Tight-Binding Model

Hongquan

June 8, 2022

Theorem 1. *Bloch Theorem.*
If the potential of the system is periodic:

$$V(\mathbf{r}+\mathbf{R}) = V(\mathbf{r}) \tag{1}$$

then the solution of the Schrödinger's equation $H\psi = E\psi$ satisfies

$$\psi(\mathbf{r}+\mathbf{R}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r}). \tag{2}$$

Proof. Since the potential is periodic, consider the translation operator(also hermitian)

$$T_{\mathbf{R}} : T_{\mathbf{R}}\left|\mathbf{r}\right\rangle = \left|\mathbf{r}+\mathbf{R}\right\rangle. \tag{3}$$

Then since H is translation invariant we have

$$T_{\mathbf{R}}^{\dagger} H T_{\mathbf{R}} = H \Leftrightarrow [H, T_{\mathbf{R}}] = 0. \tag{4}$$

So

$$T_{\mathbf{R}}\left|\alpha\right\rangle = \lambda_{\mathbf{R}}\left|\alpha\right\rangle. \tag{5}$$

Now,

$$E_\alpha\psi(\mathbf{r}+\mathbf{R}) = E_\alpha\left\langle\mathbf{r}+\mathbf{R}|\alpha\right\rangle = E_\alpha\left\langle\mathbf{r}|T|\alpha\right\rangle = \left\langle\mathbf{r}|T_{\mathbf{R}}H|\alpha\right\rangle = \left\langle\mathbf{r}|HT_{\mathbf{R}}|\alpha\right\rangle = E_\alpha\lambda_{\mathbf{R}}\psi(\mathbf{r}), \tag{6}$$

and so

$$\psi(\mathbf{r}+\mathbf{R}) = \lambda_{\mathbf{R}}\psi(\mathbf{r}). \tag{7}$$

Then we can show $\ln(\lambda_{n\mathbf{R}})$ is linear in n, and so

$$\lambda_{n\mathbf{R}} = \mathrm{e}^{n\mathbf{a}\cdot\mathbf{R}} \tag{8}$$

Since $|\lambda|^2 = 1$ for normalization, we must have

$$\lambda_{n\mathbf{R}} = \mathrm{e}^{n\mathbf{a}\cdot\mathbf{R}} = \mathrm{e}^{in\mathbf{k}\cdot\mathbf{R}}. \tag{9}$$

Therefore,

$$\psi(\mathbf{r}+\mathbf{R}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r}). \tag{10}$$

Here $\mathbf{k}$ is some real vector. Now,

$$\psi(\mathbf{r}+\mathbf{R}) = \mathrm{e}^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})}\mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}}\psi(\mathbf{r}), \tag{11}$$

and we denote $\mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}}\psi(\mathbf{r})$ by $u(\mathbf{r})$. $u(\mathbf{r})$ is periodic since

$$u(\mathbf{r}+\mathbf{R}) = \mathrm{e}^{-i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})}\psi(\mathbf{r}+\mathbf{R}) = \mathrm{e}^{-i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r}) = u(\mathbf{r}). \tag{12}$$

Therefore

$$\psi(\mathbf{r}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r}). \tag{13}$$

□

The tight-binding model assumes that the eigenstate is localized at $\mathbf{N}\cdot\mathbf{R}$. Therefore $\psi(\mathbf{r})$ is only significant at $\mathbf{r}=\mathbf{N}\cdot\mathbf{R}$. Now, let us consider a system of one atom. We consider the interaction between orbital $|\alpha\rangle$ and $|\beta\rangle$ of all sites, where the spatial origin is arbitrarily defined.

$$\langle\alpha|H|\beta\rangle = \sum_{\mathbf{R}_1,\mathbf{R}_2} \langle\alpha|\mathbf{R}_1\rangle \langle\mathbf{R}_1|H|\mathbf{R}_2\rangle \langle\mathbf{R}_2|\beta\rangle \tag{14}$$

$$= \sum_{\mathbf{R}_1,\mathbf{R}_2} \langle\mathbf{R}_1|H|\mathbf{R}_2\rangle\, u_\alpha(\mathbf{0})^* \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{R}_1} u_\beta(\mathbf{0}) \mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}_2} = \sum_{\mathbf{R}_1,\mathbf{R}_2} \langle\mathbf{R}_1|H|\mathbf{R}_2\rangle\, u_\alpha(\mathbf{0})^* u_\beta(\mathbf{0}) \mathrm{e}^{i\mathbf{k}\cdot(\mathbf{R}_2-\mathbf{R}_1)}. \tag{15}$$

