Properties of nitrogen on graphite and single-walled carbon nanotubes

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Introduction

We calculate the properties of several configurations that may exist in N-doped graphite and carbon nanotubes. The migration energy of N adatom and the activation energy for two N adatoms to form a N_2 molecule on the graphite surface are calculated.

Method

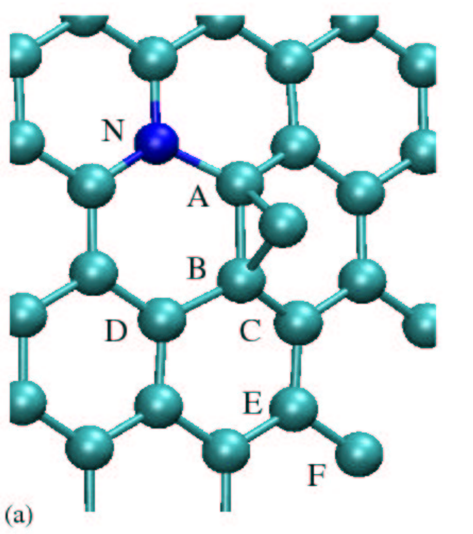
VASP code [1]:
Density functional theory with the generalized gradient approximation. Projected augmented wave potentials to describe the core electrons.

Substitutional N

System	graphite	(5, 5)	(9, 0)	(7, 0)
E_F (eV)	1.86	1.76	1.61	1.24

The formation energy $E_F = E_{(n-1)C+1N} - E_{nC}$.
The formation energy for a substitutional N atom decreases with the increase of the curvature of the tube. N atom prefers a nonplanar surrounding in graphitic materials.

Substitutional N + C Adatom



(a) a C adatom adsorbed on a N-doped graphite.

Carbon adatom forms a bridge-like structure on graphite [2]. The blue sphere is N and the green ones are C.

(b) the relative energy when the C adatom is adsorbed at different sites. The transverse coordinate is the projected distance between the N atom and the C adatom on the graphite plane.

N-A: C adatom forms bonds with atoms N and A.

A-B: C adatom forms bonds with atoms A and B.

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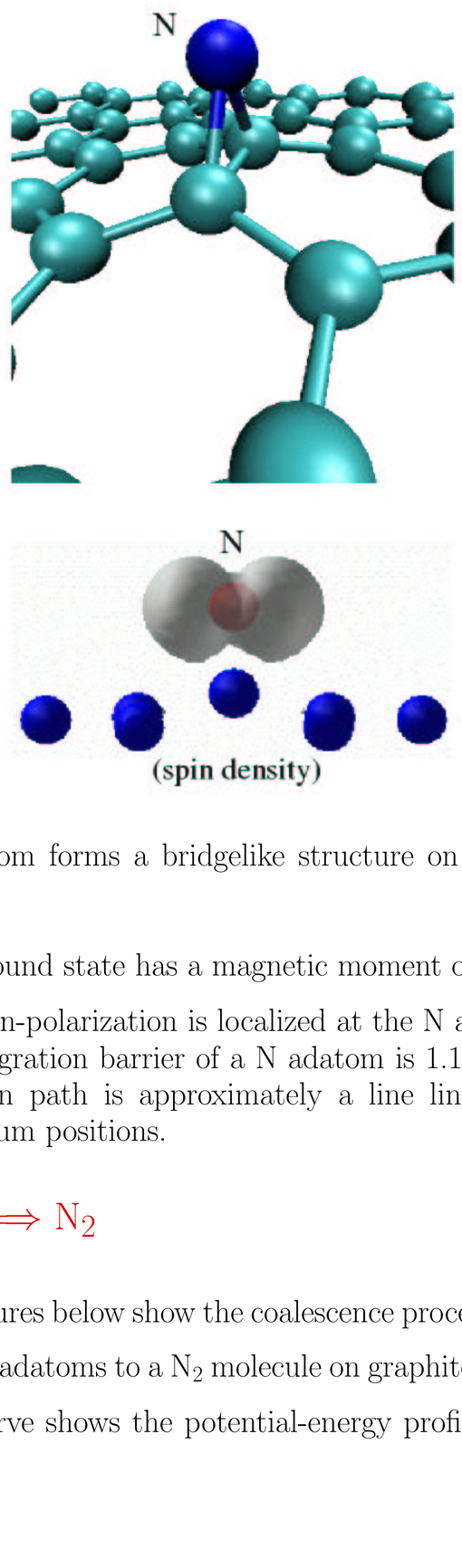
C adatom is trapped around the substitutional N atom, but could not form a bond with the N atom which is not stable.
The substitutional N could enhance the spin-polarization of the C adatom nearby.

