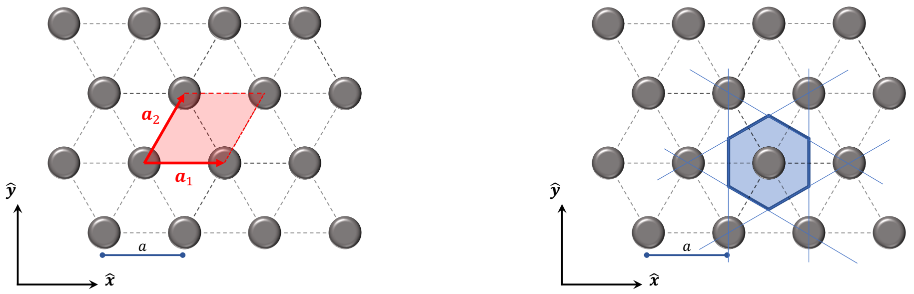
Solution of homework # 9

Exercise 1 - 2D lattices



(a) Primitive cell of the hexagonal lattice.

(b) Wigner-Seitz cell of the hexagonal lattice

Figure 1

1. There are several ways to choose the primitive vectors. One possible choice is given by:

$$\mathbf{a}_1 = a\begin{pmatrix}1\\0\end{pmatrix}, \quad \mathbf{a}_2 = a\begin{pmatrix}\frac{1}{2}\\ \frac{\sqrt{3}}{2}\end{pmatrix}. \tag{1}$$

2. The Wigner-Seitz cell can be built around an atom by drawing straight lines perpendicular to the segments connecting the atom to its nearest neighbors and passing through the midpoint of the segment.

3. The primitive vectors of the reciprocal lattice can be obtained from the orthogonality condition $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$. We get then:

$$\mathbf{b}_1 = b\begin{pmatrix}\frac{\sqrt{3}}{2}\\ -\frac{1}{2}\end{pmatrix}, \quad \mathbf{b}_2 = b\begin{pmatrix}0\\1\end{pmatrix}, \tag{2}$$

   where $b = \frac{4\pi}{a\sqrt{3}}$ and we notice that the reciprocal lattice of the hexagonal lattice is still and hexagonal lattice (with just a different orientation). The reciprocal lattice is a Bravais lattice because any vector $\mathbf{G}$ satisfying the condition $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$ (for any vector $\mathbf{R}$ of the direct lattice) can be written as a linear combination of basis vectors, where the coefficients are integer numbers. And this is exactly the defintion of a Bravais lattice.

4. The (first) Brillouin zone of the hexagonal lattice is drawn in Fig. 2.

5. The honeycomb structure is not a Bravais lattice. This can be easily shown by looking at Fig. 3. The surrounding environment seen by the atoms 1 and 2 is different, while in a Bravais lattice you should always have the same landscape.

6. To define the crystal structure of graphene, that is the honeycomb structure, we need to define a basis in addition to the primitive lattice vectors. Such structure can be described

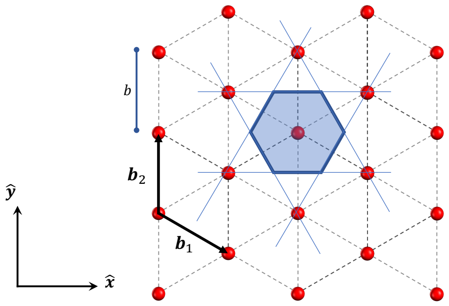
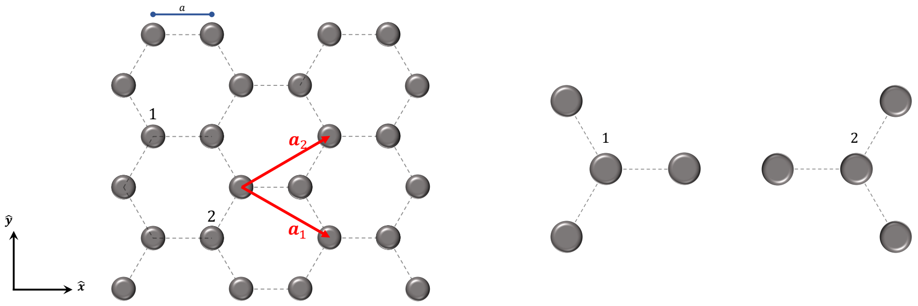


Figure 2: Reciprocal lattice and Brillouin zone of the hexagonal lattice.



