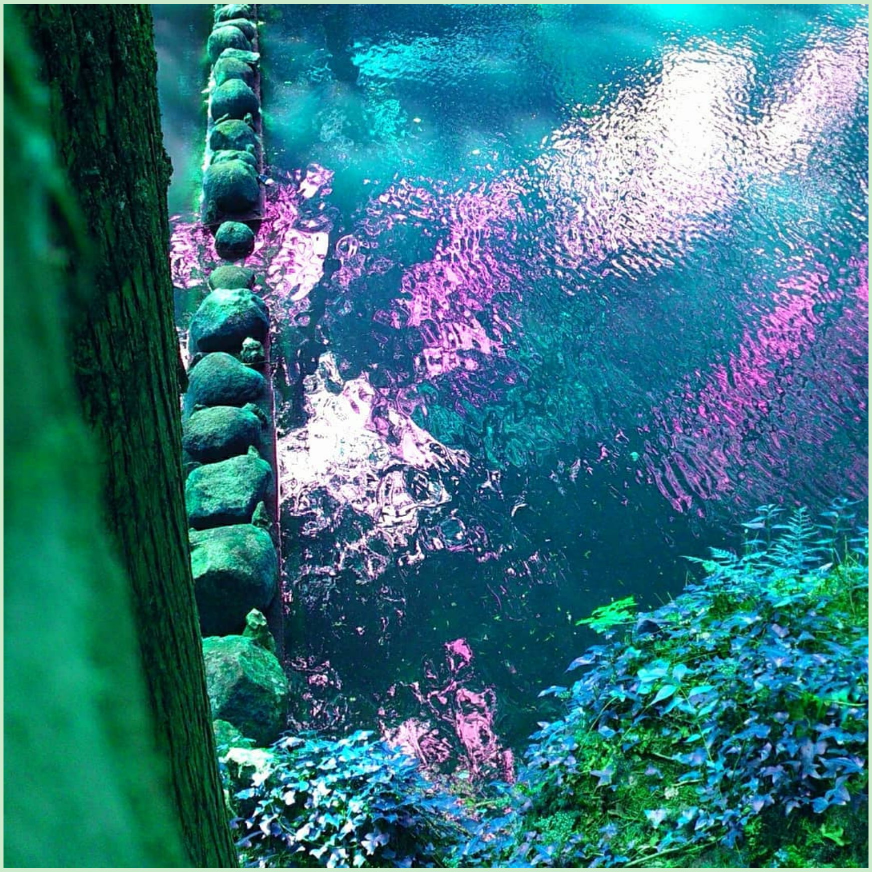
Electronic Properties of Hexagonal Boron Nitride



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I. INTRODUCTION

Hexagonal Boron Nitride (hBN) is a 2D material composed of a simple sheet of alternating boron and nitrogen atoms organized in a planar honeycomb lattice. hBN shares a lot of similarities with the infamous Graphene, also a 2D honeycomb structure but composed only of carbon atoms, although hBN has a slightly larger lattice constant $a_0 = 2.5$Å (about 1.8%). However, the most relevant distinction is that graphene behaves as a semi-metal with a zero-gap at its massless Dirac points while hBN, due to the electric repulsion between the boron and nitrogen atoms, behaves as a semiconductor and has an opening gap of about $\epsilon =$5.9eV at its Dirac points.

II. HBN DESCRIPTION IN POSITION SPACE

A. Position Space Lattice

As shown depicted in figure (1), hexagonal boron nitride (hBN) is composed of boron (depicted in red) and nitrogen (depicted in blue) atoms disposed in a two-dimensional honeycomb lattice, with a lattice constant of a_0. This honeycomb lattice can be described as a triangular Bravais lattice (depicted in gray shading) generated by the vectors basis

$$\mathbf{a}_1 = a_0 \left(\frac{1}{2}, \frac{\sqrt{3}}{2} \right), \tag{II.1}$$

$$\mathbf{a}_2 = a_0 \left(-\frac{1}{2}, \frac{\sqrt{3}}{2} \right) \tag{II.2}$$

A generic lattice vector $\mathbf{R}$ can then be written as

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2, \qquad \text{where } n_1, n_2 \in \mathbb{Z} \tag{II.3}$$

such that, a generic function $f(\mathbf{r})$ follows the periodicity of the lattice, this is

$$f(\mathbf{r}+\mathbf{R}) = f(\mathbf{r}). \tag{II.4}$$

In each unit cell (depicted by the dashed black line), we have one atom of boron and one atom of nitride, which we designate as sub-lattices A and B, of respective positions

$$\mathbf{s}_A = (0,0), \tag{II.5}$$

$$\mathbf{s}_B = \frac{a_0}{\sqrt{3}}(0,1). \tag{II.6}$$

For each site A, the first nearest neighbors of type B are given by

$$\boldsymbol{\delta}_1 = \frac{a_0}{\sqrt{3}}(0,1) \tag{II.7}$$

$$\boldsymbol{\delta}_2 = \frac{a_0}{\sqrt{3}} \left(-\frac{\sqrt{3}}{2}, -\frac{1}{2} \right) \tag{II.8}$$

$$\boldsymbol{\delta}_3 = \frac{a_0}{\sqrt{3}} \left(\frac{\sqrt{3}}{2}, -\frac{1}{2} \right) \tag{II.9}$$

B. Position Space Tight-Binding Hamiltonian

We can write this system's total Hamiltonian in real position-space and in second quantization as

