

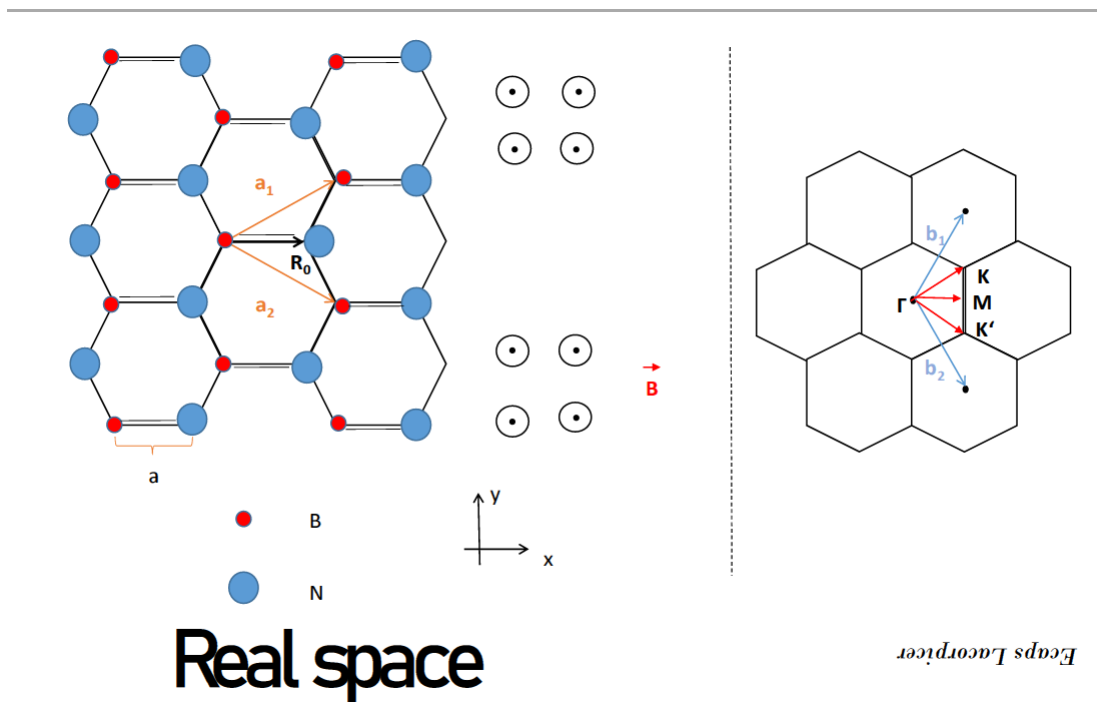
# $\pi$ electrons of a 2D material in a magnetic field

Contact: [www.martinnapetschnig.com](http://www.martinnapetschnig.com)

April 2022

Hexagonal boron nitride (h-BN) is a material that is used as a lubricant for various applications. In its most stable crystalline form, it is a layered material consisting of two dimensional atomic sheets which are loosely held together by van der Waals forces. The structure of the layers is depicted in the figure below. The B and N atoms form a hexagonal lattice. Due to the fact that the atoms in one layer are held together by covalent bonds while the different layers along the vertical  $z$ -axis are bound by the much weaker van der Waals forces, it is a valid approximation to describe h-BN as a two dimensional material.

Both the B and the N atoms are  $sp^2$  hybridised ( $2s, 2p_x, 2p_y, 2p_z \rightarrow 2sp^2, 2p_z$ ). This means that the hybrid orbital forms three planar  $\sigma$  bonds to the neighbouring atoms, while the remaining  $\pi$  bond (containing 2 electrons of one B–N bond) is orthogonal to the  $xy$  plane. In what follows, we will only focus on these two electrons of the  $\pi$  bond, as they constitute the highest occupied molecular orbital (HOMO).