(a) (b)

Figure 3: (a) The honeycomb structure and (b) the different surroundings seen by atom 1 and 2.

by a triangular lattice with primitive vectors:

$$\mathbf{a}_1 = a\begin{pmatrix} \frac{3}{2} \\ -\frac{\sqrt{3}}{2} \end{pmatrix}, \quad \mathbf{a}_2 = a\begin{pmatrix} \frac{3}{2} \\ \frac{\sqrt{3}}{2} \end{pmatrix}, \tag{3}$$

and a basis for the atomic positions inside the primitive cell:

$$\mathbf{d}_1 = \mathbf{0}, \quad \mathbf{d}_2 = a\begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{4}$$

Exercise 2 - Cubic lattices.

1. The triple product of vectors $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ can be computed by calculating the determinant of the 3×3 matrix whose columns (or lines) are the three vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$:

$$v_{\text{SC}} = a^3 \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = a^3, \quad v_{\text{BCC}} = \frac{a^3}{8} \begin{vmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{vmatrix} = \frac{a^3}{2}, \quad v_{\text{FCC}} = \frac{a^3}{8} \begin{vmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{vmatrix} = \frac{a^3}{4}. \tag{5}$$

Since in each case the primitive cell contains only one atom, the most "packed" or dense structure is the one with the smallest primitive cell, *i.e.* the FCC.

2. To calculate the primitive vectors of the reciprocal lattice we use the definition for the three-dimensional case:

$$\mathbf{b}_1 = \frac{2\pi}{v}(\mathbf{a}_2 \times \mathbf{a}_3), \quad \mathbf{b}_2 = \frac{2\pi}{v}(\mathbf{a}_3 \times \mathbf{a}_1), \quad \mathbf{b}_3 = \frac{2\pi}{v}(\mathbf{a}_1 \times \mathbf{a}_2). \tag{6}$$

Then we find

- SC: $$\mathbf{b}_1 = b\begin{pmatrix}1\\0\\0\end{pmatrix}, \quad \mathbf{b}_2 = b\begin{pmatrix}0\\1\\0\end{pmatrix}, \quad \mathbf{b}_3 = b\begin{pmatrix}0\\0\\1\end{pmatrix}; \tag{7}$$
- BCC: $$\mathbf{b}_1 = b\begin{pmatrix}0\\1\\1\end{pmatrix}, \quad \mathbf{b}_2 = b\begin{pmatrix}1\\0\\1\end{pmatrix}, \quad \mathbf{b}_3 = b\begin{pmatrix}1\\1\\0\end{pmatrix}; \tag{8}$$
- FCC: $$\mathbf{b}_1 = b\begin{pmatrix}-1\\1\\1\end{pmatrix}, \quad \mathbf{b}_2 = b\begin{pmatrix}1\\-1\\1\end{pmatrix}, \quad \mathbf{b}_3 = b\begin{pmatrix}1\\1\\-1\end{pmatrix}; \tag{9}$$

where $b = \frac{2\pi}{a}$. We notice that the reciprocal lattice of a simple cubic is still a simple cubic, while the reciprocal lattice of a body-centered cubic is a face-centered cubic and viceversa. The volumes Ω of the three Brillouin zones are:

$$\text{SC:} \quad \Omega = b^3 = \frac{8\pi^3}{a^3}, \quad \text{BCC:} \quad \Omega = 2b^3 = \frac{16\pi^3}{a^3}, \quad \text{FCC:} \quad \Omega = 4b^3 = \frac{32\pi^3}{a^3}. \tag{10}$$

3. In the SC lattice, each atom has 6 nearest neighbors (the coordination number then is 6) at a distance a. In the BCC lattice (see Fig. 4a) the coordination number is 8 and the nearest-neighbors distance is $\frac{\sqrt{3}}{2}a$. In the FCC lattice (see Fig. 4b) the coordination number is 12 and the nearest-neighbors distance is $\frac{a}{\sqrt{2}}$.