$$H = H_A + H_B + H_{\text{hop}} \tag{II.10}$$

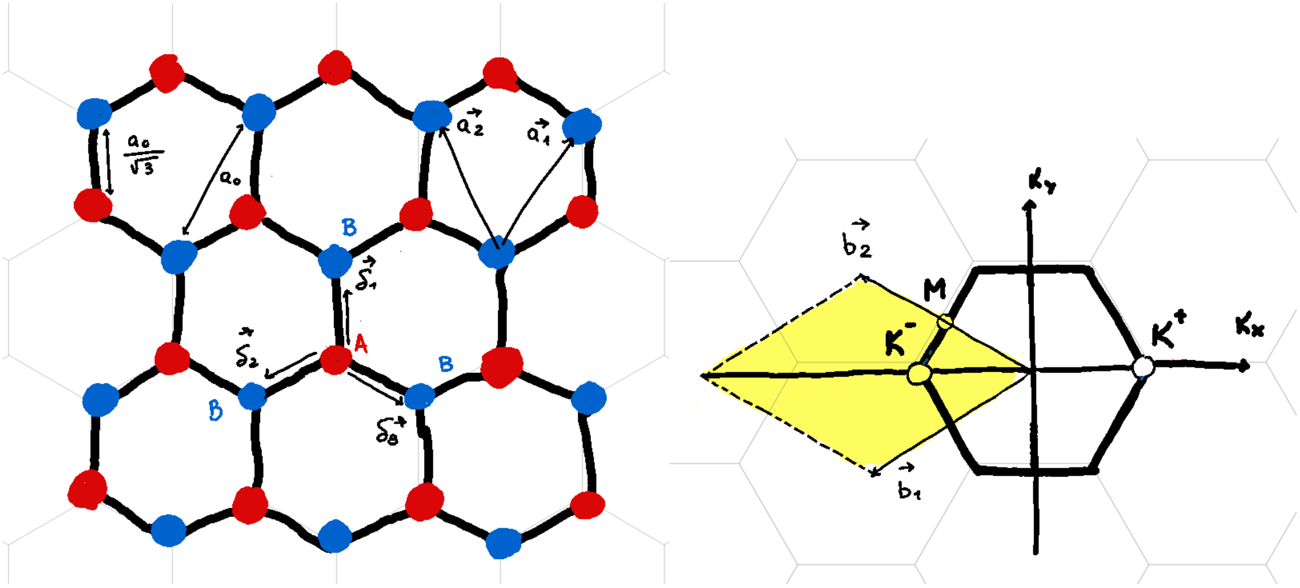


Figure 1. (a) Honeycomb lattice structure of hBN constructed by two superposed triangular sub-lattices A (red atoms) and B (blue atoms). The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are the lattice unit vectors and $\boldsymbol{\delta}_1$, $\boldsymbol{\delta}_2$ and $\boldsymbol{\delta}_3$ are the nearest-neighbor vectors. (b) Corresponding Brillouin zone. The Dirac points are located at $\mathbf{K}^+$ and $\mathbf{K}^-$. The dashed red and blue lines represent the shift of the Brillouin zone from a hexagon shape to a rectangular shape.

where

$$H_A = \sum_i \epsilon_A a_i^\dagger(\mathbf{R}) a_i(\mathbf{R}) \tag{II.11}$$

is the free-particle Hamiltonian of the boron atoms in sites A an, $a_i/a_i^\dagger$ the ladder operators in a given site i. Analogously,

$$H_B = \sum_i \epsilon_B b_i^\dagger(\mathbf{R}) b_i(\mathbf{R}) \tag{II.12}$$

is the free-particle Hamiltonian of the nitrogen atoms in sites B. Notice that, contrarily to graphene, since the atoms on sites A and B are different, the free-particle energies ϵ_A and ϵ_B are inherently different. At last, the term

$$H_{\text{hop}} = \sum_{i,j} t_{i,j}(\mathbf{R}) \left(a_i^\dagger(\mathbf{R}) b_j(\mathbf{R}) + b_j^\dagger(\mathbf{R}) a_i(\mathbf{R}) \right) \tag{II.13}$$

is the interaction Hamiltonian between neighboring sites i and j describing the possible hoppings from site B to site A and vice-versa. Considering **only first neighbors**, and since the surrounding atoms are all the same, the hopping terms is given by a constant term and can be pulled out of the sum, i.e $t_{i,j}(\mathbf{R}) \to -t$. We have

$$H_{\text{hop}} = -t \sum_{\langle i,j \rangle} \left(a^\dagger(\mathbf{R}_i) b(\mathbf{R}_i + \boldsymbol{\delta}_j) + b^\dagger(\mathbf{R}_j) a(\mathbf{R}_i - \boldsymbol{\delta}_j) \right) \tag{II.14}$$

where we denote that we are only dealing with first neighbors with $\langle i, j \rangle$ (although it's redundant since we are already specifying the first neighbors with $+\boldsymbol{\delta}_j$). Substituting back into (II.10), and making the site i explicit instead on the position $\mathbf{R}$ [i.e $a_i(\mathbf{R}) \equiv a(\mathbf{R}_i)$], the total Hamiltonian yields

$$H = \sum_i \epsilon_A a^\dagger(\mathbf{R}_i) a(\mathbf{R}_i) + \sum_i \epsilon_B b^\dagger(\mathbf{R}_i) b(\mathbf{R}_i) - t \sum_{\langle i,j \rangle} \left(a^\dagger(\mathbf{R}_i) b(\mathbf{R}_i + \boldsymbol{\delta}_j) + b^\dagger(\mathbf{R}_j) a(\mathbf{R}_i - \boldsymbol{\delta}_j) \right) \tag{II.15}$$

III. HBN DESCRIPTION IN RECIPROCAL SPACE

A. Reciprocal Space Lattice

Given the lattice periodicity described in (II.4), we can express a generic function $f(\mathbf{r})$ in reciprocal space as a Fourier series

$$f(\mathbf{r}) = \sum_{\mathbf{k}} e^{+i\mathbf{G}\cdot\mathbf{r}} f(\mathbf{k}) \tag{III.1}$$

where, given (II.4),

$$\sum_{\mathbf{k}} e^{+i\mathbf{G}\cdot\mathbf{r}} f(\mathbf{k}) = \sum_{\mathbf{k}} e^{+i\mathbf{G}\cdot(\mathbf{r}+\mathbf{R})} f(\mathbf{k})$$

$$\Rightarrow \mathbf{G}\cdot\mathbf{R} = 2\pi n, \qquad \text{where } n \in \mathbb{Z} \tag{III.2}$$

This holds true if, for a given reciprocal space translation,

$$\mathbf{G} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 \tag{III.3}$$

the two reciprocal basis vectors are such that

$$a_i \cdot b_j = \frac{1}{2\pi}\delta_{ij} \tag{III.4}$$

Thus, one choice of basis is

$$\mathbf{b}_1 = \frac{2\pi}{V}\left(\mathcal{R}_{90^{\text{o}}}\mathbf{a}_2\right) = \frac{4\pi}{\sqrt{3}a_0}\left(-\sqrt{3}, -1\right) \tag{III.5}$$

$$\mathbf{b}_2 = \frac{2\pi}{V}\left(\mathcal{R}_{90^{\text{o}}}\mathbf{a}_1\right) = \frac{4\pi}{\sqrt{3}a_0}\left(-\sqrt{3}, +1\right) \tag{III.6}$$

where $\mathcal{R}_{90^{\text{o}}}$ is a $90^{\underline{\text{o}}}$ rotation matrix and V is the volume of the unit cell,

$$V = \left|\mathbf{a}_1 \cdot \left(\mathcal{R}_{90^{\text{o}}}\mathbf{a}_2\right)\right| = \frac{\sqrt{3}a_0}{2} \tag{III.7}$$

We obtain

$$\mathbf{b}_1 = \frac{4\pi}{\sqrt{3}a_0}\left(-\sqrt{3}, -1\right) \tag{III.8}$$

$$\mathbf{b}_2 = \frac{4\pi}{\sqrt{3}a_0}\left(-\sqrt{3}, +1\right) \tag{III.9}$$

