2.1

$$\hat{H}|\psi\rangle = E|\psi\rangle \qquad (1)$$

Let $\psi = \sum_i c_i \phi_i$,

By applying $\phi_j^*$ on both sides and integrating:

$$\sum_i \int d^3r\, \phi_j^* \hat{H} c_i \phi_i = E \sum_i \int d^3r\, \phi_j^* c_i \phi_i$$

Define $S_{ji} = \int d^3r\, \phi_j^* \phi_i$, $H_{ji} = \int d^3r\, \phi_j^* \hat{H} \phi_i$

then we get $\sum_i c_i \langle \phi_j | \hat{H} | \phi_i \rangle = E \sum_i S_{ji} c_i$

$$\sum_i c_i (\hat{H}_{ji} - E S_{ji}) = 0$$

So the equation can be turned into:

$$\begin{pmatrix} H_{11} - ES_{11}, & H_{12} - ES_{12}, & \cdots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21}, & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ H_{n1} - ES_{n1}, & \cdots & & H_{nn} - ES_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0$$

seting $\det(H_{ji} - ES_{ji}) = 0$ to get eigenvalues $E_1, E_2, \cdots E_n$.

Let $(\hat{H} - E_n)\psi_n = 0$, the eigenstates are solved.

2.2 (a) Since $V(\vec{r}) = V(\vec{r}+\vec{R})$, $H = \frac{p^2}{2m} + V(\vec{r})$

$\hat{T}_{\vec{R}} H\psi(\vec{r}) = [\frac{p^2}{2m} + V(\vec{r}+\vec{R})]\psi(\vec{r}+\vec{R}) = \hat{H}\hat{T}_R\psi(\vec{r})$, so $[\hat{H}, \hat{T}_R] = 0$

$\hat{H}$ commute with $\hat{T}_{\vec{R}}$, $\hat{H}\hat{T}_{\vec{R}} = \hat{T}_{\vec{R}}\hat{H}$

So $\hat{H}\hat{T}_{\vec{R}}\psi(\vec{r}) = \hat{T}_{\vec{R}}\hat{H}\psi(\vec{r}) = \hat{T}_{\vec{R}} E\psi(\vec{r}) = E\hat{T}_R\psi(\vec{r})$

So $\hat{T}_{\vec{R}}\psi(\vec{r})$ is also an eigenstate with the same energy.

(b) From (a) we know, $\hat{H}\hat{T}_R\psi_n(\vec{r}) = E_n\hat{T}_{\vec{R}}\psi_n(\vec{r})$

and $\hat{T}_{\vec{R}}\psi_n(\vec{r}) = \psi_n(\vec{r}+\vec{R})$

Then we may get, $\hat{H}\psi_n(\vec{r}+\vec{R}) = E_n\psi_n(\vec{r}+\vec{R})$

$\psi_n(\vec{r}+\vec{R})$ and $\psi_n(\vec{r})$ are eigenstates with the same eigenvalue $E_n$.

Since $E_n$ is non-degenerate, the probability of the two states should be equal, then we get:

$|\psi_n(\vec{r}+\vec{R})|^2 = |\psi_n(\vec{r})|^2$

$\psi_n^*(\vec{r}+\vec{R})\psi_n(\vec{r}+\vec{R}) = \psi_n^*(r)\psi_n(\vec{r})$, with $e^{i\theta(\vec{R})}$, $\psi_n(\vec{r})$ can be normalized.

$\Rightarrow \psi_n(\vec{r}+\vec{R}) = e^{i\theta(\vec{R})}\psi_n(\vec{r})$

So we could write $\hat{T}_{\vec{R}}\psi_n(\vec{r}) = \psi_n(\vec{r}+\vec{R}) = e^{i\theta(\vec{R})}\psi_n(\vec{r})$.

Thus $\psi_n(\vec{r})$ is a simultaneous eigenstate of $\hat{H}$ (with eigenvalue $E_n$) and of $\hat{T}_{\vec{R}}$ (with eigenvalue $e^{i\theta(\vec{R})}$.