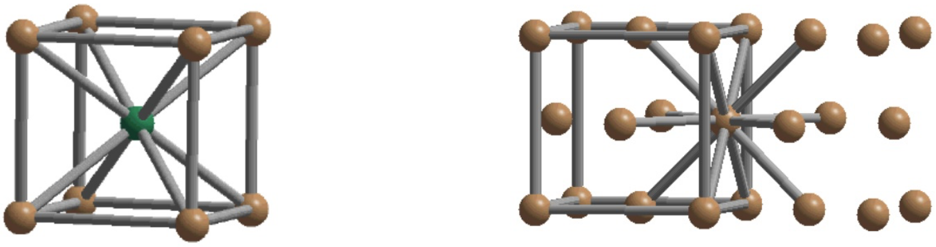

(a) (b)

Figure 4: Nearest-neighbors in the (a) body-centered and (b) face-centered cubic systems.

4. The density is an intensive quantity, so we can calculate it from the ratio between the mass contained in a primitive cell and the volume of the primitive cell. Since aluminum, copper and gold have an FCC structure, there is only one atom inside a primitive cell,

thus we find:

$$\begin{aligned}
\rho_{Al} &= \frac{4 \cdot 27 \cdot 1.66 \cdot 10^{-24}\,\text{g}}{(4.05 \cdot 10^{-8}\,\text{cm})^3} \approx 2.70 \ \text{g/cm}^3, \\
\rho_{Cu} &= \frac{4 \cdot 63.5 \cdot 1.66 \cdot 10^{-24}\,\text{g}}{(3.61 \cdot 10^{-8}\,\text{cm})^3} \approx 8.96 \ \text{g/cm}^3, \\
\rho_{Au} &= \frac{4 \cdot 197 \cdot 1.66 \cdot 10^{-24}\,\text{g}}{(4.08 \cdot 10^{-8}\,\text{cm})^3} \approx 19.3 \ \text{g/cm}^3,
\end{aligned} \tag{11}$$

where we used the previous result for the volume of the primitive cell, $v = a^3/4$.

Exercise 3 – Bloch theorem and plane waves

1. The potential term of the Hamiltonian acts on $u_{n\mathbf{k}}$ as it acts on the $\psi_{n\mathbf{k}}$, instead the kinetic term is more interesting. We focus on the momentum operator $\hat{\mathbf{p}}$, which acts on $\psi_{n\mathbf{k}}$ as follows:

$$\hat{\mathbf{p}}\, \psi_{n\mathbf{k}}(\mathbf{r}) = -i\hbar\nabla \Big[e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \Big] = e^{i\mathbf{k}\cdot\mathbf{r}} (-i\hbar\nabla + \hbar\mathbf{k}) u_{n\mathbf{k}}(\mathbf{r}), \tag{12}$$

where we just used the derivative of a product of two functions. The momentum operator acts on Bloch states in such a way that we can factor out the phase. Then, we redefine a new momentum operator which depends on the crystal momentum $\mathbf{k}$ and it acts on the periodic part only $(-i\hbar\nabla + \hbar\mathbf{k})$ - it is a gradient plus a constant term proportional to the $\mathbf{k}$ vector. Similarly, we can obtain the following expression:

$$\frac{\hat{\mathbf{p}}^2}{2m}\, \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{\hat{\mathbf{p}}^2}{2m} \Big[e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \Big] = e^{i\mathbf{k}\cdot\mathbf{r}} \frac{(-i\hbar\nabla + \hbar\mathbf{k})^2}{2m} u_{n\mathbf{k}}(\mathbf{r}). \tag{13}$$

Finally, we can write the Schödinger equation:

$$\Big(\frac{\hat{\mathbf{p}}^2}{2m} + \hat{V}_{ext} \Big) \psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}). \tag{14}$$

Using the result of Eq. (13) we can rewrite Eq. (14) as:

$$e^{i\mathbf{k}\cdot\mathbf{r}} \left(\frac{(-i\hbar\nabla + \hbar\mathbf{k})^2}{2m} + \hat{V}_{ext} \right) u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}). \tag{15}$$