The volume is given by

$$\begin{aligned} V &= \left|\mathbf{a}_1 \cdot (\mathcal{R}_{90^{\text{o}}}\mathbf{a}_2)\,\right| \\ &= \left|\frac{a_0}{2}\begin{bmatrix} 1 \\ \sqrt{3} \end{bmatrix} \cdot \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \frac{a_0}{2}\begin{bmatrix} -1 \\ \sqrt{3} \end{bmatrix}\right| \\ &= \left|\frac{a_0}{4}\begin{bmatrix} 1 \\ \sqrt{3} \end{bmatrix} \cdot \begin{bmatrix} -\sqrt{3} \\ -1 \end{bmatrix}\right| \\ &= \left|-\frac{a_0}{4}(\sqrt{3}+\sqrt{3})\right| \\ &= \frac{\sqrt{3}a_0}{2} \qquad \square \end{aligned} \tag{III.10}$$

and the reciprocal basis vectors as

$$\mathbf{b}_1 = \frac{2\pi}{V}\left(\mathcal{R}_{90^{\text{o}}}\mathbf{a}_2\right) = \frac{4\pi}{\sqrt{3}a_0}\left(-\sqrt{3}, -1\right) \tag{III.11}$$

and

$$\mathbf{b}_2 = \frac{2\pi}{V}\left(\mathcal{R}_{90^{\text{o}}}\mathbf{a}_1\right) = \frac{4\pi}{\sqrt{3}a_0}\left(-\sqrt{3}, +1\right) \tag{III.12}$$

B. Reciprocal Space Tight-Binding Hamiltonian

We can represent the total Hamiltonian (II.15) in reciprocal space, expressing the ladder operators $a/a^\dagger$ and $b/b^\dagger$ in a Fourier series given the respective periodicity $\mathbf{s}_A$ and $\mathbf{s}_B$. This is

$$a(\mathbf{R}_i) = \frac{1}{\sqrt{V}}\sum_{\mathbf{k}} e^{+i\mathbf{k}\cdot(R_i+\mathbf{s}_A)}a(\mathbf{k}) \tag{III.13}$$

$$b(\mathbf{R}_i) = \frac{1}{\sqrt{V}}\sum_{\mathbf{k}} e^{+i\mathbf{k}\cdot(\mathbf{R}_i+\mathbf{s}_B)}b(\mathbf{k}) \tag{III.14}$$

Substituting (III.13) and (III.14) into (II.15) yields

$$\begin{aligned} H &= \sum_i \epsilon_A a^\dagger(\mathbf{R}_i)a(\mathbf{R}_i) + \sum_i \epsilon_B b^\dagger(\mathbf{R}_i)b(\mathbf{R}_i) - t\sum_{\langle i,j\rangle}\left(a^\dagger(\mathbf{R}_i)b(\mathbf{R}_i+\boldsymbol{\delta}_j) + b^\dagger(\mathbf{R}_i)a(\mathbf{R}_i-\boldsymbol{\delta}_j)\right) \\ &= \frac{1}{N}\sum_i \epsilon_A\left(\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}_i+\mathbf{s}_A)}a^\dagger(\mathbf{k})\right)\left(\sum_{\mathbf{k}'} e^{+i\mathbf{k}'\cdot(\mathbf{R}_i+\mathbf{s}_A)}a(\mathbf{k}')\right) \\ &\quad + \frac{1}{N}\sum_i \epsilon_B\left(\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}_i+\mathbf{s}_B)}b^\dagger(\mathbf{k})\right)\left(\sum_{\mathbf{k}'} e^{+i\mathbf{k}'\cdot(\mathbf{R}_i+\mathbf{s}_B)}b(\mathbf{k}')\right) \\ &\quad - \frac{1}{N}t\sum_{\langle i,j\rangle}\left(\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}_i+\mathbf{s}_A)}a^\dagger(\mathbf{k})\right)\left(\sum_{\mathbf{k}'} e^{+i\mathbf{k}'\cdot(\mathbf{R}_i+\boldsymbol{\delta}_j+\mathbf{s}_B)}b(\mathbf{k}')\right) \\ &\quad + \left(\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}_i+\mathbf{s}_B)}b^\dagger(\mathbf{k})\right)\left(\sum_{\mathbf{k}'} e^{+i\mathbf{k}'\cdot(\mathbf{R}_i-\boldsymbol{\delta}_j+\mathbf{s}_A)}a(\mathbf{k}')\right) \end{aligned} \tag{III.15}$$

Given the identity

$$\delta(\mathbf{k}-\mathbf{k}') = \frac{1}{N}\sum_i e^{-i\mathbf{R}_i\cdot(\mathbf{k}-\mathbf{k}')} \tag{III.16}$$

we can rearrange (III.15) to make (III.16) explicit. It follows that

$$
\begin{aligned}
H = & \sum_{\mathbf{k},\mathbf{k}'} \left(\frac{1}{N} \sum_i e^{-i\mathbf{R}_i\cdot(\mathbf{k}-\mathbf{k}')} \right) e^{-i\mathbf{s}_A\cdot(\mathbf{k}-\mathbf{k}')} \epsilon_A a^\dagger(\mathbf{k}) a(\mathbf{k}') \\
& + \sum_{\mathbf{k},\mathbf{k}'} \left(\frac{1}{N} \sum_i e^{-i\mathbf{R}_i\cdot(\mathbf{k}-\mathbf{k}')} \right) e^{-i\mathbf{s}_B\cdot(\mathbf{k}-\mathbf{k}')} \epsilon_B b^\dagger(\mathbf{k}) b(\mathbf{k}') \\
& - t \sum_{\mathbf{k},\mathbf{k}'} \left(\frac{1}{N} \sum_i e^{-i\mathbf{R}_i\cdot(\mathbf{k}-\mathbf{k}')} \right) \left(e^{-i\mathbf{k}\cdot\mathbf{s}_A} e^{+i\mathbf{k}'\cdot\boldsymbol{\delta}_j} e^{+i\mathbf{k}'\cdot\mathbf{s}_B} \right) a^\dagger(\mathbf{k}) b(\mathbf{k}') \\
& - t \sum_{\mathbf{k},\mathbf{k}'} \left(\frac{1}{N} \sum_i e^{-i\mathbf{R}_i\cdot(\mathbf{k}-\mathbf{k}')} \right) \sum_{\langle j \rangle} \left(e^{-i\mathbf{k}\cdot\mathbf{s}_B} e^{-i\mathbf{k}'\cdot\boldsymbol{\delta}_j} e^{+i\mathbf{k}'\cdot\mathbf{s}_A} \right) b^\dagger(\mathbf{k}) a(\mathbf{k}')
\end{aligned} \tag{III.17}
$$

and thus

$$
\begin{aligned}
H = & \sum_{\mathbf{k}} \epsilon_A a^\dagger(\mathbf{k}) a(\mathbf{k}') + \sum_{\mathbf{k}} \epsilon_B b^\dagger(\mathbf{k}) b(\mathbf{k}') \\
& - t \sum_{\mathbf{k}} \left(\sum_{\langle j \rangle} e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_j + \mathbf{s}_B - \mathbf{s}_A)} \right) a^\dagger(\mathbf{k}) b(\mathbf{k}) \\
& - t \sum_{\mathbf{k}} \left(\sum_{\langle j \rangle} e^{-i\mathbf{k}\cdot(\boldsymbol{\delta}_j + \mathbf{s}_B - \mathbf{s}_A)} \right) b^\dagger(\mathbf{k}) a(\mathbf{k})
\end{aligned} \tag{III.18}
$$

