up of silicon carbide [8]. In order to study interaction of SiC nanocone and toxic gases we selected  $\text{Si}_{22}\text{C}_{22}\text{H}_{10}$  nanocone and CO and NO gases. Despite of higher stability of larger nanocones, they took much more time for optimization. Thus for a cost effective and systematic study  $\text{Si}_{22}\text{C}_{22}\text{H}_{10}$  nanocone is chosen. Table 1 shows the variation of binding energy per atom( $E_b$ ), HOMO-LUMO gap( $E_g$ ) and dipole moment(D.M.) with increasing size of nanocone by using 3-21G\* standard basis set.

Table 1. B.E. per atom( $E_b$ ), HOMO-LUMO gap( $E_g$ ) and dipole moment(D.M.) of SiC nanocones

Stoichiometry	No. of atoms	$E_b$ (eV)	$E_g$ (eV)	D.M.
$\text{Si}_6\text{C}_6\text{H}_6$	18	4.18	3.06	3.23
$\text{Si}_{11}\text{C}_{11}\text{H}_8$	30	4.46	2.38	4.55
$\text{Si}_{13}\text{C}_{13}\text{H}_8$	34	4.55	2.27	5.79
$\text{Si}_{20}\text{C}_{20}\text{H}_{10}$	50	4.74	2.23	6.79
$\text{Si}_{22}\text{C}_{22}\text{H}_{10}$	54	4.79	1.86	9.76
$\text{Si}_{27}\text{C}_{27}\text{H}_{12}$	66	4.85	2.24	6.68
$\text{Si}_{31}\text{C}_{31}\text{H}_{12}$	74	4.91	1.87	11.74
$\text{Si}_{40}\text{C}_{40}\text{H}_{14}$	94	4.99	2.14	10.65
$\text{Si}_{44}\text{C}_{44}\text{H}_{14}$	102	5.03	1.19	19.24
$\text{Si}_{55}\text{C}_{55}\text{H}_{16}$	126	5.09	1.47	19.16

The HOMO-LUMO gap is the energy involved when an electron shifts from the highest occupied molecular orbital(HOMO) to the lowest unoccupied molecular orbital(LUMO) and vice-versa. Table 1 reveals that HOMO-LUMO gap decreases with increasing size of nanocone but does not depend only on the size. Previous studies found that HOMO-LUMO gaps of all nanocones have oscillatory pattern with respect to the size of the cluster [5]. The oscillation in the HOMO-LUMO gap is due to the difference in edge structure of the nanocones when we gradually increase the size of the nanocone or cluster. Study of HOMO-LUMO orbital indicates that reactivity is more towards the opening end and tip of nanocone (Figs. 3(a) 3(b)).

Charge distribution for SiC nanocones have also been studied using LANL2DZ basis set (Fig. 3(c)). Here silicon acquired positive and carbon acquired negative charge. Least positively charged silicon atom lies at the tip and amount of charge carried by each silicon atom is increasing on going towards the middle part and becomes maximum there. It is decreased on the opening ring which is saturated by hydrogen. Similarly least negatively charged carbon atoms are towards the tip and amount of negative charge is maximum in middle part which is decreasing on going towards the opening end. Dark green colored hydrogen at opening are positively charged

while black colored hydrogen are negatively charged.

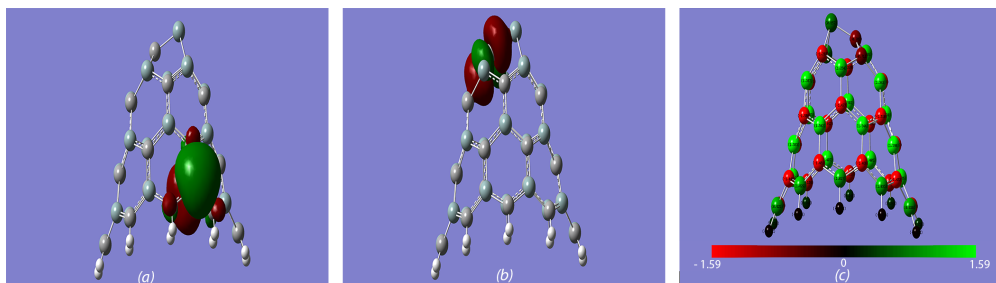


Figure 3. (a) HOMO, (b) LUMO, and (c) Charge distribution of nanocone  $\text{Si}_{22}\text{C}_{22}\text{H}_{10}$

It is found that B.E. per atom for CO molecule (4.66 eV) is greater than that for NO molecule (2.52 eV). This shows that CO is more stable than NO. Similarly, HOMO-LUMO gap of CO molecule (9.12 eV) is higher than the HOMO-LUMO gap of NO molecule (2.93 eV). But dipole moment of CO molecule (0.03 Debye) is less as compared to that of NO molecule (0.09 Debye). Also bond length of CO molecule (1.17 Å) is less than the bond length of NO molecule (1.20 Å). All these comparison between CO and NO molecules indicate that CO is more stable structure than NO. In CO molecule carbon atom is positive charge and oxygen atom is negatively charged (Fig. 4(a)). Likewise, in NO molecule nitrogen atom carry positive charge while oxygen carry equal amount of negative charge (Fig. 4(b)).

