MATSCI 302 – Solid State Physics

Lecturer – Dr. Mohamed Reyad Sakr

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QUANTUM THEORY OF ELECTRONS IN PERIODIC POTENTIALS

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1. Introduction

I find no expressing words to introduce this entry but his own words.

"When I started to think about it, I felt that the main problem was to explain why the electrons could sneak by all the ions in a metal… I found to my delight that the wave differed from a plane wave of free electron only by a periodic modulation. This was so simple that I didn't think it could be much of a discovery, but when I showed it to Heisenberg he said right away 'That's it.'."

Felix Bloch

2. Bloch's Theorem

Felix Bloch developed a quite great mathematical model of a perfectly periodic potential considering the wave–functions of electrons in periodic lattices. However, the greatness of this theorem lies in its simplicity. We will consider this beautiful theorem in two steps, as explained below.

2.1 Simple Proof Regardless the Explicit Form of the Potential

Considering a 1-D Schrödinger equation $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi=E\psi$, and $V(x)$ is such that $V(x+a)=V(x)$. Bloch tells us; hence, the solutions must satisfy the condition: $\psi(x+a)=e^{iKa}\psi(x)$.

Let's define a displacement operator $\widehat{D}$ such that $\widehat{D}\psi(x)=\psi(x+a)$. We also note that $\widehat{D}$ is a unitary operator (i.e., $\widehat{D}^{+}=\widehat{D}^{-1}$).

Moreover, it is obvious that $\left[\widehat{D},\ \widehat{H}\right]=0$, for periodic potentials.

$$[\hat{D},\hat{H}]\psi(x) = \hat{D}\left(\hat{H}(x)\psi(x)\right) - \hat{H}(x)\left(\hat{D}(x)\psi(x)\right)$$

$$= \left(\hat{H}(x+a)\psi(x+a)\right) - \hat{H}(x)\left(\psi(x+a)\right)$$

But $\hat{H}(x) = \hat{H}(x+a)$ because $V(x+a) = V(x)$.

$$\therefore \left(\hat{H}(x+a)\psi(x+a)\right) - \hat{H}(x)\left(\psi(x+a)\right) = 0. \qquad \therefore [\hat{D},\ \hat{H}] = 0.$$

$\therefore \hat{D}$ and $\hat{H}$ admit a simultaneous set of Eigen-functions. So, $\hat{H}\psi = E\psi$ and $\hat{D}\psi = \lambda\psi$. And since $\hat{D}$ is a unitary operator (i.e., $\hat{D}^{+} = \hat{D}^{-1}$), its Eigen-values are pure imaginary, which means that λ can be written as e^{iKa} where K is a real constant. Actually, λ must be an exponent!

Let $\hat{D}_a\psi(x) = \lambda(a)\,\psi(x)$ and $\hat{D}_b\psi(x) = \lambda(b)\,\psi(x)$

$\therefore \hat{D}_a\hat{D}_b\psi(x) = \lambda(a)\,\lambda(b)\,\psi(x)$ But we know $\hat{D}_a\hat{D}_b = \hat{D}_{a+b}$

$\therefore \lambda(a)\lambda(b) = \lambda(a+b)$ Hence, $\lambda(a) = e^{\gamma a}$ and $\gamma \in ¢$ in general.

Considering N atoms (i.e., N periods) and neglecting the edge effects; we can tell why the constant K is real, where $\psi(x+Na) = e^{iNKa}\psi(x) = \psi(x)$.

$$\therefore e^{iNKa} = 1 \quad \therefore K = \frac{2\pi n}{Na} \text{ and } n = 0, \pm 1, \pm 2, \ldots$$

2.2 Rigorous Proof and a More General Form of Bloch's Theorem

Consider the linear 2nd order differential equation $\frac{d^2\psi}{dx^2} + f(x)\psi = 0$, and $f(x)$ is a periodic function with period a, such that $f(x+a) = f(x)$. This equation admits two linearly independent solutions $g(x)$ and $h(x)$, for any given value of energy E such that $\psi(x) = A\,g(x) + B\,h(x)$ is the most general solution.

But because of the periodicity of $f(x)$; not only $g(x)$ and $h(x)$ are good solutions but also $g(x+a)$ and $h(x+a)$ are good. However, any solutions can be written as a linear combination of $g(x)$ and $h(x)$.

$$\therefore g(x+a) = \alpha_1\,g(x) + \alpha_2\,h(x) \text{ and } h(x+a) = \beta_1\,g(x) + \beta_2\,h(x)$$

where α_1, α_2, β_1, β_2 are constants.

Then, $\psi(x+a) = A\, g(x+a) + B\, h(x+a)$

$$= (\alpha_1 A + \beta_1 B)\, g(x) + (\alpha_2 A + \beta_2 B\,)h(x)$$

$$= \lambda\, \psi(x) \quad \text{where } \lambda \text{ is a properly chosen constant.}$$

$\therefore\ (\alpha_1 - \lambda)A + \beta_1 B = 0$ and $\alpha_2 A + (\beta_2 - \lambda)B = 0$, which is a system of homogeneous equations in A and B, that admits non-trivial solutions only if:

$$\begin{vmatrix} \alpha_1 - \lambda & \beta_1 \\ \alpha_2 & \beta_2 - \lambda \end{vmatrix} = \lambda^2 - (\alpha_1 + \beta_2)\lambda + (\alpha_1\beta_2 - \alpha_2\beta_1) = 0,$$

$$\therefore\ \lambda_{1,2} = \frac{(\alpha_1+\beta_2) \pm \sqrt{(\alpha_1+\beta_2)^2 - 4(\alpha_1\beta_2 - \alpha_2\beta_1)}}{2}$$

Then, $\psi(x+a) = \lambda_1 \psi(x)$ and $\psi(x+a) = \lambda_2\, \psi(x)$.

