



AIX-MARSEILLE UNIVERSITY

INTERNSHIP REPORT

**A "Configuration Coordinate
Diagram" study of defects in
semiconductors : the case of C
substitutional atom in hexagonal
Boron Nitride monolayer**



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25 Avril 2022 — 03 Juin 2022

1 Introduction

This internship took place at the "Physique des Interactions Ioniques et Moléculaires" (PIIM) laboratory, which is a joint research unit between the CNRS and Aix-Marseille University located in campus St.Jérôme Marseille. In particular I have been hosted by the team H2M (Hydrogène, Molécules, Matériaux). Here physicists and chemists focus their interests on two main research areas : molecules of interest for biology, astrochemistry and the atmosphere, and on extended materials of interest for magnetic fusion and more in general for optoelectronic applications.

In order to study and characterize such systems, they use different experimental techniques, like infrared, visible-UV, Raman and mass spectroscopy, electron, atomic force and confocal microscopy, and theoretical approaches, as ab initio methods based on Density Functional Theory and Many-Body Perturbation Theory.

This internship is the natural continuation of my two Science Watch projects. During this internship, we studied the electronic structure of a two-dimensional crystal lattice consisting of two atoms, Boron and Nitrogen, arranged to form a monolayer of hexagonal Boron Nitride (see Fig. 1) a 3D layered system isostructural to graphite but with very different electronic properties. Both the 3D and the 2D structure of hBN have a large band gap (>4 eV).

hBN has recently attracted a lot of interest because of its property of emitting light in ultraviolet energy range and as a consequence it can be employed for UV lamps, for disinfecting medical equipments, detecting forged banknotes or disinfecting air/water.

Perfect materials simply do not exist : every material contains defects. At crystal lattice level a defect is a local break in its periodicity.

In our case, we will study a monolayer of hBN. Starting from the pristine lattice we create a defect by replacing one Nitrogen atom with a Carbon, in its neutral form and charged one (by adding an extra electron to the system). This kind of charge capture process can be addressed by the configuration coordinate diagram which allows to reduce the multi-dimensional problem into a one-dimensional one. We will extract all the ingredients that we need to build our configuration coordinate diagram from Density Functional Theory (DFT) calculations.

In section 2 we present the direct and reciprocal lattices of monolayer hBN. In section 3, we will introduce the many-body problem and the Born-Oppenheimer approximation. In section 4, we will present DFT. Section 5 will be devoted to the discussion and interpretation of the results that we obtained. The conclusions will close the report.

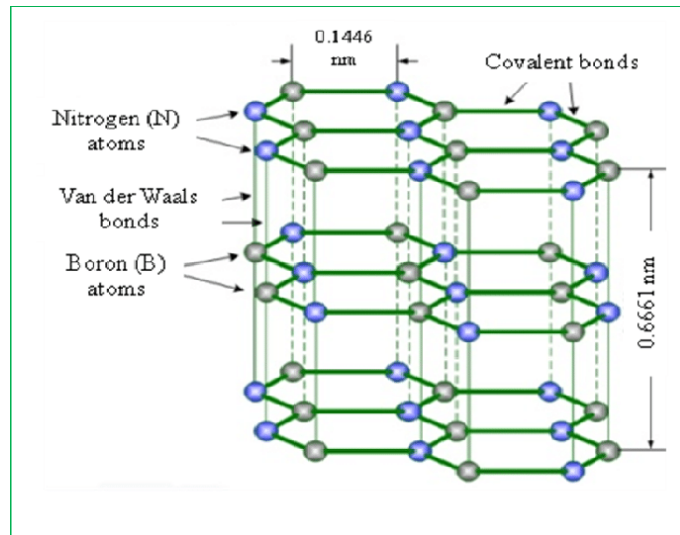


FIGURE 1 – Layered structure of hexagonal Boron Nitrides. Layers are weakly interacting through Van der Waals forces.

2 Bravais lattice, reciprocal lattice, Brillouin zone

A perfect, pure, and flawless crystal is made up of a "basic pattern" (the basis), which can be an atom or molecule, repeated periodically in space. It is completely specified by the types and positions of the nuclei (composing the basis) in the primitive unit cell, and the rules that describe the repetition. The set of points obtained by repeating the basis is a lattice of points in space called Bravais lattice. Since we are interested in a monolayer of hBN and because of its hexagonal symmetry and being bidimensional, our basis is composed of two atoms, a Boron and a Nitrogen atom (see Fig.2), arranged to form an honeycomb crystal structure.

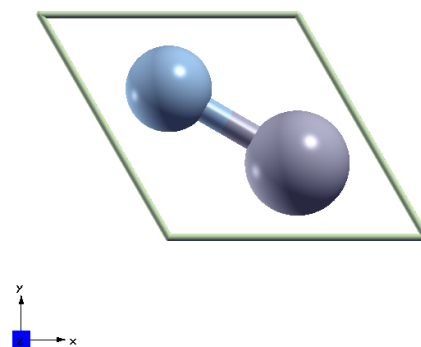


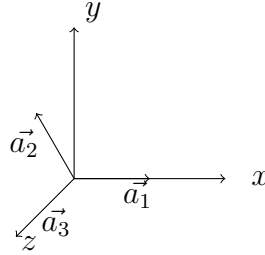
FIGURE 2 – Unit cell with Boron and Nitride atoms

The nodes of the Bravais lattice are located using a linear combination of two basis vectors \vec{a}_1, \vec{a}_2 , called primitive vectors of the lattice

$$\vec{R} = m_1 \vec{a}_1 + m_2 \vec{a}_2. \quad (1)$$

The cell parameter along the \vec{a}_1 is equal to $a = 4.717737$ a.u. Since we are simulating just a monolayer, it means that our system will be periodic on the xy plane and "isolated" along z. Anyway our simulation box will be three-dimensional, with enough vacuum along the z direction. The amount of vacuum is a parameter that will be checked later. The vector basis in crystal coordinates (with respect to the cell parameter a) are

$$a(1) = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, a(2) = \begin{pmatrix} -0.5 \\ 0.866025 \\ 0 \end{pmatrix}, \text{ et } a(3) = \begin{pmatrix} 0 \\ 0 \\ 2.605231 \end{pmatrix}.$$



While atoms are settled in their crystal positions : $B = \begin{pmatrix} 2 \\ 3 \\ 3 \\ 3 \\ 1 \\ 2 \end{pmatrix}$ and $N = \begin{pmatrix} -\frac{2}{3} \\ \frac{1}{3} \\ -\frac{1}{3} \\ \frac{1}{2} \end{pmatrix}$,

By multiplying the lattice vectors by the lattice parameter $a = 4.717737$ a.u. we obtain :

$$a(1) = \begin{pmatrix} 4.717737 \\ 0 \\ 0 \end{pmatrix}, a(2) = \begin{pmatrix} -2.3588685 \\ 4.085678185 \\ 0 \end{pmatrix}, \text{ and } a(3) = \begin{pmatrix} 0 \\ 0 \\ 12.29079468 \end{pmatrix}.$$

Here are the vectors of the primitive cell in cartesian coordinates and in a.u.