Notice that, given the definition of $\mathbf{s}_A$ and $\mathbf{s}_B$, we have that $\mathbf{s}_B - \mathbf{s}_A = \boldsymbol{\delta}_1$. We define a new operator

$$
\gamma_{\mathbf{k}} = \sum_{\langle j \rangle} e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_j + \boldsymbol{\delta}_1)}, \tag{III.19}
$$

re-express (III.18) in terms of it. The Hamiltonian in momentum space is then given by

$$
H = \sum_{\mathbf{k}} \epsilon_A(\mathbf{k}) a^\dagger(\mathbf{k}) a(\mathbf{k}) + \sum_{\mathbf{k}} \epsilon_B(\mathbf{k}) b^\dagger(\mathbf{k}) b(\mathbf{k}) - t \sum_{\mathbf{k}} \left(\gamma_{\mathbf{k}} a^\dagger(\mathbf{k}) b(\mathbf{k}) + \gamma_{\mathbf{k}}^\dagger b^\dagger(\mathbf{k}) a(\mathbf{k}) \right). \tag{III.20}
$$

We can rewrite the system's Hamiltonian in matrix form as

$$
H = \sum_{\mathbf{k}} c^\dagger(\mathbf{k}) H_{\mathbf{k}} c(\mathbf{k}). \tag{III.21}
$$

where we defined a new composite state and a new Hamiltonian as

$$
c(\mathbf{k}) = \begin{bmatrix} a(\mathbf{k}) \\ b(\mathbf{k}) \end{bmatrix} \qquad \text{and} \qquad H_{\mathbf{k}} = \begin{bmatrix} \epsilon_A & -t\gamma_{\mathbf{k}} \\ -t\gamma_{\mathbf{k}}^\dagger & \epsilon_B \end{bmatrix}. \tag{III.22}
$$

$$
\begin{aligned}
H_{int} &= \sum_{\mathbf{k}} c^\dagger(\mathbf{k}) H_{\mathbf{k}} c(\mathbf{k}) \\
&= \sum_{\mathbf{k}} \begin{bmatrix} a^\dagger(\mathbf{k}) & b^\dagger(\mathbf{k}) \end{bmatrix} \begin{bmatrix} \epsilon_A & -t\gamma_{\mathbf{k}} \\ -t\gamma_{\mathbf{k}}^\dagger & \epsilon_B \end{bmatrix} \begin{bmatrix} a(\mathbf{k}) \\ b(\mathbf{k}) \end{bmatrix} \\
&= \sum_{\mathbf{k}} \begin{bmatrix} a^\dagger(\mathbf{k}) & b^\dagger(\mathbf{k}) \end{bmatrix} \begin{bmatrix} \epsilon_A a(\mathbf{k}) - t\gamma_{\mathbf{k}} b(\mathbf{k}) \\ -\gamma_{\mathbf{k}}^\dagger a(\mathbf{k}) + \epsilon_B b(\mathbf{k}) \end{bmatrix} \\
&= \sum_{\mathbf{k}} \left(\epsilon_A(\mathbf{k}) a^\dagger(\mathbf{k}) a(\mathbf{k}) + \epsilon_B(\mathbf{k}) b^\dagger(\mathbf{k}) b(\mathbf{k}) - t\gamma_{\mathbf{k}} a^\dagger(\mathbf{k}) b(\mathbf{k}) - t\gamma_{\mathbf{k}}^\dagger b^\dagger(\mathbf{k}) a(\mathbf{k}) \right) \qquad \square
\end{aligned} \tag{III.23}
$$

IV. HBN BAND STRUCTURE

A. Finding the Eigen-Energies

To calculate the band structure we first need to find the eigenvalues of the Hamiltonian $H_{\mathbf{k}}$. This is an easy task since it's just a 2x2 matrix. We obtain

$$\begin{aligned}0 &= \det\left(H_{\mathbf{k}} - E_{\mathbf{k}}\mathbb{1}\right)\\ &= \begin{vmatrix} \epsilon_A - E_{\mathbf{k}} & -t\gamma_{\mathbf{k}} \\ -t\gamma_{\mathbf{k}}^{\dagger} & \epsilon_B - E_{\mathbf{k}} \end{vmatrix}\\ &= \left(\epsilon_A - E_{\mathbf{k}}\right)\left(\epsilon_B - E_{\mathbf{k}}\right) - t^2|\gamma_{\mathbf{k}}|^2\\ &= \epsilon_A\epsilon_B - \left(\epsilon_A + \epsilon_B\right)E_{\mathbf{k}} + E_{\mathbf{k}}^2 - t^2|\gamma_{\mathbf{k}}|^2 \end{aligned} \tag{IV.1}$$

and thus

$$\begin{aligned}E_{\mathbf{k}} &= \frac{1}{2}\left(\epsilon_A + \epsilon_B\right) \pm \frac{1}{2}\sqrt{\left(\epsilon_A + \epsilon_B\right)^2 - 4\left(\epsilon_A\epsilon_B - t^2|\gamma_{\mathbf{k}}|^2\right)}\\ &= \left(\frac{\epsilon_A + \epsilon_B}{2}\right) \pm \sqrt{\left(\frac{\epsilon_A - \epsilon_B}{2}\right)^2 + t^2|\gamma_{\mathbf{k}}|^2}\end{aligned} \tag{IV.2}$$