The phase factor $e^{i\mathbf{k}\cdot\mathbf{r}}$ appears on both sides of the Schödinger equation (15), so we can remove it. We obtain an equation of the form $\hat{H}_{\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r})$, namely

$$\underbrace{\left(\frac{(-i\hbar\nabla + \hbar\mathbf{k})^2}{2m} + \hat{V}_{ext} \right)}_{=\hat{H}_{\mathbf{k}}} u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}). \tag{16}$$

$\hat{H}_{\mathbf{k}}$ is different from $\hat{H}$ as now the kinetic part depends on $\mathbf{k}$. Hence, for each vector $\mathbf{k}$ we need to diagonalize a different Hamiltonian $\hat{H}_{\mathbf{k}}$ to get eigenvalues $\varepsilon_{n\mathbf{k}}$ and eigenvectors $u_{n\mathbf{k}}(\mathbf{r})$.

2. By definition, $u_{n\mathbf{k}}(\mathbf{r})$ is lattice-periodic on the Bravais lattice (i.e. $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})$). Hence, all the components of its plane waves expansion must be periodic at least on the Bravais lattice. We write the plane waves expansion as:

$$u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} c_{n\mathbf{k},\mathbf{G}}, \tag{17}$$

where $e^{i\mathbf{G}\cdot\mathbf{r}}$ is the plane wave, $c_{n\mathbf{k},\mathbf{G}}$ are complex-valued coefficients representing the "weight" of each plane wave, and V is the volume of the crystal ($1/\sqrt{V}$ is the normalization factor which is used to ensure the normalization of $u_{n\mathbf{k}}(\mathbf{r})$ to 1). In the following we will use a shorter notation $c_{n\mathbf{k},\mathbf{G}} \equiv c_{\mathbf{G}}$, where dependence upon the band index n and the $\mathbf{k}$ vector is implied. Now we impose the periodicity:

$$\mathbf{G}\cdot\mathbf{R} = 2\pi m, \tag{18}$$

where m are integer numbers. Hence, only a discrete set of vectors $\mathbf{G}$ is allowed, in particular every plane wave of the expansion has a vector $\mathbf{G}$ of the kind:

$$\mathbf{G} = \mathbf{b}_1 n_1 + \mathbf{b}_2 n_2 + \mathbf{b}_3 n_3, \tag{19}$$

where $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ are the primitive vectors of the *reciprocal lattice*, and n_1, n_2, and n_3 are integer numbers.

3. Let us act with momentum operator $\hat{\mathbf{p}}$ on a plane wave:

$$\hat{\mathbf{p}}\, e^{i\mathbf{G}\cdot\mathbf{r}} = -i\hbar\nabla e^{i\mathbf{G}\cdot\mathbf{r}} = \hbar\mathbf{G}e^{i\mathbf{G}\cdot\mathbf{r}}. \tag{20}$$

Hence, the plane wave $e^{i\mathbf{G}\cdot\mathbf{r}}$ is an eigenstate of the momentum operator with eigenvalue $\hbar\mathbf{G}$.

4. We start to write $\varepsilon_{n\mathbf{k}} = \langle u_{n\mathbf{k}}|\hat{H}_{\mathbf{k}}|u_{n\mathbf{k}}\rangle$ using the plane waves expansion for $u_{n\mathbf{k}}(\mathbf{r})$ given by Eq. (17).

$$\varepsilon_{n\mathbf{k}} = \langle u_{n\mathbf{k}}|\hat{H}_{\mathbf{k}}|u_{n\mathbf{k}}\rangle = \frac{1}{V}\int_V d\mathbf{r}\sum_{\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}}c^*_{\mathbf{G}}\left(\frac{(-i\hbar\nabla+\hbar\mathbf{k})^2}{2m} + V_{ext}(\mathbf{r})\right)\sum_{\mathbf{G}'} e^{i\mathbf{G}'\cdot\mathbf{r}}c_{\mathbf{G}'}. \tag{21}$$