We now want to calculate the vectors of the reciprocal space lattice. Since the Bravais lattice is periodic, the potential felt by the electrons (related to the presence of ions of the lattice acting on the electron) has the same periodicity

$$V(\vec{r} + \vec{R}) = V(\vec{r}), \quad (2)$$

where \vec{R} is defined by Eq.(1). It can be written in the form of a Fourier series because it is periodic :

$$V(\vec{r}) = \sum_{\vec{K}} V(\vec{K}) e^{i\vec{K} \cdot \vec{r}}. \quad (3)$$

From Eq. (2) we have that

$$\sum_{\vec{k}} V(\vec{K}) e^{i\vec{K} \cdot (\vec{r} + \vec{R})} = \sum_{\vec{k}} V(\vec{K}) e^{i\vec{K} \cdot \vec{r}}. \quad (4)$$

This leads to

$$e^{i\vec{K} \cdot \vec{R}} = 1 \quad (5)$$

and therefore to

$$\vec{K} \cdot \vec{R} = 2\pi n \quad (6)$$

where n is a integer. The vectors \vec{K} are

$$\vec{K} = l_1 \vec{b}_1 + l_2 \vec{b}_2 + l_3 \vec{b}_3. \quad (7)$$

The existence of a lattice in direct space (the space of positions), implies the existence of a lattice in wave vector space \vec{k} , called reciprocal space. The basis vectors of the reciprocal lattice are the vectors \vec{b}_j defined by

$$\vec{b}_j = \frac{2\pi\delta_{ij}}{a_j} \quad (8)$$

Most physical properties of solids are calculated in wave vector space using the reciprocal lattice. The vectors \vec{K} belong to wave vector space, they characterize the periodicity of the reciprocal lattice.

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \wedge \vec{a}_3}{\Omega} \quad (9)$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \wedge \vec{a}_1}{\Omega} \quad (10)$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \wedge \vec{a}_2}{\Omega} \quad (11)$$

With Ω is the volume

$$\Omega = \vec{a}_1 \cdot (\vec{a}_2 \wedge \vec{a}_3) = 236.9071(a.u.)^3 \quad (12)$$

in our case.

So we can calculate the values of the reciprocal lattice in crystal coordinates (coordinates with respect to the lattice parameters) :

if we divide by $2\pi \cdot 4.717737$ we obtain $\vec{b}_1 = \begin{pmatrix} 1 \\ 0.577350 \\ 0 \end{pmatrix}$, $\vec{b}_2 = \begin{pmatrix} 0 \\ 1.154701 \\ 0 \end{pmatrix}$, and

$$\vec{b}_3 = \begin{pmatrix} 0 \\ 0 \\ 0.383843 \end{pmatrix}.$$

Here we show the direct and reciprocal lattices of one monolayer of graphite.

As we said at the beginning the hBN and graphite are isostructural, so the reciprocal spaces are equivalent.

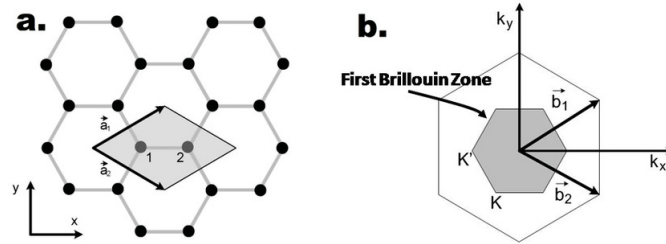


FIGURE 3 – This is graphene, a two-dimensional crystal made up of carbon atoms black dots on the left arranged in a hexagonal lattice. It has two atoms per elementary cell.

2.1 Defects : Definition

Perfect materials simply do not exist : every material contains defects. At crystal lattice level a defect is a local break in its periodicity.

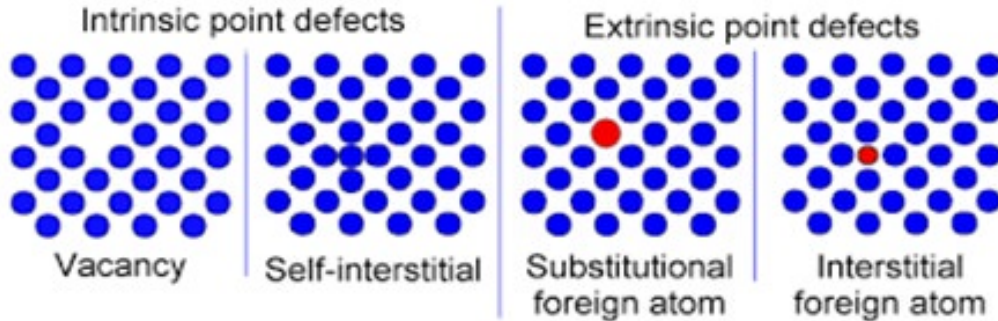


FIGURE 4 – Intrinsic and extrinsic defects

Defects can be intrinsic (when an atom is missing or is in an irregular position) or extrinsic (impurities). Impurities are unintentionally present in the growth or processing environment or intentionally introduced to tailor the properties of materials (doping of semiconductors with acceptors and donors for electronic and optoelectronic applications).

Since defects are unavoidable, the effects they have on the properties of materials merit to be studied. For example mechanic properties of a material are linked to the mobility of dislocations (function of point defects); atomic transport (diffusion) is linked to the presence of point defects. Defects with energy levels within the band gap can act as recombination centers, impeding carrier collection in a solar cell or light emission from a light-emitting diode. Sometimes, these effects can be used to our advantage : luminescence centers in wide-band-gap materials can be used to emit light at specified wavelengths.

All of these scenarios require control over the defect population. Such control, in turn, requires accurate knowledge of the mechanisms by which defects incorporate and affect materials properties. Over the past 60 years, tremendous progress has been made in the experimental and theoretical characterization of defects in semiconductors.