In frequency space, $|\gamma_{\mathbf{k}}|^2$ is given by

$$\begin{aligned}|\gamma_{\mathbf{k}}|^2 &= \left(\sum_{\langle j\rangle} e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_j+\boldsymbol{\delta}_1)}\right)\left(\sum_{\langle j'\rangle} e^{-i\mathbf{k}\cdot\left(\boldsymbol{\delta}_{j'}+\boldsymbol{\delta}_1\right)}\right)\\ &= \left(e^{+i\mathbf{k}\cdot\boldsymbol{\delta}_1} + e^{+i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{+i\mathbf{k}\cdot\boldsymbol{\delta}_3}\right)e^{+i\mathbf{k}\cdot\boldsymbol{\delta}_1}\left(e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_1} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_3}\right)e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_1}\\ &= \left(e^{+i\mathbf{k}\cdot\boldsymbol{\delta}_1} + e^{+i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{+i\mathbf{k}\cdot\boldsymbol{\delta}_3}\right)\left(e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_1} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_3}\right)\\ &= 1 + e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_1-\boldsymbol{\delta}_2)} + e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_1-\boldsymbol{\delta}_3)} + e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_2-\boldsymbol{\delta}_1)} + 1 + e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_2-\boldsymbol{\delta}_3)} + e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_3-\boldsymbol{\delta}_1)} + e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_3-\boldsymbol{\delta}_2)} + 1\\ &= 3 + \left(e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_1-\boldsymbol{\delta}_2)} + e^{-i\mathbf{k}\cdot(\boldsymbol{\delta}_1-\boldsymbol{\delta}_2)}\right) + \left(e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_1-\boldsymbol{\delta}_3)} + e^{-i\mathbf{k}\cdot(\boldsymbol{\delta}_1-\boldsymbol{\delta}_3)}\right) + \left(e^{+i\mathbf{k}\cdot(\boldsymbol{\delta}_2-\boldsymbol{\delta}_3)} + e^{-i\mathbf{k}\cdot(\boldsymbol{\delta}_2-\boldsymbol{\delta}_3)}\right)\\ &= 3 + 2\cos(\boldsymbol{\delta}_1 - \boldsymbol{\delta}_2) + 2\cos(\boldsymbol{\delta}_1 - \boldsymbol{\delta}_3) + 2\cos(\boldsymbol{\delta}_2 - \boldsymbol{\delta}_3)\end{aligned} \tag{IV.3}$$

Given the definition in (II.7), (II.8) and (II.9) we have

$$|\gamma_{\mathbf{k}}|^2 = 3 + 2\cos\left(\frac{a_0}{2}\left[k_x + \sqrt{3}k_y\right]\right) + 2\cos\left(\frac{a_0}{2}\left[-k_x + \sqrt{3}k_y\right]\right) + 2\cos\left(-a_0k_x\right) \tag{IV.4}$$

Using the identity

$$\begin{aligned}\cos(a+b) + \cos(a-b) &= (\cos a\cos b - \sin a\sin b) + (\cos a\cos(-b) - \sin a\sin(-b))\\ &= (\cos a\cos b - \sin a\sin b) + (\cos a\cos b + \sin a\sin b)\\ &= 2\cos a\cos b\end{aligned} \tag{IV.5}$$

we obtain

$$|\gamma_{\mathbf{k}}|^2 = 3 + 4\cos\left(\frac{a_0}{2}k_x\right)\cos\left(\frac{a_0\sqrt{3}}{2}k_y\right) + 2\cos\left(a_0k_x\right) \tag{IV.6}$$

Substituting (IV.6) directly into (IV.2) yields

$$E_{\mathbf{k}}^{\pm}(k_x, k_y) = \left(\frac{\epsilon_A + \epsilon_B}{2}\right) \pm \sqrt{\left(\frac{\epsilon_A - \epsilon_B}{2}\right)^2 + t^2\left[3 + 2\cos\left(a_0k_x\right) + 4\cos\left(\frac{a_0\sqrt{3}}{2}k_y\right)\cos\left(\frac{a_0}{2}k_x\right)\right]}. \tag{IV.7}$$

Notice that, if $\epsilon_A = \epsilon_B$, as is the case for graphene, the term $((\epsilon_A - \epsilon_B)/2)^2$ is zero and the band gap closes at the so called Dirac points (for reason we will see later),

$$\mathbf{K}^{+} = \left(+\frac{4\pi}{3a_0}, 0\right) \tag{IV.8}$$

$$\mathbf{K}^{-} = \left(-\frac{4\pi}{3a_0}, 0\right) \tag{IV.9}$$

since

$$\begin{aligned}
0 &= 3 + 2\cos\left(a_0 K_x^{\pm}\right) + 4\cos\left(\frac{a_0\sqrt{3}}{2}K_y^{\pm}\right)\cos\left(\frac{a_0}{2}K_x^{\pm}\right)\\
&= 3 + 2\cos\left(\pm a_0\frac{2\pi}{a_0}\frac{2}{3}\right) + 4\cos\left(0\right)\cos\left(\pm\frac{a_0}{2}\frac{2\pi}{a_0}\frac{2}{3}\right)\\
&= 3 + 2\cos\left(\pm(\pi/3+\pi)\right) + 4\cos\left(\pm(\pi-\pi/3)\right)\\
&= 3 - 2\cos\left(\pi/3\right) - 4\cos\left(\pi/3\right)\\
&= 3 - 2\frac{1}{2} - 4\frac{1}{2}\\
&= 3 - 1 - 2\\
&= 0 \quad \square
\end{aligned} \tag{IV.10}$$

On the other hand, in the case for hBN, at this $\mathbf{K}$ points we have a band of $(\epsilon_A + \epsilon_B)/2 \equiv 0$. It has been demonstrated that this indirect-gap semiconductor has a band-gap of $\epsilon = 5.95$ eV. If we define the zero energy point at $(\epsilon_A - \epsilon_B)/2 \equiv \epsilon$ such that $\epsilon_A \equiv \epsilon$ and $\epsilon_A \equiv -\epsilon$ we obtain

$$E_{\mathbf{k}}^{\pm}(k_x, k_y) = \pm\sqrt{\epsilon^2 + t^2\left[3 + 2\cos\left(a_0 k_x\right) + 4\cos\left(\frac{a_0\sqrt{3}}{2}k_y\right)\cos\left(\frac{a_0}{2}k_x\right)\right]}. \tag{IV.11}$$

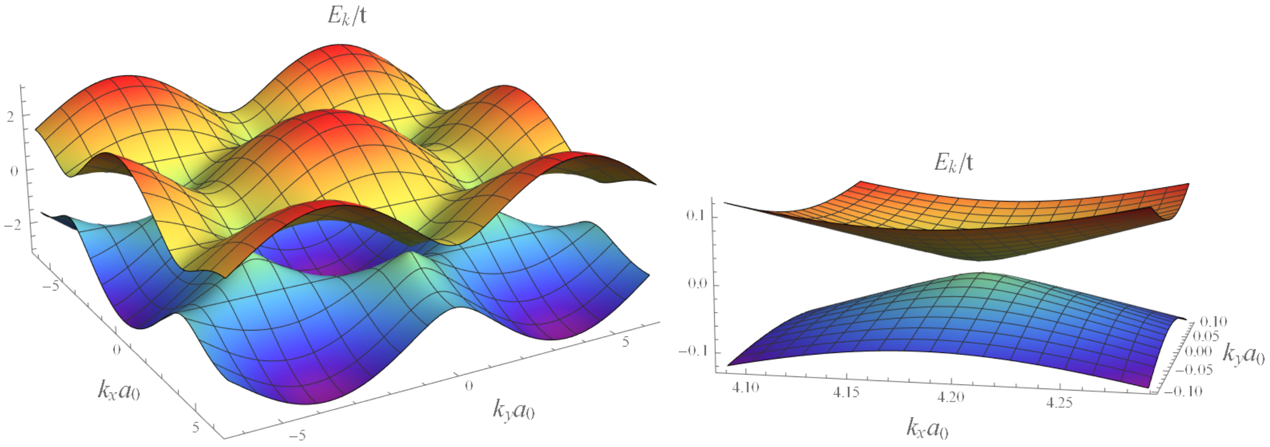


Figure 2. hBN band structure within the first Brillouin zone with parameters $t = 1$ eV and **(a)** $\epsilon = 5.9$eV **(b)** and with $\epsilon = 0.01$eV (just to make the parabolic shape of the band gap more explicit) near the $\mathbf{K}$ points.