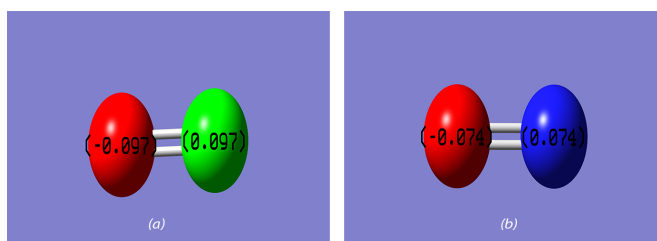


Figure 4. Charge distribution of optimized (a) CO, and (b) NO molecule. Here, red represents oxygen, green represents carbon and blue represents nitrogen respectively.

Table 2 shows that binding energy of the system for Oxygen approaching case lies within the physisorption range. But for Carbon approaching case, binding energy of the system falls slightly outside the range of physisorption. Although it is physisorption and the results suggests that CO will not be absorbed in SiC nanocone as in chemisorption. Binding energy of the interacting system is extremely less in comparison with binding energy of individual nanocone and gas. This indicates that the system becomes unstable when CO gas molecule approaches SiC nanocone. HOMO-LUMO gap of the system is very close to the HOMO-LUMO gap of nanocone.

HOMO (Fig. 5(a)) and LUMO (Fig. 5(b)) for Oxygen approaching case are towards the apex of nanocone which clearly tells that reactivity is more towards the apex. Bond length of CO molecule after optimization is not changed significantly. Bond angle between tip of nanocone and gas molecule in the input was set at  $180^\circ$

but it is decreased after optimization. In O approaching case it is seen that carbon atom gained more positive charge(0.09) but negativity of oxygen atom is slightly decreased(0.017) whereas amount of positive charge on silicon atom at the tip is also slightly decreased(0.14) (Fig. 5(c)).

Table 2. B.E. of system( $E_b$ ) in eV, HOMO-LUMO gap( $E_g$ ) in eV, dipole moment(D.M.) in Debye, bond length( $l_b$ ) of CO in angstrom, distance between tip of the nanocone and approaching atom of the gas( $l_{gn}$ ) in angstrom and bond angle between tip of nanocone and gas molecule(A) in degree.

	Optimization O approaching	C approaching
$E_b$	0.06	0.18
$E_g$	1.63	1.64
D.M.	9.51	9.45
$l_b$	1.17	1.17
$l_{gn}$	3.72	2.96
A	110.57°	139.06°

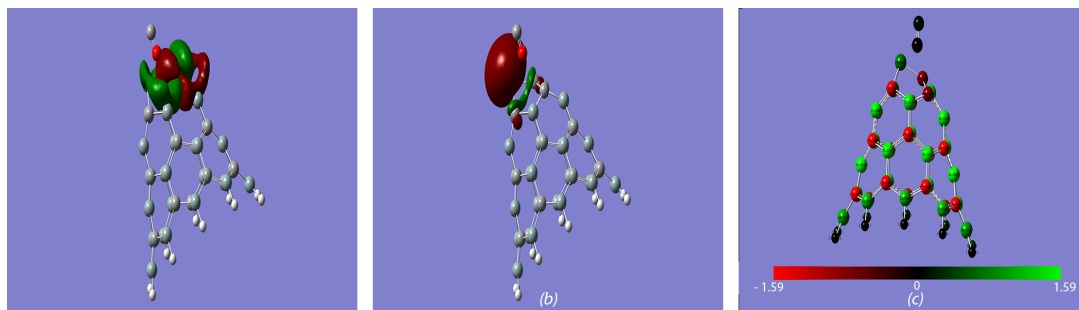


Figure 5. (a) HOMO, (b) LUMO, and (c) Charge distribution for the interaction of nanocone  $Si_{22}C_{22}H_{10}$  and CO gas molecule in O approaching case

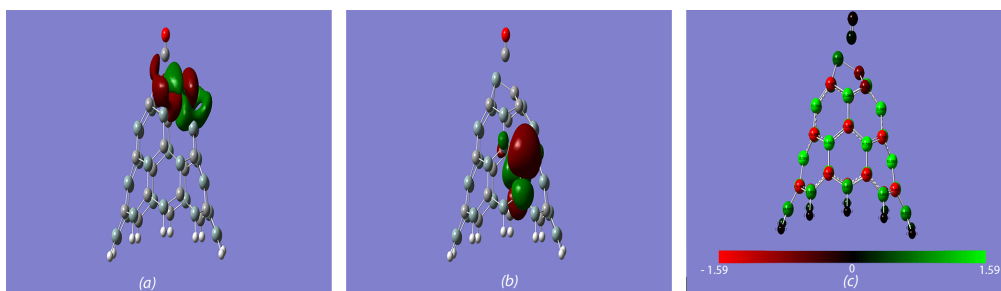


Figure 6. (a) HOMO, (b) LUMO, and (c) Charge distribution for the interaction of nanocone  $Si_{22}C_{22}H_{10}$  and CO gas molecule in C approaching case

HOMO (Fig. 6(a)) and LUMO (Fig. 6(b)) for Carbon approaching case are towards the apex of nanocone which clearly tells that reactivity is more towards the apex. In C approaching case carbon atom gained a little positive charge(0.002) but oxygen atom neither lost nor gained charge. But silicon atom at the tip of nanocone gained slightly more positive charge(0.002). (Fig. 6(c)).