(c) (i) $\psi_n(\vec{r}+\vec{R_1}+\vec{R_2}) = e^{i\theta(\vec{R_1}+\vec{R_2})}\psi_n(\vec{r})$ (1)

(ii) $\psi_n(\vec{r}+\vec{R_1}) = e^{i\theta(\vec{R_1})}\psi_n(\vec{r})$

So $\psi_n(\vec{r}+\vec{R_1}+\vec{R_2}) = e^{i\theta(\vec{R_1})} \cdot e^{i\theta(\vec{R_2})}\psi_n(\vec{r})$ (2)

compare (1) and (2), we have $\theta(\vec{R_1}+\vec{R_2}) = \theta(\vec{R_1}) + \theta(\vec{R_2})$

If $\theta(\vec{R})$ is a linear in $R$, we have

$\theta(\vec{R_1}) = A_1R_x + B_1R_y + C_1R_z$

$\theta(\vec{R_2}) = A_2R_x + B_2R_y + C_2R_z$

So, $\theta(\vec{R_1})+\theta(\vec{R_2}) = (A_1+A_2)R_x + (B_1+B_2)R_y + (C_1+C_2)R_z$ (3)

Consider (i) : $\psi_n(\vec{r}+\vec{R_1}+\vec{R_2}) = e^{i\theta(\vec{R_1}+\vec{R_2})}\,\psi_n(\vec{r})$ (4)

Consider (ii) : $\psi_n(\vec{r}+\vec{R_1}) = e^{i\theta(\vec{R_1})}\psi_n(\vec{r}) = e^{i(A_1R_x+B_1R_y+C_1R_z)}\psi_n(\vec{r})$

$$\psi_n(\vec{r}+\vec{R_1}+\vec{R_2}) = e^{i(A_1R_x+B_1R_y+C_1R_z)}\cdot e^{i(A_2R_x+B_2R_y+C_2R_z)}\psi_n(\vec{r})$$

$$= e^{i[(A_1+A_2)R_x+(B_1+B_2)R_y+(C_1+C_2)R_z]}\psi_n(\vec{r}) \quad (5)$$

Compare (4),(5), we have $\theta(\vec{R_1}+\vec{R_2}) = (A_1+A_2)R_x + (B_1+B_2)R_y + (C_1+C_2)R_z$ (6)

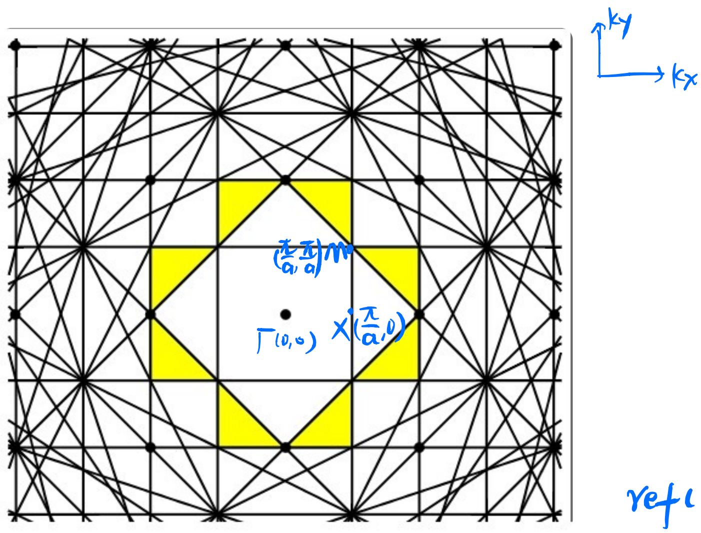
compare (3) and (6), $\theta(\vec{R_1})+\theta(\vec{R_2}) = \theta(\vec{R_1}+\vec{R_2})$ is satisfied.

(d) $\theta(\vec{R}) = AR_x + BR_y + CR_z = (A, B, C)\begin{pmatrix} R_x \\ R_y \\ R_z \end{pmatrix} = \vec{k}\cdot\vec{R}$

So $\hat{T}_{\vec{R}}\psi_n(\vec{r}) = \psi_n(\vec{r}+\vec{R}) = e^{i\theta(\vec{R})}\psi_n(\vec{r}) = e^{i\vec{k}\cdot\vec{R}}\psi_n(\vec{r})$

That is Bloch's theorem: $\psi_n(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi_n(\vec{r})$, with eigenvalue $E_n(\vec{k})$

2.3.




ref(1)

First, here shows how to sketch the energy versus k from $\Gamma \to X \to M \to \Gamma$ where k belongs to 1st B.Z.