By periodicity,

$$\langle\mathbf{R}_1|H|\mathbf{R}_2\rangle = \langle\mathbf{0}|H|\mathbf{R}_2-\mathbf{R}_1\rangle\,. \tag{16}$$

So the expression is simplified to

$$\sum_{\mathbf{R}_1}\sum_{\mathbf{R}} \langle\mathbf{0}|H|\mathbf{R}\rangle\, u_\alpha(\mathbf{0})^* u_\beta(\mathbf{0}) \mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}} = N\sum_{\mathbf{R}} H_{\alpha\beta}(\mathbf{R})\mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}}, \text{ after we replace } \mathbf{R}_2-\mathbf{R}_1 \text{ with } \mathbf{R}. \tag{17}$$

Here N is the number of sites, and $H_{\alpha\beta}(\mathbf{R}) := \langle\mathbf{0}|H|\mathbf{R}\rangle\, |u_\alpha(\mathbf{0})^* u_\beta(\mathbf{0})$. By periodicity, the situation for all sites are identical so we would only consider the state at the origin. This is simply to consider a Hamiltonian

$$H_{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{R}} H_{\alpha\beta}(\mathbf{R})\mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}}. \tag{18}$$

Now we consider the slab Hamiltonian given by the tight-binding model. Suppose we would like to stack N layers of unit cells along some direction, and the slab surface is characterized by two vectors inside, call them $\mathbf{u}$ and $\mathbf{v}$. Let them be the minimal linear combination of $\mathbf{a}_{1,2,3}$ over $\mathbb{Z}$. Before we only have one site with n orbitals in a unit cell, and now we would have N sites with $n\times N$ orbitals in a unit cell. The additional sites are contributed from other layers, so their locations are simply $n\xi$, where ξ is the shortest off-plane vector. And the orbitals now are extended to be

$$|\alpha,0\rangle\,,...,|\beta,0\rangle\,;|\alpha,\xi\rangle\,,...,|\beta,\xi\rangle\,;...;|\alpha,N\xi\rangle\,,...,|\beta,N\xi\rangle\,. \tag{19}$$

It will be better to treat the Hamiltonian H block-by-block-ly. Now what we have here should be $H_{\alpha\beta,m_1,m_2}$, which is the interaction between different layers. Each layer is symmetric to another one so by symmetry

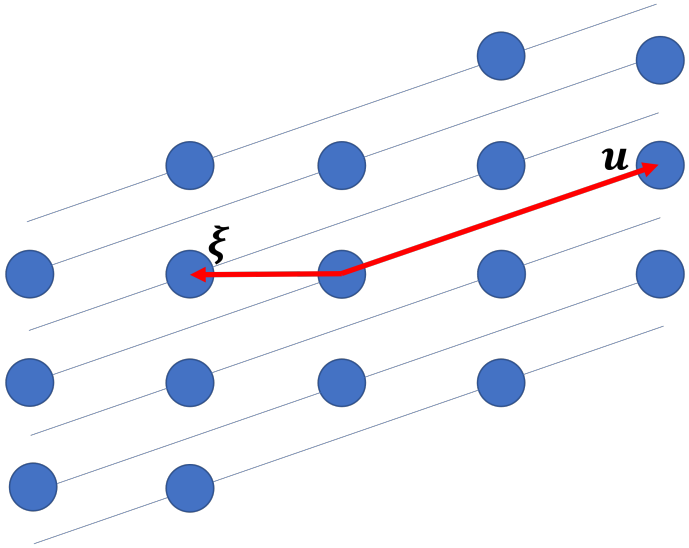
$$H_{\alpha\beta,n} := H_{\alpha\beta,0,n} = H_{\alpha\beta,m_1,m_2}, \quad n=m_2-m_1. \tag{20}$$

Easily, we can see that

$$H_{\alpha\beta,n}(N_1\mathbf{u}+N_2\mathbf{v}) = H_{\alpha\beta}(n\xi+N_1\mathbf{u}+N_2\mathbf{v}), \tag{21}$$

since they naturally differ by $n\xi$ within the cell.