In case of NO, it is seen that binding energy of the system for both the cases is outside the range of physisorption but it is physisorption phenomena. It is found that binding energy of the system is extremely low than that of nanocone and NO gas molecule. This signifies that system becomes unstable when NO gas approaches SiC nanocone. HOMO-LUMO gap of the system is also decreased. Dipole moment of system is increased which indicate the increased polarity of the system. Also bond length of NO molecule is slightly increased which because of the fact that bond strength of NO is lowered due to the influence of nanocone.

Study of HOMO-LUMO orbital in both Oxygen approaching and Nitrogen approaching case reveals that reactivity of the system more towards apex and middle part of nanocone than towards opening end (Figs. 7(a-b) and Figs. 8(a-b)).

Table 3. B.E. of the system( $E_b$ ) in eV, HOMO-LUMO gap( $E_g$ ) in eV, dipole moment(D.M.) in Debye, bond length( $l_b$ ) of NO in angstrom, distance between tip of the nanocone and approaching atom of the gas( $l_{gn}$ ) in angstrom and bond angle between tip of nanocone and gas molecule(A) in degree.

Optimization	O approaching	N approaching
$E_b$	0.56	0.15
$E_g$	1.41	1.76
D.M.	11.57	11.51
$l_b$	1.37	1.27
$l_{gn}$	1.76	1.86
A	129.54	123.41

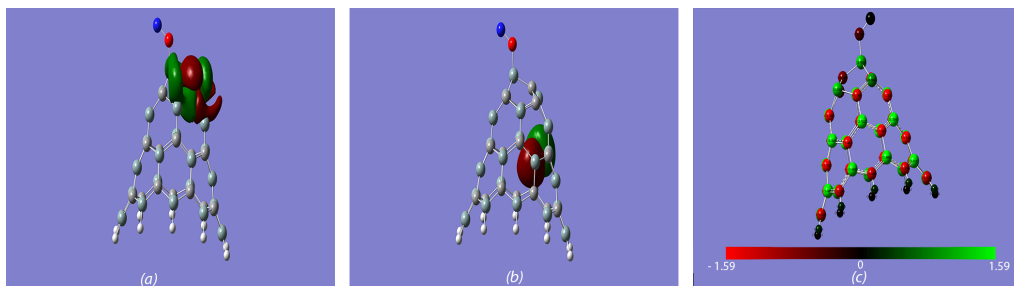


Figure 7. (a) HOMO, (b) LUMO, and (c) Charge distribution for the interaction of nanocone  $\text{Si}_{22}\text{C}_{22}\text{H}_{10}$  and NO gas molecule in O approaching case

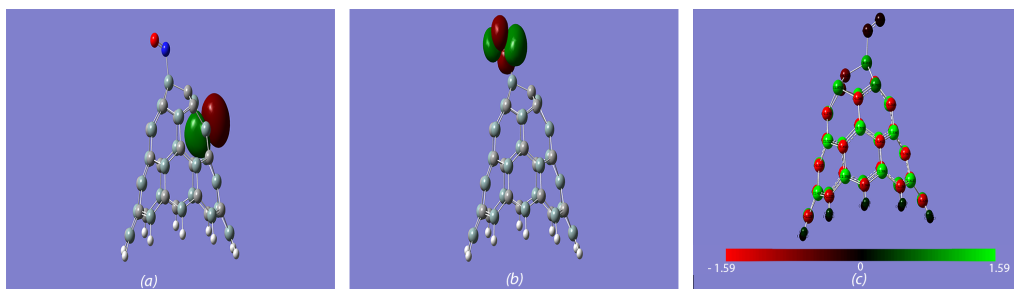


Figure 8. (a) HOMO, (b) LUMO, and (c) Charge distribution for the interaction of nanocone  $\text{Si}_{22}\text{C}_{22}\text{H}_{10}$  and NO gas molecule in N approaching case



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## 4. Conclusions

When CO and NO gas molecules approach to SiC nanocone there are significant changes in electronic properties of the system. Binding energies of the system of interaction of toxic gases and nanocone SiC indicates that, it is a physisorption process. This is favorable point for proving that SiC could be a promising gas sensor. It is strong enough to be detected and small enough to be removed the toxic gases from nanocone. After optimization there is transfer of charge among silicon atom at the tip of nanocone and atoms of gas molecule. All these changes in physical and electronic properties show that SiC nanocone can be promising gas sensor. Among two gases, NO gas can be detected effectively by a silicon carbide nanocone.

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