3 Many-body problem

A solid is made up of a very large number of atoms which themselves are made up of a heavy, positively charged central nucleus (protons + neutrons), a negatively charged core electron cloud strongly bound to the nucleus, and valence electrons, weakly bound to the nucleus. The central nucleus plus core electrons is seen as a $+Ze$ charge ion. For some materials (alkali metals), the internal degrees of freedom of the ions are not significant. The solid can therefore be seen as lattice of positive ions immersed in a valence electron gas. The system is then described by the many-body Hamiltonian

$$H = H_{el} + H_{ions} + H_{el-ions}, \quad (13)$$

$$H_{el} = - \sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}, \quad (14)$$

where $\nabla_i^2 = \partial_{x_i}^2 + \partial_{y_i}^2 + \partial_{z_i}^2$ and ϵ_0 is the vacuum permittivity. The vectors $\vec{R}_{\alpha,\beta}$ and $\vec{r}_{i,j}$ refer to the positions of ions and valence electrons respectively.

The first term corresponds to the kinetic energy of the valence electrons of mass m and the second term is the repulsive Coulomb potential between the valence electrons of charge $-e$. Here the presence of the factor $1/2$ is due to the fact that we have a double sum over the positions of the electrons, which amounts to counting each interaction twice. Then we have :

$$H_{ions} = - \sum_{\alpha} \frac{\hbar^2 \nabla_{\alpha}^2}{2M} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z^2 e^2}{4\pi\epsilon_0 |\vec{R}_{\alpha} - \vec{R}_{\beta}|}, \quad (15)$$

the first term corresponds to the repulsive energy between ions of mass M , and the second term is the attractive Coulomb potential between valence electrons and ions. The presence of the $1/2$ factor, as in H_{el} , comes from the fact that we have a double sum over the positions of the ions

$$H_{el-ions} = - \sum_{i,\alpha} \frac{Ze^2}{4\pi\epsilon_0 |\vec{R}_{\alpha} - \vec{r}_i|}, \quad (16)$$

corresponds to the attractive Coulomb potential between the electrons and the ions.

The corresponding Schrodinger equation of the system, composed of moving electrons and atoms both interacting each others doesn't have a solution. We need to introduce appropriate approximations.

3.1 Born-Oppenheimer approximation

The ions move very slowly compared to the time scale characterizing the movement of the electrons. We can therefore assume that the electrons are in the ground state for a particular configuration of the ions, this is the adiabatic approximation. It is thus possible to isolate in the Schrödinger equation the part that acts on the electronic degrees of freedom, this approximation is valid in the limit $M \gg m$. It is necessary to separate the dynamics of the electrons from the dynamics of the ions, the wave function which describes the complete system is written :

$$\Psi(\vec{r}, \vec{R}) = \Psi_{el}(\vec{r}, \vec{R}) \Phi_{ions}(\vec{R}) \quad (17)$$

where $\vec{r} = \{\vec{r}_i\}$ is the set of positions of the valence electrons and $\vec{R} = \{R_{\alpha}\}$ is the set of positions of the ions. The Born-Oppenheimer approximation consists in assuming that Ψ_{el} satisfies the Schrödinger equation :

$$(H_{el} + H_{el-ions}) \Psi_{el}(\vec{r}, \vec{R}) = E_{el}(\vec{R}) \Psi_{el}(\vec{r}, \vec{R}), \quad (18)$$

with E_{el} which depends on the configuration of the ions but not on that of the electrons. However even the solution of equation {18} is a formidable task.

4 Density Functional Theory

As in so many areas of solid-state physics, density functional theory (DFT) has emerged as the most powerful approach for assessing the properties of defects. DFT calculations, typically carried out in a supercell geometry, yield reliable information about atomic structure, vibrational properties, and allow to predict formation energies and transition levels of native defects and impurities.

These physical quantities are in tight relation with information obtained from some experimental technique. For example the nature and local structure of the defect can be identified by vibrational spectroscopy techniques. A defect modifies the vibrational spectrum of the solid. To clarify, let's consider a linear monatomic chain of atoms connected by bonds with equal force constants. If one of the host atoms is replaced by a lighter impurity, this atom and its nearest neighbors vibrate appreciably (with higher frequencies with respect to the host atoms), giving origin to localized vibrational mode (LVM). Raman spectroscopy or Fourier-transform infrared spectroscopy can detect the LVM, which can be predicted by first principles calculations.

Optical signatures of defects with high resolution can be identifying with the photoluminescence (PL) experiment. It consists in exciting electrons from the valence band to the conduction band (or alternatively from or to defect levels) with a above-gap light. Then the excited electrons emit light to transit to lower energy levels in order to conserve energy. A peak in the PL spectrum then appears. The PL intensity is measured as a function of excitation photon energy. This gives an absorption profile for the defect. The limit of this experiment is we cannot identify the nature or character of the defect. Comparison with first-principles calculations can be particularly powerful here.

To studied the electronic structure of a two-dimensional crystalline lattice consisting of two atoms, a Boron atom and a Nitrogen atom, the Nitrogen atom will be replaced by a Carbon atom, we need the Schrodinger equation. The Schrodinger equation provides all the information sought about the material, by studying the Hamiltonian. This Hamiltonian is the sum of the ionic Hamiltonian and the electronic Hamiltonian, by fixing the electrons in the material we will only study the electronic Hamiltonian, thanks to the Born-Oppenheimer approx. The complexity comes from the fact that the material contains a very large number of electrons. This is where the density functional theory comes in, with the Kohn-Sham asatz theorem, which allows us to solve a many-body problem by considering a one-body problem, where there is no interaction between the electrons and where the external potential is the same. The basic DFT theorem (Hohenberg-Theorem) states that an exact representation of the ground state properties of a stationary, non relativistic many-particle system in terms of the exact ground state density is possible. In studying ground-state electronic properties one can replace the ground-state electronic wave function $\Psi(x_1, \dots, x_N)$ with the simple electron density $n(r)$. In other words one can use the electron density as fundamental variable : the ground state wave function is a functional of the electron density, $\Psi = \Psi[n]$.

The physics of an interacting electronic system perturbed by an external potential can be described writing the Hamiltonian like

In order to describe the system, we have to calculate the total Hamiltonian :

$$H_{tot} = H + H_{ext} = T + V + H_{coul} + H_{ext} \quad (19)$$

with H_{ext} an external perturbation. Consider an auxiliary system of N non-interacting particles described by the Hamiltonian :

$$H_s = T + V_s \quad (20)$$

The Hohenberg-Kohn theorem tells us that there exists a unique energy functional

$$E_s[n] = T_s[n] + \int V_s(r)n(r)dr \quad (21)$$

for which the variational principle yields the exact ground state density $n_s(r)$ corresponding to H_s . $T_s[n]$ denotes the universal kinetic functional of non-interacting particles.