use free particle Hamiltonian, $E(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m}$, $\vec{k} = (k_x, k_y)$

$E(\vec{k}) = \frac{\hbar^2}{2m}(k_x^2 + k_y^2)$, Let $\Gamma(0,0)$, $X(\frac{\pi}{a}, 0)$, $M(\frac{\pi}{a}, \frac{\pi}{a})$

So $\Gamma$: $E(0,0) = 0$

$X$: $E(\frac{\pi}{a}, 0) = \frac{\hbar^2}{2m}(\frac{\pi}{a})^2 = \varepsilon$

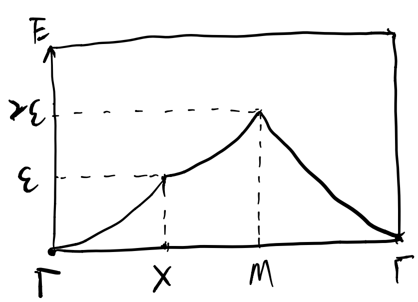
$M$: $E(\frac{\pi}{a}, \frac{\pi}{a}) = \frac{\hbar^2}{2m}(\frac{\pi}{a})^2 \times 2 = 2\varepsilon$

From $\Gamma$ to $X$, $E = \frac{\hbar^2}{2m} k_x^2$

From $X$ to $M$, $E = \frac{\hbar^2}{2m}(\frac{\pi}{a})^2 + \frac{\hbar^2}{2m} k_y^2$

From $M$ to $\Gamma$, $E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2) = \frac{\hbar^2}{m} k_x^2$ $\quad (k_x^2 = k_y^2)$

We can plot:



$\psi(r) = e^{i\vec{k}\cdot\vec{r}}$,

when $\vec{k}$ is outside the 1st B.Z., the eigenfuction can be writtern in Bloch form with $\vec{k}'$ inside the first B.Z.

$\psi(r) = e^{i\vec{k}'\cdot\vec{r}} \cdot e^{i\vec{G}_n\vec{r}}$, where $\vec{k} = \vec{k}' + \vec{G}_n$, the energy is:

$$E(k) = \frac{\hbar^2(\vec{k}'+\vec{G}_n)^2}{2m}$$

Then we may find the energy of those k, which can be translated to $\Gamma$, X, M in 1st B.Z:

$$E_n(k) = \frac{\hbar^2}{2m}(k'+G_n)^2, \quad \Gamma(0,0)\ X(\tfrac{\pi}{a},0), M(\tfrac{\pi}{a},\tfrac{\pi}{a})$$

let $G_1 = (0,0)$, $G_2 = (-2\pi/a, 0)$ $G_3 = (0, -2\pi/a)$ $G_4 = (-2\pi/a, -2\pi/a)$, $G_5 = (\frac{2\pi}{a}, 0)$, $G_6 = (0, \frac{2\pi}{a})$

$n=1$, all $k \in$ 1st B.Z. $E_\Gamma = 0$; $E_X = \frac{\hbar^2}{2m}(\frac{\pi}{a})^2 = \varepsilon$, $E_M = \frac{\hbar^2}{2m}(\frac{\pi}{a})^2 \times 2 = 2\varepsilon$

$n=2$, $E_\Gamma = \frac{\hbar^2}{2m}(\frac{2\pi}{a})^2 = 4\varepsilon$, $E_X = \frac{\hbar^2}{2m}(\frac{\pi}{a})^2 = \varepsilon$, $E_M = \frac{\hbar^2}{2m}(\frac{\pi}{a})^2 \times 2 = 2\varepsilon$

$n=3$. $E_\Gamma = 4\varepsilon$, $E_X = \frac{\hbar^2}{2m}\left[(\frac{\pi}{a})^2 + (\frac{2\pi}{a})^2\right] = 5\varepsilon$, $E_M = 2\varepsilon$