The rod Hamiltonian is deduced similarly and more easily, for we only need one $\mathbf{u}$ to specify the "surface". $\mathbf{v}$ no longer exists. ξ still plays the same role.



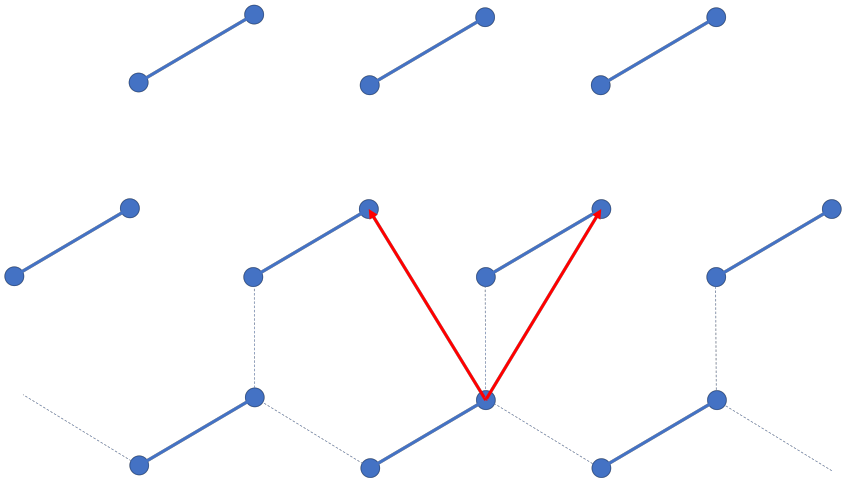
Now, let us examine the simplest example: a cubic. Suppose we are stacking the layers along the z-direction. Therefore $\mathbf{u}, \mathbf{v}$ are simply $\mathbf{a}_1, \mathbf{a}_2$ and $\xi = \mathbf{a}_3$. Hence $H_{\alpha\beta,R_z} = H_{\alpha\beta}(N_1\mathbf{a}_1 + N_2\mathbf{a}_2 + R_z\mathbf{a}_3)$. Therefore the whole Hamiltonian should be

$$H(\mathbf{k}) = \sum_{N_1,N_2} \begin{bmatrix} H(N_1,N_2,0) & H(N_1,N_2,1) & \cdots & H(N_1,N_2,R_z) \\ H(N_1,N_2,-1) & H(N_1,N_2,0) & \cdots & H(N_1,N_2,R_z-1) \\ \vdots & \vdots & \ddots & \vdots \\ H(N_1,N_2,-R_z) & H(N_1,N_2,-R_z+1) & \cdots & H(N_1,N_2,0) \end{bmatrix} \exp\{i\mathbf{k}\cdot(N_1\mathbf{a}_1 + N_2\mathbf{a}_2)\}. \tag{22}$$

Furthermore, let us consider a honeycomb lattice in 2D. Here $\mathbf{a}_1 = (1/2, \sqrt{3}/2); \mathbf{a}_2 = (-1/2, \sqrt{3}/2)$. So we need one vector to specify the surface and one vector to specify the direction along the N_{slab} number of layers. For a zigzag surface, we have

$$\mathbf{u} = \hat{\mathbf{x}} = \mathbf{a}_1 - \mathbf{a}_2; \quad \xi = \mathbf{a}_1. \tag{23}$$

Of course, we could have chosen ξ to be $\mathbf{a}_2$. They are just symmetric.



Now, our Hamiltonian consists of

$$H_n(\mathbf{R}) = H(N\mathbf{u} + n\xi) = H(N(\mathbf{a}_1 - \mathbf{a}_2) + n\mathbf{a}_1) = H(N+n, -N), \tag{24}$$

so

$$H(\mathbf{k}) = \sum_{N} \begin{bmatrix} H(N,-N) & H(N+1,-N) & \cdots & H(N+N_{\text{slab}}-1,-N) \\ H(N-1,-N) & H(N,-N) & \cdots & H(N+N_{\text{slab}}-2,-N) \\ \vdots & \vdots & \ddots & \vdots \\ H(N-N_{\text{slab}}+1,-N) & H(N-N_{\text{slab}}+2,-N) & \cdots & H(N,-N) \end{bmatrix} \exp\{i\mathbf{k}\cdot(N\mathbf{u})\}. \tag{25}$$