The Kohn-Sham ansatz leads to independent particle equation for the non interacting system (soluble numerically) with all the difficult many-body terms incorporated into an exchange-correlation functional of the density $E_{xc}[n]$. Solving equation one finds the ground state density and energy of the original interacting. The Kohn-Sham scheme is : for any interacting system, there exists a local single-particle potential $V_s(\vec{r})$ such that the exact ground state density $n(r)$ of the interacting system equals the ground state density of the auxiliary problem.

$$n(r) = n_s(r) \quad (22)$$

with

$$n(r) = \sum_{i=1\dots N} |\phi_i(r)|^2 \quad (23)$$

The Schrödinger equation :

$$H_s\phi_i(r) = \epsilon_i\phi_i(r) \quad (24)$$

$$\left[-\frac{\Delta^2}{2} + V_s(r)\right]\phi_i(r) = \epsilon_i\phi_i(r) \quad (25)$$

Now consider a particular interacting system with external potential $V_0(r)$ and ground state density $n_0(r)$. To determine the auxiliary potential $V_{s,0}(r)$ which generates $n_0(r)$ via

$$n_0(r) = \sum_{1\dots N} |\phi_{i,0}(r)|^2 \quad (26)$$

The Schrödinger equation :

$$H_{s,0}\phi_i(r) = \epsilon_i\phi_i(r) \quad (27)$$

$$\left[-\frac{\Delta^2}{2} + V_{s,0}(r)\right]\phi_{i,0}(r) = \epsilon_{i,0}\phi_{i,0}(r) \quad (28)$$

The unique energy functional by Hohenberg-Kohn theorem is

$$E_{V_0}[n] = F_{HK}[n] + \int V_0(r)n(r)dr \quad (29)$$

with

$$F_{HK}[n] = \langle \psi[n] | T + H_{coul} | \psi[n] \rangle \quad (30)$$

The functional $F_{HK}[n]$ is universal in the sense that it does not depend on V_0 . So $E_{V_0}[n]$ is

$$E_{V_0}[n] = F_{HK}[n] + \int V_0(r)n(r)dr + T_s[n] - T_s[n] + \frac{1}{2} \int dr \int n(r)v(r,r')n(r')dr' \quad (31)$$

$$- \frac{1}{2} \int dr \int n(r)v(r,r')n(r')dr'$$

$$E_{V_0}[n] = T_s[n] + \int V_0(r)n(r)dr + \frac{1}{2} \int dr \int n(r)v(r,r')n(r')dr' + E_{xc}[n] \quad (32)$$

with

$$E_{xc}[n] = E_{HK}[n] - T_s[n] - \frac{1}{2} \int dr \int n(r)v(r,r')n(r')dr' \quad (33)$$

with $v(r, r')$ the Coulomb interaction.

The Hohenberg-Kohn variational principle ensures that $E_{V_0}[n]$ is stationary for small variation $\delta n(r)$ around the minimum density $n_0(r)$. If we define

$$V_{xc}([n_0], r) = \left. \frac{\delta E_{xc}[n]}{\delta n(r)} \right|_{n_0} \quad (34)$$

The Kohn-Sham ansatz ensures that the system is non-interacting representable also for small deviations around the $[n_0(r) + \delta n_0(r)]$ allows to write, by neglecting second order terms,

$$\delta T_s = - \int V_{s,0}(r)\delta n(r)dr \quad (35)$$

Thus one is left with the final expression

$$V_{s,0}(r) = V_0(r) + \int v(r, r')n_0(r')dr' + V_{xc}([n_0], r) \quad (36)$$

So what we solve in practice are the ? called Kohn-Sham equations :

$$[T + V_{s,0}(\vec{r})]\Phi_{i,0}(\vec{r}) = \epsilon_{i,0}\Phi_{i,0}(\vec{r}) \quad (37)$$

These equations are solved in an iterative scheme until self-consistency is reached.

5 Configuration coordinate diagrams

In studying defects, one is faced with a variety of different phenomena as for solids in general : electronic and nuclear magnetism, thermodynamics, optical properties, mechanical properties, transport, etc. Here we focus on the properties of deep, localized defects and on the coupling of electronic and atomic structure, described in terms of configuration coordinate diagrams, defined below. The analysis of experimental results in terms of these diagrams provides a lot of insight about defects.

Consider a diatomic model, where an impurity atom attaches to a host atom and the defect is an acceptor (negatively charged). We see that the electronic ground state is negative and the excited levels are neutral, when the Fermi Level is at the maximum of the conduction band (see Figure 3).

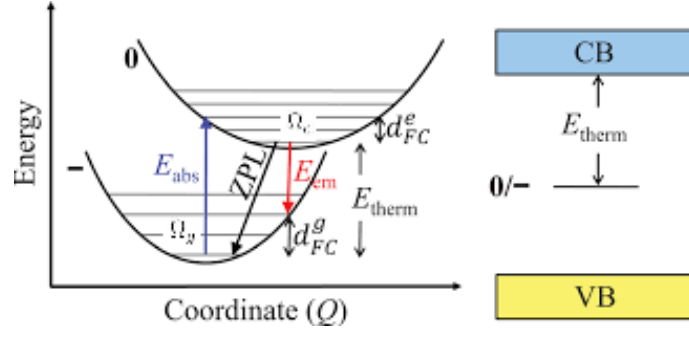


FIGURE 5 – Configuration coordinate diagram showing energies and optical transitions

The defect is described by a configuration coordinate (cc) Q , which in this simple picture is proportional to the bond length of the diatomic molecule. At equilibrium, the energy E is minimized at a specific value of Q . To first order, the bond behaves like harmonic spring, so $E \sim Q^2$. Starting from the acceptor in its ground state, the interpretation of the diagram goes through the following steps :

- (i) a photon is absorbed by an electron which instantaneously jumps from the VB to the CB (Franck Condon approximation), this gives us the classical absorption energy E_{abs}
- (ii) the acceptor loses 1 electron and it is consequently neutralized
- (iii) the system relaxes to a new equilibrium Q value, by losing energy d_{FC}^e called Franck-Condon shift. Here we have that the

$$E_{abs} = E_{therm} + d_{FC}^e \quad (38)$$

where E_{therm} is the energy separation between the equilibrium configurations in the ground and the excited state.