N Adatom



N adatom forms a bridgelike structure on graphite surface.

The ground state has a magnetic moment of 0.6 μ_B.

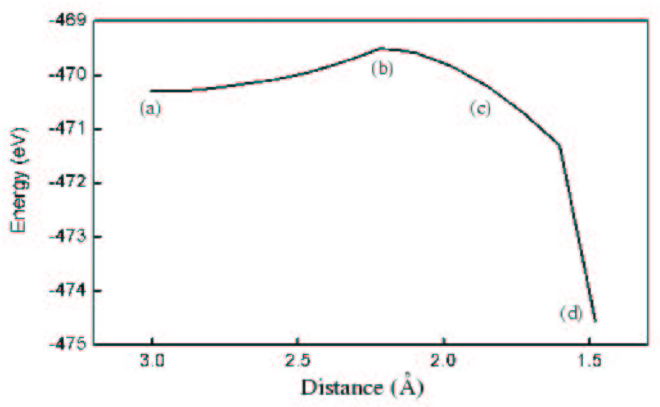
The spin-polarization is localized at the N adatom.
The migration barrier of a N adatom is 1.1 eV. The migration path is approximately a line linking two equilibrium positions.

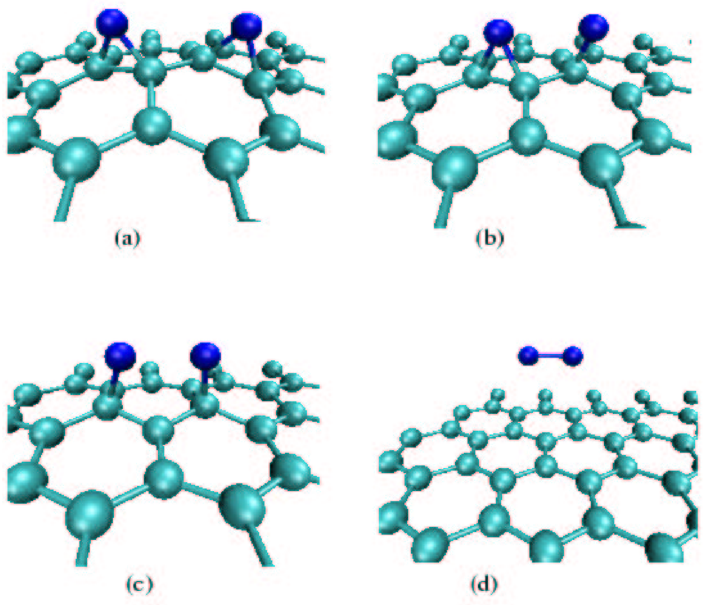
N+N $\Longrightarrow$ N_2

The figures below show the coalescence process of two single N adatoms to a N_2 molecule on graphite surface.

The curve shows the potential-energy profile during the coalescence process as a function of the projected distance between the two N atoms on the graphite plane.

The activation energy for the reaction is 0.80 eV.





(a) The local stable state just before two single N atoms coalescence. Both the N atoms form bridge-like structures with the substrate.

(b) The maximum energy state during the coalescence process. One N atom forms bridge-like structure, the other one form one bond with the substrate.

(c) The state when the distance between the two N atoms is 1.9 Å. Each N atom forms a bond with the substrate.

(d) The state when the distance between the two N atoms is 1.5 Å. A N_2 molecule is formed and leaves the graphite surface. (The bond length of a free N_2 molecule is 1.11 Å).

References

[1] G. Kresse and J. Furthmüller, PRB 54, 11169 (1996)

[2] P. O. Lehtinen, *et al.*, PRL 91, 017202 (2003).