We start using the results of the previous answers and we act with the Hamiltonian on the plane waves:

$$\begin{aligned}
\varepsilon_{n\mathbf{k}} &= \frac{1}{V}\int_V d\mathbf{r}\sum_{\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}}c^*_{\mathbf{G}}\left(\frac{(-i\hbar\nabla+\hbar\mathbf{k})^2}{2m} + V_{ext}(\mathbf{r})\right)\sum_{\mathbf{G}'} e^{i\mathbf{G}'\cdot\mathbf{r}}c_{\mathbf{G}'} && (22)\\
&= \frac{1}{V}\int_V d\mathbf{r}\sum_{\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}}c^*_{\mathbf{G}}\sum_{\mathbf{G}'} c_{\mathbf{G}'}e^{i\mathbf{G}'\cdot\mathbf{r}}\left(\frac{(\hbar\mathbf{G}+\hbar\mathbf{k})^2}{2m} + V_{ext}(\mathbf{r})\right) && (23)\\
&= \frac{1}{V}\sum_{\mathbf{G}}\sum_{\mathbf{G}'} c^*_{\mathbf{G}}c_{\mathbf{G}'}\int_V d\mathbf{r}e^{-i\mathbf{G}\cdot\mathbf{r}}e^{i\mathbf{G}'\cdot\mathbf{r}}\left(\frac{(\hbar\mathbf{G}+\hbar\mathbf{k})^2}{2m} + V_{ext}(\mathbf{r})\right) && (24)\\
&= \sum_{\mathbf{G}}\sum_{\mathbf{G}'} c^*_{\mathbf{G}}c_{\mathbf{G}'}\left(\frac{(\hbar\mathbf{G}+\hbar\mathbf{k})^2}{2m}\delta_{\mathbf{G},\mathbf{G}'} + \frac{1}{V}\int_V d\mathbf{r}e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}V_{ext}(\mathbf{r})\right) && (25)\\
&= \sum_{\mathbf{G}}|c_{\mathbf{G}}|^2\frac{(\hbar\mathbf{G}+\hbar\mathbf{k})^2}{2m} + \sum_{\mathbf{G}}\sum_{\mathbf{G}'} c^*_{\mathbf{G}}c_{\mathbf{G}'}\tilde{V}_{ext}(\mathbf{G}-\mathbf{G}'), && (26)
\end{aligned}$$

where $\tilde{V}_{ext}(\mathbf{G})$ is the Fourier transform of the external potential $V_{ext}(\mathbf{r})$. In Eqs. (20)-(21) we used the fact that the first part of the integral (kinetic term) is different from zero only when $\mathbf{G}=\mathbf{G}'$, and $\int_V d\mathbf{r} = V$.

5. It is a straightforward exercise in vector algebra to show that the volume of the Brillouin zone is $V_{BZ} = \frac{(2\pi)^3}{V_c}$ where V_c is the volume of the *primitive unit cell.* You can prove it by taking the definition of the primitive cell vectors and compute the volume. In a fcc lattice,

the primitive cell has a volume $V_c = a^3/4$. In fact, the primitive unit cell has one atom per cell while the conventional fcc cell has four atoms per cell (see exercise 2, point 1, of this homework). For aluminium $a = 4.05\mathring{A}$ and

$$V_{\mathrm{BZ}} = \frac{(2\pi)^3 \cdot 4}{a^3}. \tag{27}$$

The volume of the sphere of radius G_{max} is:

$$V_{\mathrm{sphere}} = \frac{4}{3}\pi G_{max}^3 = \frac{4\pi(2\pi/\delta)^3}{3}. \tag{28}$$

Finally, the ratio between these two volumes gives the number of plane waves (PW):

$$N_{\mathrm{PW}} = \frac{V_{\mathrm{sphere}}}{V_{\mathrm{BZ}}} = \frac{4\pi(2\pi/\delta)^3 a^3}{3(2\pi)^3 \cdot 4} = \frac{\pi}{3}\left(\frac{a}{\delta}\right)^3 = \frac{\pi}{3}\left(\frac{4.05\mathring{A}}{0.1 \cdot 0.529\mathring{A}}\right)^3 \approx 470 \times 10^3. \tag{29}$$

As we can see, we need a huge number of plane waves (almost half a million) in the expansion of Bloch's wave-functions in order to describe fine details in the electronic structure which vary on a length scale of $\delta = 0.1$ a.u.