The basis of the hexagonal lattice consists of one B=N double bond. The interatomic distance has a length  $a$ . The lattice vectors in real space,  $\mathbf{a}_1$  &  $\mathbf{a}_2$ , and the first Brillouin zone in reciprocal space (with the symmetry points  $\Gamma$ ,  $K$ ,  $K'$  and  $M$ ) are shown in the figure as well. The single electron wavefunction in the h-BN sheet is approximated by a linear combination of atomic orbital

(LCAO) wavefunctions of the atoms in the basis. Furthermore, only the  $2p_z$  orbitals will be considered, such that the only the two functions  $\phi_B(\mathbf{r}) \equiv \phi_{p_z}^{(B)}(\mathbf{r})$  and  $\phi_N(\mathbf{r}) \equiv \phi_{p_z}^{(N)}(\mathbf{r})$  form the set of basis functions of the single electron wavefunction  $\Psi_k(\mathbf{r})$ . Following this approach, the following ansatz for the wavefunction is used:

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} (c_B \phi_B(\mathbf{r} - \mathbf{R}) + c_N \phi_N(\mathbf{r} - \mathbf{R} - \mathbf{R}_0)). \quad (1)$$

In the equation above,  $N$  is the total number of possible lattice vectors,  $\mathbf{k}$  is the wave number that labels the function  $\Psi_{\mathbf{k}}(\mathbf{r})$ ,  $\mathbf{R}$  labels all possible lattice vectors in real space,  $\mathbf{R}_0$  is the vector between the B and N atoms in the basis and  $c_B$  &  $c_N$  are complex coefficients. This wavefunction satisfies the stationary *Schrödinger equation*:

$$\hat{H}\Psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}}\Psi_{\mathbf{k}}(\mathbf{r}) \quad (2)$$

where  $\varepsilon_{\mathbf{k}}$  is the energy of the electron and  $\hat{H}$  is the Hamiltonian of the system. The specific form of  $\phi_B(\mathbf{r})$  &  $\phi_N(\mathbf{r})$  is not needed, as we parametrise the theory as follows:

$$\int d^3r \phi_B^*(\mathbf{r}) H \phi_B(\mathbf{r} - \mathbf{R}) = \varepsilon_B \delta(\mathbf{R}), \quad (3)$$

$$\int d^3r \phi_N^*(\mathbf{r}) H \phi_N(\mathbf{r} - \mathbf{R}) = \varepsilon_N \delta(\mathbf{R}), \quad (4)$$

$$\int d^3r \phi_B^*(\mathbf{r}) H \phi_N(\mathbf{r} - \mathbf{R} - \mathbf{R}_0) = t \theta(a - |\mathbf{R} - \mathbf{R}_0|). \quad (5)$$

The on-site energies for B and N orbitals are given by  $\varepsilon_B$  &  $\varepsilon_N$ , respectively and  $t$  is the transition matrix element between neighbouring atoms. The  $\delta$  and Heaviside  $\theta$  functions express the fact only matrix elements on the same atomic site or between neighbouring atoms are non-vanishing. Overlap integrals with a larger spatial separation are zero, because the atomic orbital functions are sharply localised at the position of the atoms. In addition to that, the following identities hold:

$$\int d^3r \phi_B^*(\mathbf{r}) \phi_B(\mathbf{r} - \mathbf{R}) = \delta(\mathbf{R}) = \int d^3r \phi_N^*(\mathbf{r}) \phi_N(\mathbf{r} - \mathbf{R}), \quad (6)$$

$$\int d^3r \phi_N^*(\mathbf{r}) \phi_B(\mathbf{r} - \mathbf{R}) = 0. \quad (7)$$

This is the **Tight Binding** (TB) method.

## 1 Band Structure

- From the figure shown above, determine the lattice vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , the reciprocal lattice vectors  $\mathbf{b}_1$  &  $\mathbf{b}_2$  and the vectors to the symmetry points  $\Gamma$ ,  $K$ ,  $K'$  &  $M$ , in reciprocal space<sup>1</sup>.
- Exploiting the crystal symmetry, show that the ansatz (1) satisfies Bloch's theorem, i.e. that

$$\Psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \Psi_{\mathbf{k}}(\mathbf{r}) \quad (8)$$

holds.

- Derive a matrix relation for the coefficients  $c_B$  &  $c_N$  of the form:

$$\begin{pmatrix} H_{BB}(\mathbf{k}) & H_{BN}(\mathbf{k}) \\ H_{BN}^*(\mathbf{k}) & H_{NN}(\mathbf{k}) \end{pmatrix} \begin{pmatrix} c_B \\ c_N \end{pmatrix} = \varepsilon_{\mathbf{k}} \begin{pmatrix} c_B \\ c_N \end{pmatrix} \quad (9)$$

<sup>1</sup>Hint: The reciprocal lattice vectors satisfy  $a_i b_j = \delta_{ij}$ ,  $i, j = 1, 2$

by projecting both sides of the Schrödinger equation (2) one time with  $\int d^3r \phi_B^*(\mathbf{r}) \cdot$  and another time with  $\int d^3r \phi_N^*(\mathbf{r}) \cdot$ . To arrive at closed expressions, you need to use the tight binding identities shown above.