B. Low Energies Regime

In the low energy regime, around the $\mathbf{K}$ points, i.e within $[\mathbf{K}-\mathbf{p},\mathbf{K}+\mathbf{p}]$ with $\mathbf{p}\to 0$, we can expand the ... as

$$\begin{aligned}
\gamma_{\mathbf{K}+\mathbf{p}} &= \sum_{\langle j\rangle} e^{+i(\mathbf{K}+\mathbf{p})\cdot(\boldsymbol{\delta}_j+\boldsymbol{\delta}_1)} \\
&= e^{+i(\mathbf{K}+\mathbf{p})\cdot\boldsymbol{\delta}_1}\sum_{\langle j\rangle} e^{+i\mathbf{K}\cdot\boldsymbol{\delta}_j}e^{+i\mathbf{p}\cdot\boldsymbol{\delta}_j} \\
&\approx (...)\sum_{\langle j\rangle} e^{+i\mathbf{K}\cdot\boldsymbol{\delta}_j}\left(1+i\mathbf{p}\cdot\boldsymbol{\delta}_j\right) \\
&= (...)\sum_{\langle j\rangle} e^{+i\mathbf{K}\cdot\boldsymbol{\delta}_j} + i\mathbf{p}\cdot\sum_{\langle j\rangle} e^{+i\mathbf{K}\cdot\boldsymbol{\delta}_j}\boldsymbol{\delta}_j
\end{aligned} \tag{IV.12}$$

As we already saw, we have that

$$\begin{aligned}
\sum_{\langle j\rangle} e^{+i\mathbf{K}\cdot\boldsymbol{\delta}_j} &= e^{i\mathbf{K}\cdot\boldsymbol{\delta}_1}+e^{i\mathbf{K}\cdot\boldsymbol{\delta}_2}+e^{i\mathbf{K}\cdot\boldsymbol{\delta}_3} \\
&= e^{i\frac{2\pi}{a_0}\left(\frac{2}{3},0\right)\cdot\frac{a_0}{\sqrt{3}}(0,1)} + e^{i\frac{2\pi}{a_0}\left(\frac{2}{3},0\right)\cdot\frac{a_0}{\sqrt{3}}\left(-\frac{\sqrt{3}}{2},-\frac{1}{2}\right)} + e^{i\frac{2\pi}{a_0}\left(\frac{2}{3},0\right)\cdot\frac{a_0}{\sqrt{3}}\left(\frac{\sqrt{3}}{2},-\frac{1}{2}\right)} \\
&= e^{i0}+e^{-i\frac{2\pi}{3}}+e^{+i\frac{2\pi}{3}} \\
&= 1+2\cos(2\pi/3) \\
&= 1-1=0
\end{aligned} \tag{IV.13}$$

And thus

$$\begin{aligned}
\gamma_{\mathbf{K}+\mathbf{p}} &= i\mathbf{p}\cdot\sum_{\langle j\rangle} e^{+i\mathbf{K}\cdot\boldsymbol{\delta}_j}\boldsymbol{\delta}_j \\
&= i\mathbf{p}\cdot\frac{a_0}{\sqrt{3}}\left(e^{i0}(0,1)+e^{-i\frac{2\pi}{3}}\left(-\frac{\sqrt{3}}{2},-\frac{1}{2}\right)+e^{+i\frac{2\pi}{3}}\left(\frac{\sqrt{3}}{2},-\frac{1}{2}\right)\right) \\
&= i\mathbf{p}\cdot\frac{a_0}{\sqrt{3}}\left((0,1)+\left(\frac{\sqrt{3}}{2}\left[e^{+i\frac{2\pi}{3}}-e^{-i\frac{2\pi}{3}}\right],-\frac{1}{2}\left[e^{+i\frac{2\pi}{3}}+e^{-i\frac{2\pi}{3}}\right]\right)\right) \\
&= i\mathbf{p}\cdot\frac{a_0}{\sqrt{3}}\left((0,1)+\left(\frac{\sqrt{3}}{2}2i\sin(\frac{2\pi}{3}),-\frac{1}{2}2\cos(\frac{2\pi}{3})\right)\right) \\
&= i\mathbf{p}\cdot\frac{a_0}{\sqrt{3}}\left((0,1)+\left(\sqrt{3}i\frac{\sqrt{3}}{2},-(-\frac{1}{2})\right)\right) \\
&= i\left(p_x,p_y\right)\cdot\frac{a_0}{\sqrt{3}}\frac{3}{2}\left(i,1\right) \\
&= -\frac{\sqrt{3}a_0}{2}\left(p_x-ip_y\right)
\end{aligned} \tag{IV.14}$$

Substituting in the Hamiltonian yields

$$\begin{aligned} H_{\mathbf{K+p}} &= \begin{bmatrix} \epsilon & -t\gamma_{\mathbf{K+p}} \\ -t\gamma^{\dagger}_{\mathbf{K+p}} & -\epsilon \end{bmatrix} \\ &= \begin{bmatrix} \epsilon & t\frac{\sqrt{3}a_0}{2}\left(p_x - ip_y\right) \\ t\frac{\sqrt{3}a_0}{2}\left(p_x + ip_y\right) & -\epsilon \end{bmatrix} \\ &= \begin{bmatrix} \epsilon & 0 \\ 0 & -\epsilon \end{bmatrix} + t\frac{\sqrt{3}a_0}{2}\begin{bmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{bmatrix} \\ &= \epsilon\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} + t\frac{\sqrt{3}a_0}{2}\left(p_x\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + p_y\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\right) \\ &= \epsilon\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} + t\frac{\sqrt{3}a_0}{2}\left(\left(p_x, p_y\right)\cdot\left(\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\right)\right) \end{aligned} \tag{IV.15}$$

If can invoke the Pauli matrices

$$\boldsymbol{\sigma} = \left(\sigma_x, \sigma_y, \sigma_z\right) \quad \text{where} \quad \begin{cases} \sigma_{\mathrm{x}} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ \sigma_{\mathrm{y}} = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \\ \sigma_{\mathrm{z}} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \end{cases} \tag{IV.16}$$