Since $\mathbf{u} = \hat{\mathbf{x}}$, the effective part of $\mathbf{k}$ is just $k_x\hat{\mathbf{x}}$ where $k_x \in [0, 2\pi)$. So the above expression is in fact,

$$H(\mathbf{k}) = \sum_{N} \begin{bmatrix} H(N,-N) & H(N+1,-N) & \cdots & H(N+N_{\text{slab}}-1,-N) \\ H(N-1,-N) & H(N,-N) & \cdots & H(N+N_{\text{slab}}-2,-N) \\ \vdots & \vdots & \ddots & \vdots \\ H(N-N_{\text{slab}}+1,-N) & H(N-N_{\text{slab}}+2,-N) & \cdots & H(N,-N) \end{bmatrix} \exp(ik_xN). \tag{26}$$

In those papers, they never provide us with $H(\mathbf{R})$! But only with $H(\mathbf{k})$! So we have to transform $H(\mathbf{k})$ into $H(\mathbf{R})$, which is way more useful. We already know that,

$$H(\mathbf{k}) = \sum_{N_1,N_2,N_3} H(N_1,N_2,N_3)\exp\{i\mathbf{k}\cdot(N_1\mathbf{a}_1+N_2\mathbf{a}_2+N_3\mathbf{a}_3)\} \tag{27}$$

Here $\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3$ with $k_{1,2,3} \in [0,1)$ and $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. Nobody can stop me from calculating

$$\sum_{k_1\in[0,1)} H(\mathbf{k})\mathrm{e}^{-ik_1\mathbf{b}_1\cdot n_1\mathbf{a}_1} \tag{28}$$

$$= \sum_{N_1,N_2,N_3}\sum_{k_1\in[0,1)} H(N_1,N_2,N_3)\exp\{ik_1\mathbf{b}_1\cdot((N_1-n_1)\mathbf{a}_1+N_2\mathbf{a}_2+N_3\mathbf{a}_3)\} \tag{29}$$

$$= \sum_{N_1,N_2,N_3} H(N_1,N_2,N_3)\sum_{k_1\in[0,1)}\mathrm{e}^{2\pi ik_1(N_1-n_1)} \tag{30}$$

$$= \#\{k_1\}\sum_{N_1,N_2,N_3} H(N_1,N_2,N_3)\delta_{N_1,n_1} = \#\{k_1\}\sum_{N_2,N_3} H(n_1,N_2,N_3). \tag{31}$$

Therefore

$$\frac{1}{\#\{k_1\}\#\{k_2\}\#\{k_3\}}\sum_{k_1,k_2,k_3\in[0,1)} H(\mathbf{k})\exp\{-i\mathbf{k}\cdot(n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3)\} = H(n_1,n_2,n_3). \tag{32}$$

For 2D cases, we would simply have

$$\frac{1}{\#\{k_1\}\#\{k_2\}}\sum_{k_1,k_2\in[0,1)} H(\mathbf{k})\exp\{-i\mathbf{k}\cdot(n_1\mathbf{a}_1+n_2\mathbf{a}_2)\} = H(n_1,n_2). \tag{33}$$

Now let us consider the case of band-folding, acquired by making copies of the previous unit cell, and merging them into a bigger new unit cell. The goal is to build a new tight-binding model. In fact, this is similar to the surface state calculation, but with fewer layers. However, we still need to consider the periodic boundary conditions.

Let us first consider the simplest case: a 2-D point with orbital $|\alpha\rangle$. Now, let us make a copy of the unit cell—making it a 2×1 unit cell.

For $\mathbf{R} = (R_x, R_y)$, we have $|\alpha_1,\mathbf{R}\rangle$ located at $[2R_x, R_y]^T$ and $|\alpha_2,\mathbf{R}\rangle$ located at $[2R_x+1, R_y]^T$. More generally, if we label α_1 by $\mathbf{0}$ and α_2 by $[1,0]^T$ we would have $|\alpha_1,\mathbf{R}\rangle$ and $|\alpha_1,\mathbf{R}\rangle$ located at

$$\mathrm{diag}[2,1][R_x,R_y]^T + \mathbf{0}; \quad \mathrm{diag}[2,1][R_x,R_y]^T + [1,0]^T. \tag{34}$$