- (iv) The acceptor in the excited state can recapture the electron and jumps to the ground state, by losing energy E_{em} and emitting a photon (\rightarrow luminescence).

- (v) Finally the system relaxes to its ground state by losing more energy d_{FC}^g . Since $E_{em} < E_{abs}$ we can define the Stokes shift as

$$E_{abs} - E_{em} = d_{FC}^e + d_{FC}^g \quad (39)$$

The Franck-Condon approximation is useful to interpret optical experiments, because it allows to distinguish between electrical and optical properties of the same defect. It is also possible to include the vibrational broadening of the transitions in absorption and emission (the vibrational sub-levels). Always in the case of a diatomic molecule, we define two effective frequencies as linear vibrations of the molecule in the excited level, Ω_e and in the ground state Ω_g . If

$$\Omega_e = \Omega_g = \Omega_0 \quad (40)$$

the curvature of two parabolas is identical. Beyond the Franck-Condon approximation, we must consider the transitions between vibronic levels. If the transition occurs between the zero-phonon vibrational states in the ground and excited state configurations, we define the zero phonon line (ZPL), as an alternative to either E_{therm} or E_{abs} .

In the literature this model is used in the study of several different cases. But in our case, what we have studied is much in adherence to the subsection below.

Being the first time that we applied this type of analysis and given that we had a little trouble finding consistency in the notation used in the literature, we made the choice to replace nitrogen by a carbon with 1 more electron and then by a simple carbon, to be able to be in the case of a "Non radiative capture of charge carriers." For this, we also made the choice to follow the parabola parameter calculation procedures presented below.

5.1 Nonradiative capture of charge carriers

A configuration coordinate diagram can also be used to understand nonradiative capture of a hole by a negatively charged acceptor which occurs into two steps, and illustrated in Figure 4 :

- (i) Capture of a carrier from a delocalized bulk-like state to a localized defect state (the electronic energy is conserved) \implies the system ends up in a vibrationally excited state
- (ii) Phonon relaxation \implies the vibrationally excited state returns to local equilibrium.

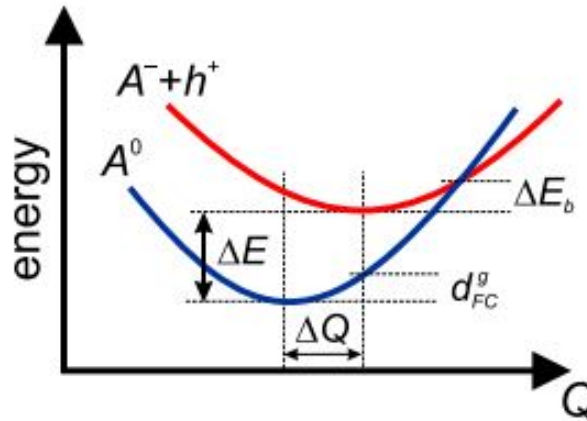


FIGURE 6 – Configuration coordinate diagram illustrating nonradiative capture of a hole by a deep acceptor

The ground state corresponds to the neutral state of charge (blue curve) and the excited state to the negative charge (red curve). Here, the charge exchange takes place in the valence band. ΔE is the energy difference between the two states, ΔQ is the horizontal shift between the minima of the two curves. d_{FC}^g is the Franck-Condon shift, corresponding to the vertical shift between the minimum of the blue curve and the intersection of the dotted lines at the level of the minimum of the red curve with the blue curve.

$$\Delta E_b = \frac{(\Delta E - d_{FC}^g)^2}{4d_{FC}^g} \quad (41)$$

is the classical barrier for a transition, corresponding to the vertical offset between the intersection between the blue and red curve and the minimum of the red curve.

5.2 Electronic structure and geometry relaxation calculations

Our aim is to build our configuration coordinate diagram in order to describe the capture of an electron. We first generated a 4x4 supercell. Knowing that the position of the substitutional carbon atom with respect to the supercell is completely arbitrary, we replaced one atom of nitrogen with an atom of carbon (see Fig.7).

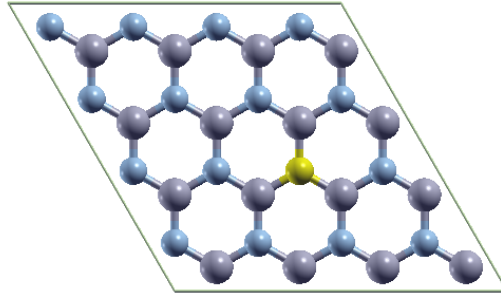


FIGURE 7 – Primitive cell with Carbon atom represented in yellow. The blue atoms are the nitrogen atoms and the violet are the boron atoms.

After relaxing the system, i.e. searching for the atomic configuration which minimizes the total energy, we observe in Fig.8 how the lattice deforms itself around the substitutional atom : the closest boron and nitrogen atoms tend to get far from the C atom.

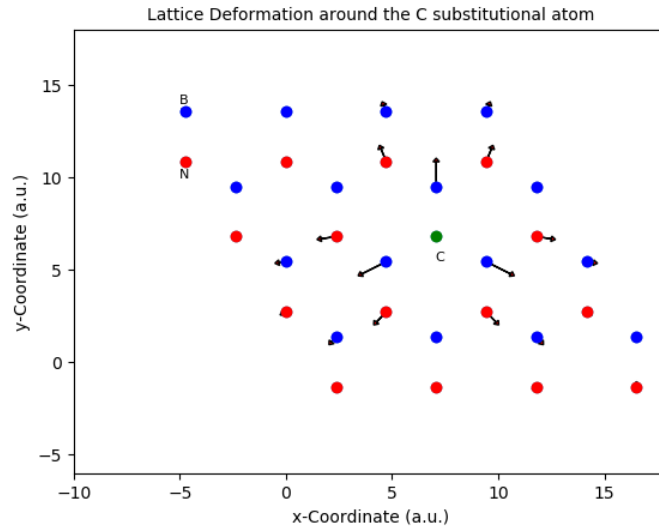


FIGURE 8 – Lattice deformation, represented by black arrows, around the carbon substitutional atom from pristine lattice.

We have the force

$$F_i = -\frac{\partial E}{\partial \vec{R}_i} = 0 \quad (42)$$

if it is not equal to 0 atoms are moved according to the forces acting on them, in order to go towards a configuration which minimizes the forces.

