Ex: Bloch's theorem (partial solution)

(5) For a fixed k value we have to solve

$$\left[\frac{(k-k')^2}{2}-\varepsilon\right] C_\varphi(k-k') + \sum_{k''} V_{k''-k'}\, C_\varphi(k-k'')=0 \leftarrow \text{Eq(2)}$$

* We introduce the k-dependent vector $\underline{X}(k)$ whose components are $\underbrace{X_{k'}(k)}_{\parallel\; C_\varphi(k-k')}$ with $k' \in \frac{2\pi}{a}\mathbb{Z}$ i.e.

$$\underline{X}(k) = \begin{bmatrix} \vdots \\ C_\varphi(k+\frac{2\pi}{a}) \\ C_\varphi(k) \\ C_\varphi(k-\frac{2\pi}{a}) \\ C_\varphi(k-\frac{4\pi}{a}) \\ \vdots \end{bmatrix}$$

this vector has an infinite dimension (dimension of $\mathbb{Z}$)

* Eq.(2) can be rewritten as follows

$$\underbrace{\left[\frac{(k-k')^2}{2}-\varepsilon\right] X_{k'}(k)}_{\left(\sum_{k''}\delta_{k'k''}\frac{(k-k')^2}{2}X_{k''}(k)\right)-\varepsilon X_{k'}(k)} + \sum_{k''} V_{k''-k'}\, X_{k''}(k)=0$$

$$\Leftrightarrow \sum_{k''} \underbrace{\left[\frac{(k-k')^2}{2}\delta_{k'k''} + V_{k''-k'}\right]}_{\parallel \text{ definition } H_{k'k''}(k)} X_{k''}(k) = \varepsilon X_{k'}(k)$$

$H_{k'k''}(k) \leftarrow$ Hamiltonian matrix element

$$\Leftrightarrow \left[\underline{\underline{H}}(k)\underline{X}(k)\right]_{k'} = \varepsilon\left[\underline{X}(k)\right]_{k'} \quad \forall k'$$

Hamiltonian matrix

$$\Leftrightarrow \boxed{\underline{\underline{H}}(k)\underline{X}(k) = \varepsilon\,\underline{X}(k)} \quad \text{Eq(3)}$$

Eq.(3) is solved for a given k value. Therefore, $\varepsilon = \varepsilon(k)$ will depend on k.

(6) Eq.(3) is an eigenvalue equation. The number of solutions is the rank of the Hamiltonian matrix (infinite here). We denote $\underline{X}^{(n)}(k)$ one solution:

$$\underline{\underline{H}}(k)\,\underline{X}^{(n)}(k) = \varepsilon^{(n)}(k)\,\underline{X}^{(n)}(k)$$

"molecular orbital" energy in the chemist's language

The components of this vector will be $\left\{C_\varphi^{(n)}(k-k')\right\}_{k' \in \frac{2\pi}{a}\mathbb{Z}}$

What is the one-electron wavefunction that corresponds to these coefficients?

We start from the general expression $\varphi(x) = \int_{-\infty}^{+\infty} dk'\, C_\varphi(k')\, e^{ik'x}$

The only coefficients $C_\varphi(k')$ that are in fact needed to express a solution to the Schrödinger equation are

$$C_\varphi(k') \longrightarrow C_\varphi(k-k') \text{ where } k \text{ is fixed and } k' \text{ varies in } \frac{2\pi}{a}\mathbb{Z}.$$

The solution $\varphi^{(n)}(k,x)$ which is a function of x where n and k are fixed is obtained from the following simplification

$$\int_{-\infty}^{+\infty} dk' \longrightarrow \sum_{\substack{k' = k - k' \\ k' \in \frac{2\pi}{a}\mathbb{Z}}}$$

In other words, the only values of k' in $\mathbb{R}$ that are needed to express a solution to the Schrödinger equation are expressed as $k - \frac{2\pi m}{a}$ where $m \in \mathbb{Z}$.

Thus leading to

$$\underbrace{\varphi^{(n)}(k, x)}_{k \text{ fixed!}} = \sum_{k' \in \frac{2\pi}{a}\mathbb{Z}} C_\varphi^{(n)}(k-k')\, e^{i(k-k')x} \qquad \text{Eq.(14)}$$

(7) According to Eq.(4)

$$\varphi^{(n)}(k,x) = \sum_{k' \in \frac{2\pi}{a}\mathbb{Z}} C_\varphi^{(n)}(k-k')\, \underbrace{e^{ikx}}_{\text{does not depend on } k'} e^{-ik'x}$$

$$= e^{ikx} \underbrace{\sum_{k' \in \frac{2\pi}{a}\mathbb{Z}} C_\varphi^{(n)}(k-k')\, e^{-ik'x}}_{\text{definition!}\ \parallel\ u^{(n)}(k,x)}$$

Note that $u^{(n)}(k,x)$ is periodic:

$$u^{(n)}(k, x+a) = \sum_{k' \in \frac{2\pi}{a}\mathbb{Z}} C_\varphi^{(n)}(k-k')\, e^{-ik'x} \underbrace{e^{-ik'a}}$$

since $k' = \frac{2\pi}{a} m'$ where $m' \in \mathbb{Z}$ we have $e^{-ik'a} = e^{-i\frac{2\pi}{\cancel{a}} m' \cancel{a}}$

$= +1$

Therefore $\boxed{u^{(n)}(k, x+a) = u^{(n)}(k,x)}$