Therefore,

$$H(\mathbf{R}) = H(R_x,R_y) = \begin{bmatrix} H_0(2R_x,R_y) & H_0(2R_x+1,R_y) \\ H_0(2R_x-1,R_y) & H_0(2R_x,R_y)\end{bmatrix}. \tag{35}$$

What is left now is just to compute

$$H(\mathbf{k}) = \sum_{\mathbf{R}} H(\mathbf{R})\mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}}. \tag{36}$$

Having known the special case, we may turn to the general case now. The unit cell has become, say $m\times n\times r$. Now, there should be exactly $m\times n\times r$ copies of the previous orbitals located respectively at $[0,m-1]\times[0,n-1]\times[0,r-1]$. Using the same argument as before, if we label α_l by $\mathbf{r}_l$ we easily see its location to be

$$\begin{bmatrix} m & 0 & 0 \\ 0 & n & 0 \\ 0 & 0 & r\end{bmatrix}\begin{bmatrix} R_x \\ R_y \\ R_z\end{bmatrix} + \mathbf{r}_l = \begin{bmatrix} mR_x \\ nR_y \\ rR_z\end{bmatrix} + \mathbf{r}_l. \tag{37}$$

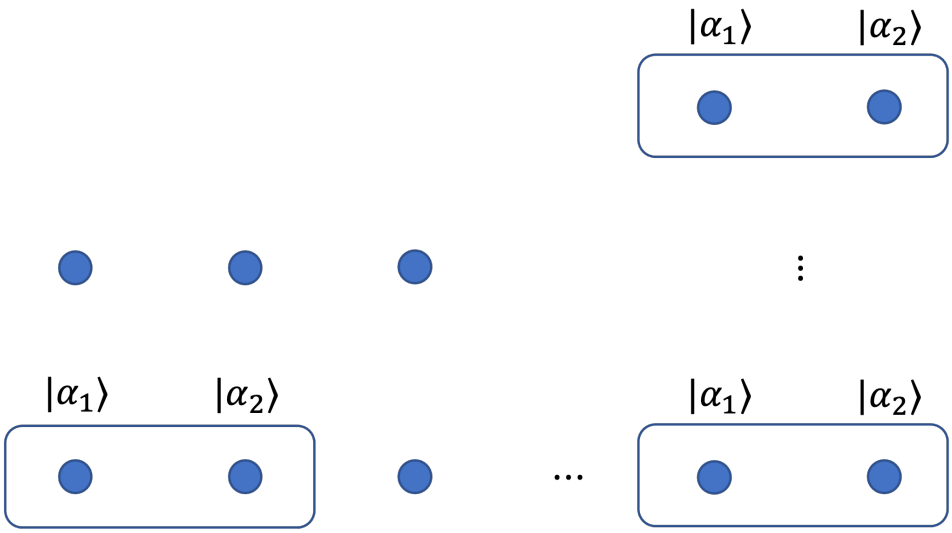
We place the orbitals in the way we did for the surface states: $|\alpha_0\rangle, \cdots, |\beta_0\rangle, \cdots, |\alpha_l\rangle, \cdots, |\beta_l\rangle, \cdots$. So

$$H(\mathbf{R}) = H(R_x, R_y, R_z) = \begin{bmatrix} H^{1,1} & H^{1,2} & \cdots & H^{1,m\times n\times r} \\ H^{2,1} & H^{2,2} & \cdots & H^{2,m\times n\times r} \\ \vdots & \vdots & \ddots & \vdots \\ H^{m\times n\times r,1} & H^{m\times n\times r,2} & \cdots & H^{m\times n\times r,m\times n\times r} \end{bmatrix}, \tag{38}$$

where

$$H^{pq}(\mathbf{R}) = H(\mathbf{x}), \mathbf{x} = \begin{bmatrix} mR_x \\ nR_y \\ rR_z \end{bmatrix} + \mathbf{r}_q - \mathbf{r}_p. \tag{39}$$

Here $\mathbf{x}$ is simply the difference of the locations between site p at $\mathbf{0}$ and site q at $\mathbf{R}$.



In fact, a special case for this is the surface state, in which we make N copies of the cell along the normal direction and killing the periodicity in that direction. In other words, only in the directions parallel to the surface could we have periodicity.