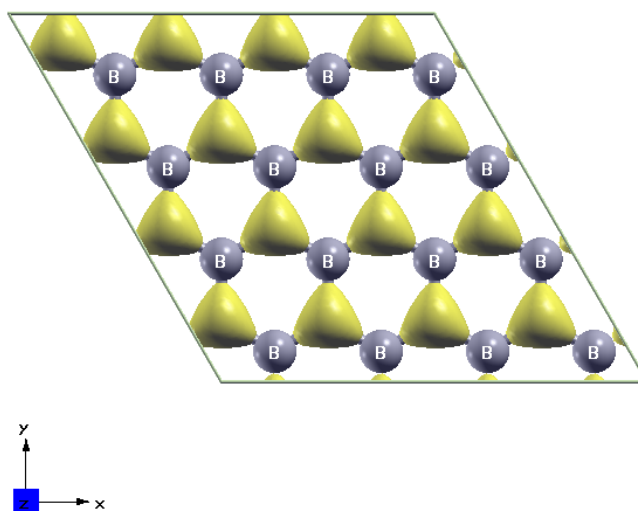


FIGURE 9 – Representation of the electron density of the system without defects.

The yellow and blue areas represent the probability of finding the electrons around the Nitrogen and Boron atoms respectively. We notice that the yellow surfaces are denser than the blue ones, indeed the nitrogen is more electronegative. That's why too that the electron density is concentrated around nitrogen because it is the most electronegative atom in the system.

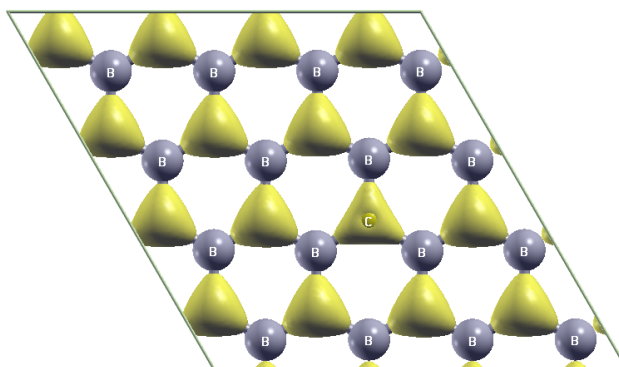


FIGURE 10 – Representation of the electron density of the system with the defect, carbon, in the neutral state

Nitrogen atom is more electronegative than Boron but less than Nitrogen. Note that its surface is less rounded.

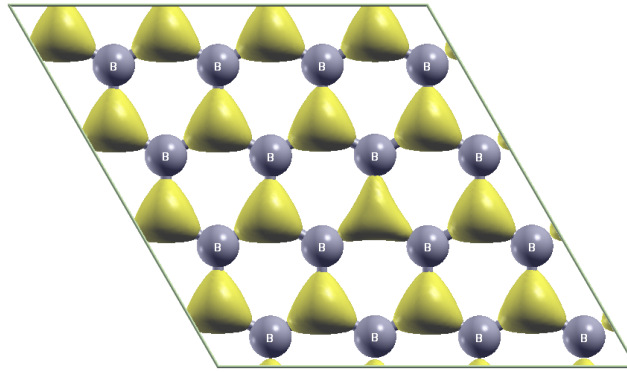


FIGURE 11 – Representation of the electron density of the system with the defect, carbon, in the excited state

We see a slight difference, the C of the carbon is covered by the added electron.

The goal is to calculate the key ingredients in order to build the configuration coordinate diagram of the "Nonradiative capture of charge carriers" and in particular to calculate the classical barrier. To do that, it first had was necessary to understand it.

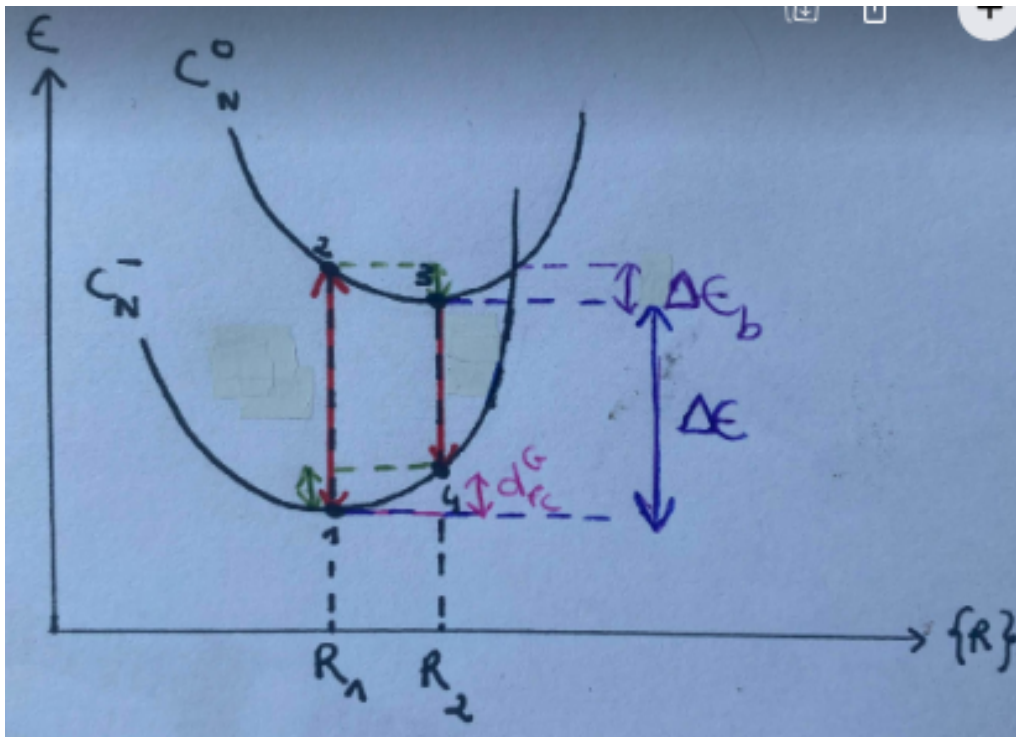


FIGURE 12 – Configuration coordinate diagram by hand

Indeed, we thought that the lowest energy curve was the excited state because there was the C_N^- and the curve above, of higher energy was the neutral state with the C_N^0 , but it is the reverse. The filling of the electron shells : $C : 1s^2 2s^2 2p^2$. With oxidation, we have $C^{+/-4}$ because we can fill up to 6 electrons in $2p^2$ or remove 4 in $2s^2 2p^2$.