$n=4$, $E_\Gamma = 8\varepsilon$, $E_X = 5\varepsilon$, $E_M = 2\varepsilon$

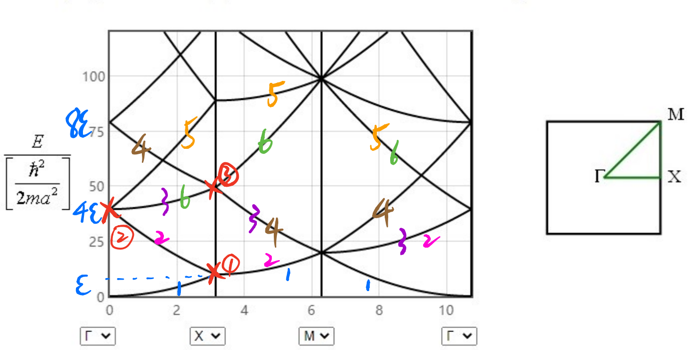
$n=5$, $E_\Gamma = 4\varepsilon$, $E_X = 9\varepsilon$, $E_M = 10\varepsilon$

$n=6$, $E_\Gamma = 4\varepsilon$, $E_X = 5\varepsilon$, $E_M = 10\varepsilon$

And sketch out the band along the path $\Gamma \to X \to Y \to \Gamma$ :

The number labeled in the plot is $n$.

**Empty lattice approximation for a 2-D square lattice**




ref(2)

Then, let's pick 2 places, marked with crossings

(i) First begin with the easier one, point ①, corresponding to two $k$, one is $(\frac{\pi}{a}, 0)$, the other is $(-\frac{\pi}{a}, 0)$, they have the same $E$, which is $\varepsilon$. They are translated by $\vec{G_1}$, $\vec{G_2}$ to $X(\frac{\pi}{a}, 0)$, respectively.

(ii) For point ②, there are four $k$, belonging to 2nd B.Z., they have the same energy $E = 4\varepsilon$, they are $(-\frac{2\pi}{a}, 0)$, $(0, -\frac{2\pi}{a})$ $(\frac{2\pi}{a}, 0)$ $(0, \frac{2\pi}{a})$ translated by $\vec{G_2}$, $\vec{G_3}$, $\vec{G_5}$, $\vec{G_6}$ to $\Gamma(0, 0)$ respectively.

(iii) For point ③, they are $(\frac{\pi}{a}, -\frac{2\pi}{a})$ $(-\frac{\pi}{a}, \frac{-2\pi}{a})$, $(\frac{\pi}{a}, \frac{2\pi}{a})$ $(-\frac{\pi}{a}, \frac{2\pi}{a})$ translated by $\vec{G_3}$, $\vec{G_4}$, $\vec{G_6}$, $\vec{G_8}(-\frac{2\pi}{a}, \frac{2\pi}{a})$ to $X(\frac{\pi}{a}, 0)$ respectively

Figure Sources：

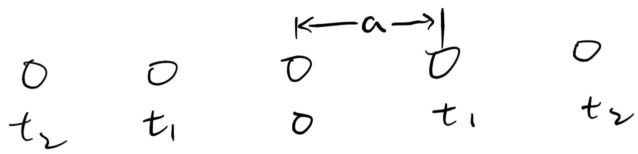
Ref (1) B.Z. of the 2D square lattice

https://demonstrations.wolfram.com/2DBrillouinZones/

(Ref 2) Band structure of the 2D square lattice

http://lampx.tugraz.at/~hadley/ss1/empty/disp2dsquare.html?

2.4




$$E(k) = \varepsilon_{atom} - \alpha + \sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}} F(\vec{R})$$

where $F(\vec{R}) = \int \phi^*(\vec{r}-\vec{R})\, U_{atom}(\vec{r}-\vec{R})\, \phi(\vec{r})\, d^3r$. $\alpha$ is a constant shift.

Taking the nearest-neighboring (n.n.) and next n.n. hopping terms:

$$E(k) = \varepsilon_{atom} - \alpha + e^{ika} F(a) + e^{-ika} F(-a) + e^{2ika} F(2a) + e^{-2ika} F(-2a)$$

$F(a)$ and $F(-a)$ are the same according to the integrals' meaning

let $F(a) = F(-a) = -t_1$, $F(2a) = F(-2a) = -t_2$, so

$$E(k) = \varepsilon_{atom} - \alpha - t_1(e^{ika} + e^{-ika}) - t_2(e^{2ika} + e^{-2ika})$$

$$= \varepsilon_{atom} - \alpha - 2t_1 \cos ka - 2t_2 \cos 2ka$$

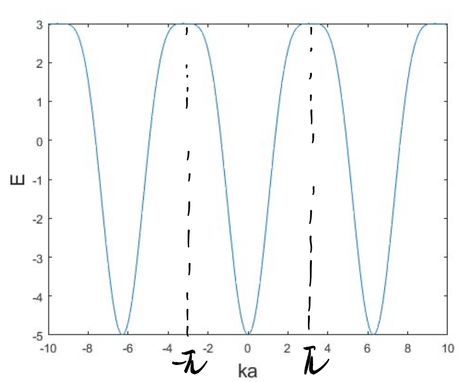
When sketching the band and finding the band width, there are 2 cases:

case 1: when $t_1 \geqslant 4t_2$,

$E_{max} = \varepsilon_{atom} - \alpha + 2t_1 - 2t_2$ (the edge of 1st B.Z)