- (d) We would like to investigate the electronic structure in the vicinity of the symmetry point  $K$  in the long wavelength limit. To this end, expand the Hamiltonian matrix  $\hat{H}(\mathbf{k} = \mathbf{K} + \mathbf{k}')$  to first order in  $k'_x, k'_y$  around  $\mathbf{K}$  ( $|\mathbf{k}'| \ll |\mathbf{K}|$ ).
- (e) With the Hamiltonian found, calculate the energy eigenvalues  $\varepsilon_{\pm}$  of the matrix eigenvalue problem (9). Determine the Fermi energy  $\varepsilon_F$ , the band gap at  $\mathbf{k}' = 0$ ,  $\varepsilon_g$ , and the effective mass array of electrons in the conduction band,  $\mathbf{m}_e^*$ , and of holes in the valence band,  $\mathbf{m}_h^*$ , given by:

$$\varepsilon_F = \frac{\varepsilon_+ + \varepsilon_-}{2}, \quad (10)$$

$$\varepsilon_g = \varepsilon_+ - \varepsilon_-, \quad (11)$$

$$m_i^* = \frac{\hbar^2}{\left. \frac{d^2 E}{dk_i^2} \right|_{\mathbf{k}'=0}}, \quad i = x, y \quad (12)$$

Are the effective masses isotropic? What is the relation between  $\mathbf{m}_e^*$  and  $\mathbf{m}_h^*$ ? Are you aware of a material that has zero band gap and zero effective masses at the symmetry point  $K$ ?

## 2 Effective Hamiltonian in amagnetic field

In this part of the exercise we would like to investigate the behaviour of charge carriers in a constant magnetic field in the above approximation. The magnetic field is taken to be perpendicular to the  $xy$  plane:  $\mathbf{B} = B\mathbf{e}_z$

- (a) To set up the Schrödinger equation for this system, consider the *reduced Hamiltonian*  $\hat{H}_R = \hat{H} - \varepsilon_F \mathbb{1}$  and promote the wavenumber  $\mathbf{k}$  to an operator according to the *Peierls substitution*:  $\mathbf{k} \rightarrow \mathbf{k}' = -i\vec{\nabla} + \frac{q}{\hbar}\mathbf{A}$ . For the vector potential  $\mathbf{A}$  use the Landau gauge  $\mathbf{A} = Bx\mathbf{e}_y$ .
- (b) The system of equations can be decoupled by writing down the squared Schrödinger equation  $\hat{H}_R^2 \Psi(x, y) = \varepsilon_R^2 \Psi(x, y)$ . Use the ansatz  $\Psi(x, y) = e^{ik_y y} \varphi(x)$  to obtain an ordinary differential equation in  $x$  for  $\varphi(x)$ . It might be convenient to make the substitution  $x \rightarrow x' = x - x_0$  with a suitable variable  $x_0$ .
- (c) The obtained equation can be solved by introducing suitable creation and annihilation operators  $\hat{a}$  &  $\hat{a}^\dagger$  as a linear combination  $\hat{a} = \alpha \frac{d}{dx} + \beta x$ ;  $\alpha, \beta \in \mathbb{C}$  and rewriting  $\hat{H}_R$  in terms of these new operators. The ladder operators should be normalised such that they satisfy the commutation relation  $[\hat{a}, \hat{a}^\dagger] = \mathbb{1}$ . Write down the discrete energy spectrum  $\varepsilon_n$ .
- (d) As the eigenenergies found do not depend on  $k_y$ , each energy level is highly degenerate. To obtain the degeneracy  $n_y$  for a given magnetic field, use the quantisation of  $k_y$  and the trivial fact that  $0 \leq x_0 \leq L_x$ . Given a fixed number  $\mathcal{N}$  of electrons in the conduction band/holes in the valence band and a magnetic field  $B$ , how many energy levels are populated ( $n_{\max} = ?$ ) and up to what energy ( $\varepsilon_{n_{\max}} = ?$ ). Neglect spin and assume zero temperature for this task.