We have a C atom with 3 B atoms around it. Carbon is more electronegatif than Boron,

so each Boron atom will give 1 electron to Carbon. We will therefore have $1s^2 2s^2 2p^1$ for Carbon. For the excited state we will have $1s^2 2s^2 2p^{5+1}$. Instead of replacing the Nitrogen atom with a Carbon atom, we replace it with a negatively charged Carbon atom, so that in the excited state we have the charge of 0. So we add 1 electron (we add it to the system, it's not an impurity) so that the p orbital is full. We will therefore have $2 + 3 + 1 = 6$.

Now that we understood it, we can use the code which calculates the forces numerically in order to minimize the energy, this is called system relaxation.

But we first checked, once set the simulation box (as explained in section 2), that enough vacuum has been included along the z axis, large enough to avoid interactions between electrons from one layer to the other. We find $l = 12, 29$ a.u with Quantum Espresso. We performed three calculations, by verifying the size of the simulation box along z (l) and we noted the total energy values, see table 1.

We launched three calculations with the "Quantum Espresso", in 1x1, for three different values of the distance of the simulation box along the z axis ;

l (a.u)	12.29	12.0	12.5
E (Ry)	-26.80987267	-26.80975481	-26.80994870

Table 1 : Values of energy depending of the values of the distance of the simulation box along the z axis

The minimum value is the last for a length of 12.5, but we notice that the difference is only on the fourth significant digit, so we can keep our base value of 12.29 a.u for the rest of our calculations and simulations.

So, we impose the atomic configuration R_1 to the excited state, and we relax the system again in order to have the minimum energy in the excited state at the atomic configuration R_2 .

We have the electronic configurations in the excited state and the neutral state, in alat (4.79..) and we want them in Cartesian coordinates, so we multiply them by a_1, a_2 and a_3 . We do this on excel in a table. We followed the procedure described in the article "Multiphonon hole trapping from first principles" by Schanovsky, Gos and Grasser in Microelectronics and Nanometer Structures. We define $\vec{m} = \vec{e}_{x_+ - x_0} = \sum_i C_i \vec{e}_i$, where C_i are the components of the modal vector in Cartesian coordinates, is the difference between the electronic configuration of the excited state and the neutral state, it is a vector. We can check the calculations with quantum espresso. Then we have the associated modal mass $M = \sum_i c_i^2 M_i$ with the coefficient obtained for m.

5.3 Calculation of the line-shape function

The determining elements of the line-shape function are the overlaps of the vibrational wave functions and their corresponding defect energies. This, requires the calculation of the potential energy surfaces. The system can be described by a single configuration vector \vec{R} that holds all $3N$ coordinates of the N atoms under consideration. By setting the charge state of the system and applying a suitable optimization algorithm, one can obtain the optimum structure for the neutral \vec{R}_1 and the charged \vec{R}_2 defects along with the respective energies. The energies obtained from DFT will be denoted $E_0^{DFT}(\vec{R})$ and

$E_+^{DFT}(\vec{R})$ for the neutral and the charged calculations, respectively. The first assumption of single mode coupling is that only one vibrational mode contributes to the electronic transition, which is considered a first-order approximation. The director vector is given as the direction from the initial configuration to the final one, i.e. the neutral and charged :

$$\vec{m} = e \vec{R}_2 - \vec{R}_1 = \sum_i c_i \vec{e}_i \quad (43)$$

with

c_i are the components of the modal vector in the Cartesian base of the system.

$$M = \sum_i c_i^2 M_i \quad (44)$$

is the modal mass associated while M_i are the atomic masses in atomic mass units. We assume parabolic energy surfaces for the neutral and charged state of the defect. So :

$$E_0^d(q) = \frac{1}{2} M \omega_0^2 q^2 \quad (45)$$

and

$$E_+^d(q) = \frac{1}{2} M \omega_+^2 (q - q_s)^2 + E_s \quad (46)$$

with

$$q_s = |\vec{R}_1 - \vec{R}_2| \quad (47)$$

$$E_s = E_+^{DFT}(\vec{R}_2) - E_0^{DFT}(\vec{R}_1) \quad (48)$$

The parameters ω_0 and ω_+ are chosen such that

$$E_0^d(q_s) = E_0^{DFT}(\vec{R}_2) \quad (49)$$

and

$$E_+^d(0) = E_+^{DFT}(\vec{R}_1) \quad (50)$$

describe the relaxation energies in the approximate treatment.

5.3.1 Electronic configurations

We obtained the electronic configurations of the excited state and the neutral state thanks to "Quantum Espresso". We introduced them in an excel table, converted them into cartesian coordinates, then made the difference between the two states and finally normalized them. Thus we obtained all the useful values for our calculations.

5.3.2 Energies and pulse values

In this subsection we will calculate the important values of the configuration coordinate diagram and the classical barrier.

We have for the neutral state :

$$E_0^d(q) = \frac{1}{2} M \omega_0^2 q^2 \quad (51)$$

$$E_0^d(0) = 0 \quad (52)$$

and

$$E_0^d(q = q_s) = \frac{1}{2}M\omega_0^2q_s^2 \quad (53)$$

$$E_0^d(q = q_s) - E_0^d(q) = \frac{1}{2}M\omega_0^2q_s^2 \quad (54)$$

So

$$\omega_0 = \sqrt{\frac{2E_0^d(q)}{Mq_s^2}} \quad (55)$$

$$E_0^d(q) = -419.62734737 + 419.6359324 = 8.58503.10^{-3}\text{Ry. Or } 1\text{Ry} = 2.1798741.10^{-18}\text{J}$$

$$E_0^d(q) = 1.871428454.10^{-20}\text{J}$$

$$M = 10,93475599 \text{ atomic mass unit, but } 1 \text{ atomic mass unit} = 1.66054.10^{-27}\text{kg}$$

$$M = 1.815759971.10^{-26}\text{kg}$$

$$q_s = 0.117803336\text{Bohr, but } 1\text{Bohr} = 5.29177.10^{-11}\text{m}$$

$$q_s = 6.233881593.10^{-12}\text{m}$$

$$\omega_0 = 2.303105562.10^{14}\text{rad/s}$$

Excited state :

$$E_+^d(q) = \frac{1}{2}M\omega_0^2(q - q_s)^2 + E_s \quad (56)$$

$$E_+^d(q) = E_+^d(0) - E_+^d(q_s) = \frac{1}{2}M\omega_+^2q_s^2 \quad (57)$$

$$\omega_+ = \sqrt{\frac{2E_+^d(q)}{Mq_s^2}} \quad (58)$$

$$E_+^d(q) = -419.54883334 + 419.55839696 = 9.56362.10^{-3}\text{Ry} = 2.084748754.10^{-20}\text{J}$$

$$M = 1.815759971.10^{-26}\text{kg}$$

$$E_s = -419.55839696 + 419.54883334 = 9.56362.10^{-3}\text{Ry} = 2.084748754.10^{-20}\text{J}$$

$$\omega_+ = 2.428904834.10^{14}\text{rad/s}$$

So the values of the four points are :

	R_1	R_2
$E_0(R_1/R_2)$ (Ry)	-419.63593242	-419.62734737
$E_+(R_1/R_2)$ (Ry)	-419.54883334	-419.55839696

Table 1 : Values of our four points.