$E_{min} = \varepsilon_{atom} - \alpha - 2t_1 - 2t_2$

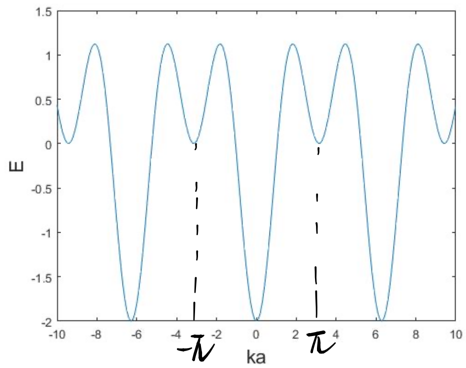
Band width: $\Delta E = E_{max} - E_{min} = 4t_1$



case 2: When $t_1 < 4t_2$,

$$E_{max} = \varepsilon_{atom} - \alpha + \frac{t_1^2}{4t_2} + 2t_2 \quad \text{(within 1st B.Z)}$$

Band width: $\Delta E = E_{max} - E_{min} = \frac{t_1^2}{4t_2} + 4t_2 + 2t_1$




$$\frac{dE(k)}{dk} = 2at_1 \sin ka + 4at_2 \sin 2ka$$

the slope of the band at $k = \frac{\pi}{a}$: $2at_1 \sin \pi + 4at_2 \sin 2\pi = 0$

Remark: This is a general result. Here we use a complicated band structure to show the general result.

Near bottom of band,

$$E(k) \simeq \varepsilon_{atom} - \alpha - 2t_1\left(1 - \frac{k^2a^2}{2}\right) - 2t_2\left(1 - \frac{4k^2a^2}{2}\right)$$

$$= \underbrace{(\varepsilon_{atom} - \alpha - 2t_1 - 2t_2)}_{\text{bottom of band}} + k^2a^2t_1 + 4k^2a^2t_2$$

So $\frac{\hbar^2k^2}{2m^*} = k^2a^2t_1 + 4k^2a^2t_2$

$$\Rightarrow \quad m^* = \frac{\hbar^2}{2a^2t_1 + 8a^2t_2}$$

2.5. Since $|\Psi'_{GS}\rangle$ is not a ground state of H, and $|\Psi_{GS}\rangle$ is not a ground state of H', we write:

$H = T + V + U_{el-el}$

$H' = T + V' + U_{el-el}$

Based on variational principle:

$$E_{GS} = \langle \Psi_{GS} | T + V + U_{el-el} | \Psi_{GS} \rangle < \langle \Psi'_{GS} | T + V + U_{el-el} | \Psi'_{GS} \rangle \quad (1)$$

$$E'_{GS} = \langle \Psi'_{GS} | T + V' + U_{el-el} | \Psi'_{GS} \rangle < \langle \Psi_{GS} | T + V' + U_{el-el} | \Psi_{GS} \rangle \quad (2)$$

when $n(\vec{r}) = n'(\vec{r})$

From (1): $E_{GS} < \langle \Psi'_{GS} | H' + V - V' | \Psi'_{GS} \rangle = E'_{GS} + \int [V(\vec{r}) - V'(\vec{r})] n(\vec{r}) d\vec{r}$ (3)

From (2): $E'_{GS} < \langle \Psi_{GS} | H + V' - V | \Psi_{GS} \rangle = E_{GS} + \int [V'(\vec{r}) - V(\vec{r})] n(\vec{r}) d\vec{r}$ (4)

(3)+(4), leads to the contradictory statement:

$$E_{GS} + E'_{GS} < E_{GS} + E'_{GS}$$

Thus, the external potential $V(\vec{r})$ is closely related to the particle density $n(\vec{r})$.