We can rewrite the Hamiltonian (IV.15) in terms of them as

$$\boxed{H_{\mathbf{K+p}} = \epsilon\sigma_z + t\frac{\sqrt{3}a_0}{2}\left(\mathbf{p}\cdot\boldsymbol{\sigma}\right) \qquad \text{(IV.17)}}$$

Clearly, the Hamiltonian (IV.17) resembles the Dirac Hamiltonian in two-dimension,

$$H_{\mathrm{Dirac}} = \sigma_z mc^2 + c\left(\mathbf{p}\cdot\boldsymbol{\sigma}\right) \tag{IV.18}$$

where m is the rest mass and c is the speed of light. We can now work backwards and calculate the band structure by finding the eigenvalues of the Hamiltonian $H_{\mathbf{K+p}}$. We obtain

$$\begin{aligned} 0 &= \det\left(H_{\mathbf{K+p}} - E_{\mathbf{K+p}}\mathbb{1}\right) \\ &= \begin{vmatrix} \epsilon - E_{\mathbf{K+p}} & v_F\left(p_x - ip_y\right) \\ v_F\left(p_x + ip_y\right) & -\epsilon - E_{\mathbf{K+p}} \end{vmatrix} \\ &= E^2_{\mathbf{K+p}} - \epsilon^2 - v_F^2\left(p_x^2 + p_y^2\right) \\ &= E^2_{\mathbf{K+p}} - \left(\left(m_{\text{eff}}v_F^2\right)^2 + v_F^2p^2\right) \end{aligned} \tag{IV.19}$$

The eigen energies are

$$\boxed{E_{\mathbf{K+p}}(p) = \pm\sqrt{p^2v_F^2 + m_{\text{eff}}^2v_F^4} \qquad \text{(IV.20)}}$$

which is exactly one would aspect. Notice that, for the case of graphene, the term $\epsilon\sigma_z$ in (IV.17) would not appear since the band gap is zero. This implies that, for low energies, electrons behave as if they are massless.

V. HBN DENSITY OF STATES

A. Analytical Evaluation for Low Energies Regime

Consider, in reciprocal space, the plane $k_x k_y$, discretized into small intervals of allowed momentum k_x and k_y. The volume of each small interval is then given by

$$\Delta k = \frac{(2\pi)^2}{A} \tag{V.1}$$

where we A is the area of the hexagonal Brillouin unit cell. The number of states per area is given by

$$\mathcal{N}(k) = \frac{1}{A}\frac{\pi k^2}{\Delta k} = \frac{1}{4\pi}k^2. \tag{V.2}$$

If we account for the spin degeneracy (×2) and for the valley degeneracy (×2) of the $\mathbf{K}^{\pm}$ points, we instead obtain

$$\mathcal{N}(k) = \frac{2}{\pi}k^2. \tag{V.3}$$

Given the low energy energy dispersion expressed in equation (IV.20) we have that

$$k^2 = \frac{1}{v_F^2}\left(E^2 - \epsilon^2\right) \tag{V.4}$$

And thus, the number of states in terms of the energies is given by

$$\mathcal{N}(E) = \frac{2}{\pi}\frac{1}{v_F^2}\left(E^2 - \epsilon^2\right) \tag{V.5}$$

Notice that, given the bandgap ϵ there is certainly no states for energies below $E < \epsilon$. The density of states, being the number of states per energies per area, is then defined as

$$DoS\left(E\right) = \frac{d\mathcal{N}(E)}{dE} \tag{V.6}$$

and thus

$$\boxed{DoS_{\mathbf{K+p}}\left(E\right) = \frac{4}{\pi}\frac{1}{v_F^2}E, \qquad E \notin [-\epsilon, +\epsilon] \qquad \text{(V.7)}}$$

B. Numerical evaluation for all energies

In this section, we show the relevant bits of a possible numerical implementation of the hBN density of states in the programming language *Julia*. Since the code is self-explanatory we will not make any extra regards concerning the implementations. However, in the oral presentation, a discussion will be made. [If one wishes to obtain the full code or a detailed explanation, refer to franciscolobo1880@gmail.com]

```julia
function kgrid(Nkpts, b1, b2)

    kpts = Vector{Float64}[]

    for j in 1:Nkpts
        for i in 1:Nkpts

            k = (2*i - Nkpts - 1)/(2Nkpts) * b1 + (2*j - Nkpts - 1)/(2Nkpts) * b2

            push!(kpts, k)

        end
    end

    return kpts
end

# where k is defined in the mean points
```

```
kgrid (generic function with 1 method)
```

```julia
# with the reciprocal basis vector being:
b1 = (4π/sqrt(3))*[-sqrt(3), -1];
b2 = (4π/sqrt(3))*[-sqrt(3), +1];
```

Figure 3. **Building the reciprocal lattice grid.** Numerical implementation of the k points within the first Brillouin zone.

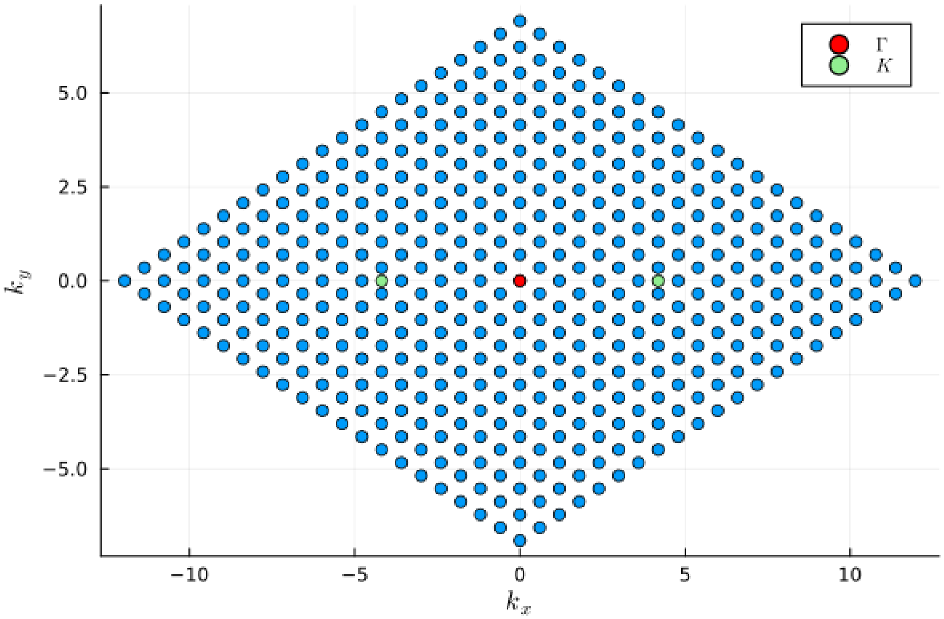


Figure 4. Brillouin zone grid built from the reciprocal basis vectors $\mathbf{b}_1$ and $\mathbf{b}_2$.