$\hbar\omega_0$ (meV)	151.6050855
$\hbar\omega_+$ (meV)	159.8859953

Table 2 : Values of our frequency.

We can calculate : $E_{abs} = E_+(R_1) - E_0(R_1) + \frac{1}{2}\hbar\omega_0 = 1.260845185eV$
 $E_{em} = E_+(R_2) - E_{R_4} + \frac{1}{2}\hbar\omega_+ = 1.018060554eV$
 $E_{therm} = E_{R_3} - E_0(R_2) = 1.054923042eV$

We have : $d_{FC}^+ = E_+(R_1) - E_+(R_2) = 0.1301196008eV$

And we have $d_{FC}^0 = (E_0(R_2) - E_0(R_1)) = 0.1168054857eV$

So we can estimate, the classical barrier from equation [41] : $\Delta E_{b0} = 1.883611328eV$
and $\Delta E_{b+} = 1.643221606eV$

We can have the classical barrier only when the two parabolas have the same curvature, indeed we have seen that the values of the frequencies ω_0 and ω_+ are very close.

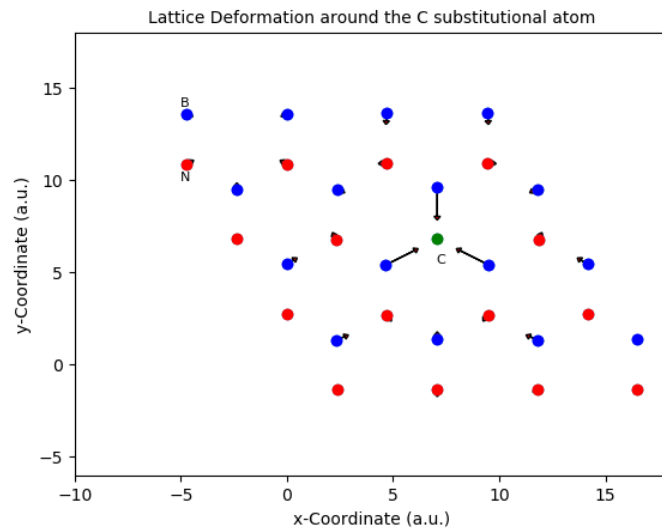


FIGURE 13 – Lattice deformation around the carbon substitutional atom, where we have added 1 electron. From neutral state to excited state.

Note that borons are attracted to carbon which is more electronegative.

We can represent the energy bands of the defects :



FIGURE 14 – The level of the defect in red, the valence band in violet and the conduction band in blue.

6 Conclusion

We were able to view the two-dimensional crystal lattice made up of Boron and Nitrogen, forming a monolayer of hBN. The elementary cell therefore has hexagonal symmetry, is two-dimensional and has a honeycomb crystal structure. Thanks to "Quantum Expresso", we obtained the primitive and reciprocal vectors of this cell and the positions of our two atoms.

The Born-Oppenheimer approximation allowed to neglect the ions by considering only the electrons in our system. The Kohn-Sham theorem transformed a many-body problem into a one-body problem, where there is no interaction between electrons.

DFT allowed to study the properties of the ground state of a system with several stationary particles, in terms of the density of the ground state; the fundamental variable.

We replaced Nitrogen atom with Carbon atom. For the neutral state we left the molecule as it is, while for the excited state, as the nitrogen atom has an extra electron, we add an electron to stabilize the molecule. We therefore had the electronic configurations in the excited state and in the neutral state thanks to the code which calculates the forces numerically in order to minimize the energy of the system by relaxation. We found $E_0^d(q) = 8.58503.103\text{Ry}$ and $E_+^d(q) = 9.56362.103\text{Ry}$.

We were therefore able to calculate the important values of the configuration coordinate diagram, we obtained : $E_0(R1) = -419.63593242\text{Ry}$, $E_0(R2) = -419.62734737\text{Ry}$, $E_+(R1) = -419.54883334\text{Ry}$ and $E_+(R2) = -419.55839696\text{Ry}$. Note that $E_+(R1) > E_+(R2) > E_0(R2) > E_0(R1)$, corresponding to points 2>3>4>1 of figure 6. Thanks from these values, it was possible to calculate the value of the effective frequencies as linear vibrations of the molecule, the energy of absorption, emission, thermal and the Franck-Condon shift. We obtained : $\hbar\omega_0 = 151.6050855\text{meV}$ and $\hbar\omega_+ = 159.8859953\text{meV}$, $E_{abs} = 1.260845185\text{eV}$, $E_{em} = 1.018060554\text{eV}$, $E_{therm} = 1.054923042\text{eV}$, $d_{FC}^e = 205.922133\text{meV}$ and $d_{FC}^g = 36.862498\text{meV}$. For the classical barrier we have $\Delta E_{b0} = 7.029144303\text{eV}$ and $\Delta E_{b+} = 0.8750911485\text{eV}$, we see that $E_{b0} > E_{b+}$. Thus we were able to represent the energy bands of the defects, we found an energy difference of 5 meV

between the valence band and the conduction band, and of 0.93 meV between the valence band and the level of the defect. The level of the defect is located in the gap close to the valence band, in fact as the carbon has one less electron (in the neutral state) the impurity is of the acceptor type.

We calculated the classical barrier, which represents the potential barrier that must be overcome to capture the electron, this is called charge transfer.

We could have made much more precise calculations with larger supercells to best simulate the isolated fault, but the calculation time would have been too long.

We chose to replace nitrogen with carbon because it is a more frequent source of defects in this type of material.

We did not take into account the spin of the system because it was out of the scope of the internship.

We could have tried to replace the Boron by a Carbon, the Boron having 3 valence electrons and nitrogen 5, we would have had 2 impurities, holes, therefore acceptors. Thus we would have had to add 2 electrons to stabilize the molecule. The level of the defect would have been even closer to the valence band, so the semiconductor would have been barely a better insulator.

7 Bibliographie

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