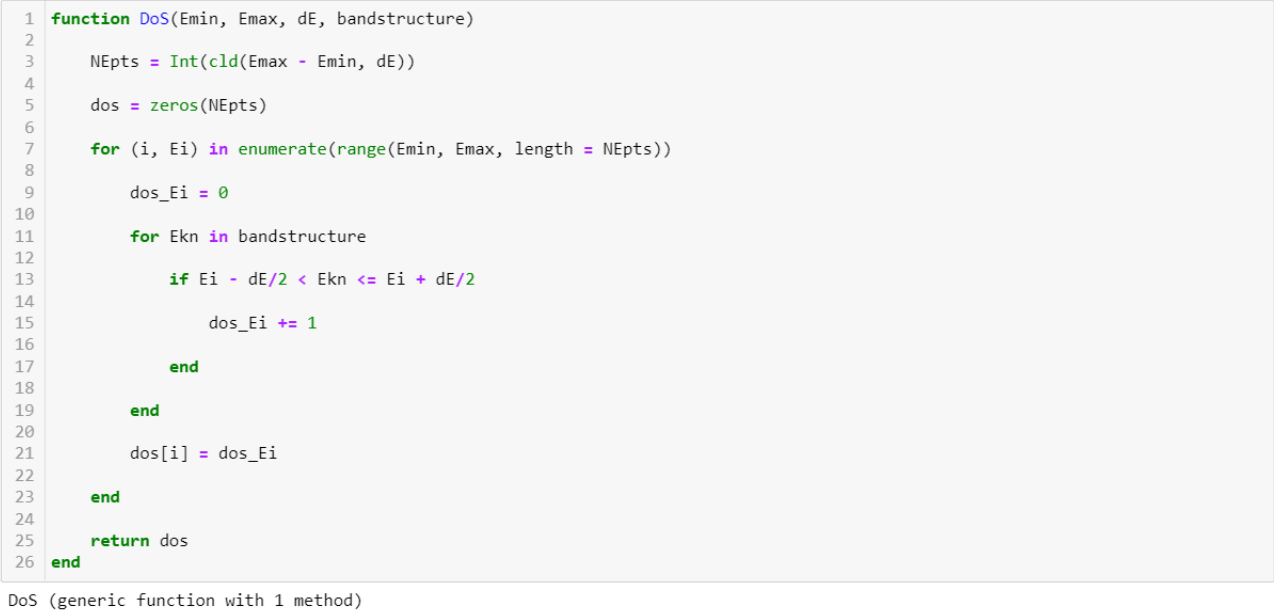
```
const ϵ  = 0.2 ;
const t  = 1   ;
const a0 = 1   ;
```

```
E(k) = sqrt( ϵ^2 + t^2 * ( 3 + 2*cos( a0 * k[1] ) + 4*cos( a0*sqrt(3)/2 * k[2] ) * cos( a0/2 * k[1] ) ) );

# where k is a vector from the grid
```

```
function bandstructure(kpts)

    Nkpts = length(kpts)
    band = zeros(Nkpts)

    for (i, k) in enumerate(kpts)
        band[i] = E(k)
    end

    return band

end

# returns a matrix with the values of E(kx,ky) for every k in the grid
```

```
bandstructure (generic function with 1 method)
```

Figure 5. **Calculating all the possible energies.** Numerical implementation of the energy spectrum within the first Brillouin zone.



```
function DoS(Emin, Emax, dE, bandstructure)

    NEpts = Int(cld(Emax - Emin, dE))

    dos = zeros(NEpts)

    for (i, Ei) in enumerate(range(Emin, Emax, length = NEpts))

        dos_Ei = 0

        for Ekn in bandstructure

            if Ei - dE/2 < Ekn <= Ei + dE/2

                dos_Ei += 1

            end

        end

        dos[i] = dos_Ei

    end

    return dos
end
```

```
DoS (generic function with 1 method)
```

Figure 6. **Counting the Number of States.** Numerical implementation of the energy spectrum within the first Brillouin zone.

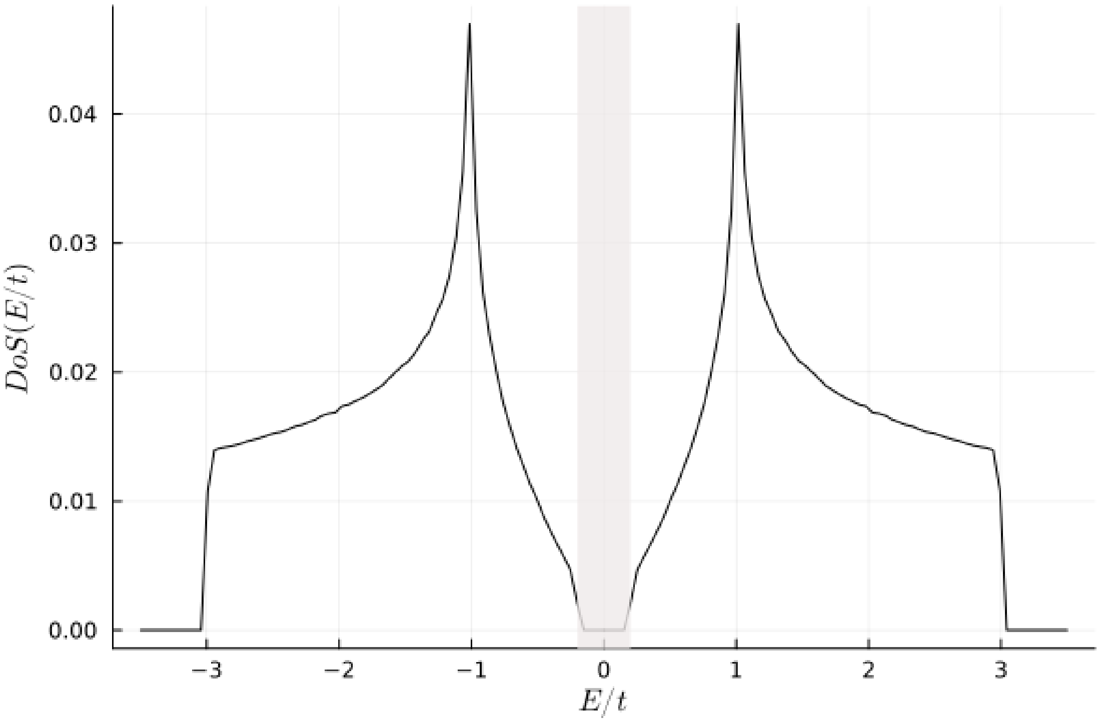


Figure 7. Numerical results for the hBN density of energy states. The bandgap region $[-\epsilon, +\epsilon]$ is depicted in gray. As expected, the density of energy states is zero within this region. Furthermore, for energies $|E/t| > 3$, we also have a null density of energy states since the two depicted band cap at those energy levels [as one seen also in Fig(1)]