We can define K_1 and K_2 such that:

$$\lambda_1 = e^{iK_1 a} \quad \text{and} \quad \lambda_2 = e^{iK_2 a},$$

Also, we can define $u_{K_1}(x)$ and $u_{K_2}(x)$ such that:

$$u_{K_1}(x) = e^{-iK_1 x}\psi(x) \quad \text{and} \quad u_{K_2}(x) = e^{-iK_2 x}\psi(x).$$

Now, it is clear that:

$$u_{K_1}(x+a) = e^{-iK_1(x+a)}\, \psi(x+a) = e^{-iK_1(x+a)}\lambda_1\, \psi(x)$$

$$= e^{-iK_1(x+a)} e^{iK_1 a}\, \psi(x) = u_{K_1}(x).$$

Similarly, $u_{K_2}(x+a) = u_{K_2}(x)$.

$\therefore\ u_K(x)$ is a periodic function with period *a* and it is called Bloch's wave.

In 3-D Bloch's Theorem reads: $\psi_{\boldsymbol{K}}(x) = e^{i\boldsymbol{K}\cdot\boldsymbol{r}} u_{\boldsymbol{K}}(x)$.

Hence, all-electron wave-functions can be expressed in this way which is a plane wave propagation with a ***K***-vector modulated by a periodic function whose periodicity is that of the lattice itself. However, crystals admit finite extent which leads to physical boundary conditions. Then, the above solutions must satisfy the Schrödinger equation and the boundary conditions. Thus, there will be certain discrete energy eigenvalues.

For example, consider N atoms (i.e., N periods) and let's assume it is a closed ring lattice. Hence, $\psi(x)$ has to be a single-valued function.

$\therefore \psi(x+Na) = e^{iNKa}\psi(x) = \psi(x)$, $\therefore e^{iNKa} = 1$, $\therefore K = \frac{2\pi n}{Na}$ and $n = 0, \pm1, \pm2, \ldots$

3. Specific Famous Models of a Periodic Potential

The above discussion did not specify, at any point, any form of potential. The only information we know, so far, is that the potential must be periodic (i.e., $V(x+a) = V(x)$). Let's now consider two famous models of periodic potentials and investigate the physics underlying Bloch's Theorem.

3.1 The 1-D Model Dirac Comb Model

Actually, this model is the simplest possible model of a perfect periodic potential, and yet it captures a lot of interesting details about how electrons behave in such a potential. The 1-D Dirac Comb consists of many delta-function spikes that are evenly spaced, as the figure below shows.

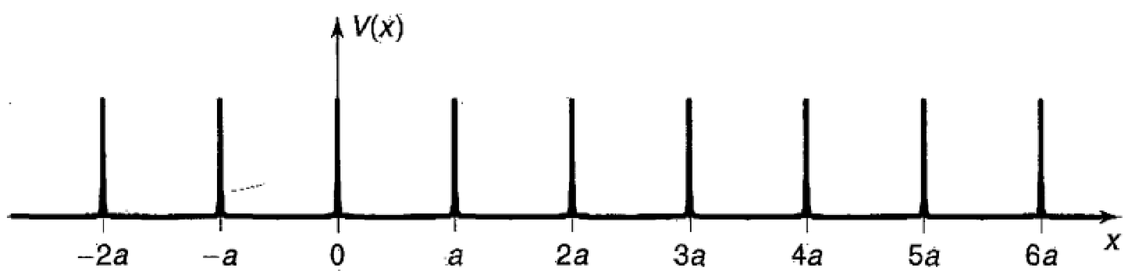

Figure (3.1) I: The Dirac Comb.

Credits to: Griffith Quantum Mechanics (2nd ed.)

$$\therefore V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja)$$

where $j = 0, \pm 1, \pm 2, ...$ and $\alpha > 0$ because we are considering scattering states (i.e., $\mathrm{E} > 0$).

So, in the first unit cell $(0 < x < a)$; Schrödinger equation reads $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$, which can be written as $\frac{d^2\psi}{dx^2} = -k^2\psi$, and $k^2 = \frac{2mE}{\hbar^2}$.

The strategy, from here, is to get a solution for one cell (i.e., $0 < x < a$), followed by getting the allowed states and the allowed spectrum. We now proceed writing the general solution: $\psi(x) = A\, sin(kx) + B\cos(kx)$, and $(0 < x < a)$. But according to Bloch's theorem, we can immediately write a solution to the next unit cell as follows: $\psi(x) = e^{-iKa}\,[A\sin k(x+a) + B\cos k(x+a)]$, and $(-a < x < 0)$.

Using the continuity of ψ at $x = 0$ yields: $B = e^{-iKa}\,[A\sin(ka) + B\cos(ka)]$. However, ψ' is discontinuously well-behaved at $x = 0$ because the discontinuity here is proportional to α, the delta-function strength factor. This returns another equation: $kA - e^{-iKa}\,k[A\sin(ka) + B\cos(ka)] = \frac{2m\alpha}{\hbar^2}B$.

Solving the last two equations of B yields: $\cos(Ka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka)$. This equation tells about the possible values of k and hence, the allowed spectrum of energies. It can be written as: $f(z) = \cos(z) + \beta\frac{\sin(z)}{z}$, where $z = ka$ and $\beta = \frac{m\alpha\, a}{\hbar^2}$.

Before plotting $f(z)$ for some finite β, there is a notable thing about $f(z)$ which is; its solutions only exist in $(-1, +1)$.

The figures below show the behavior of $f(z)$ at some finite value of β.

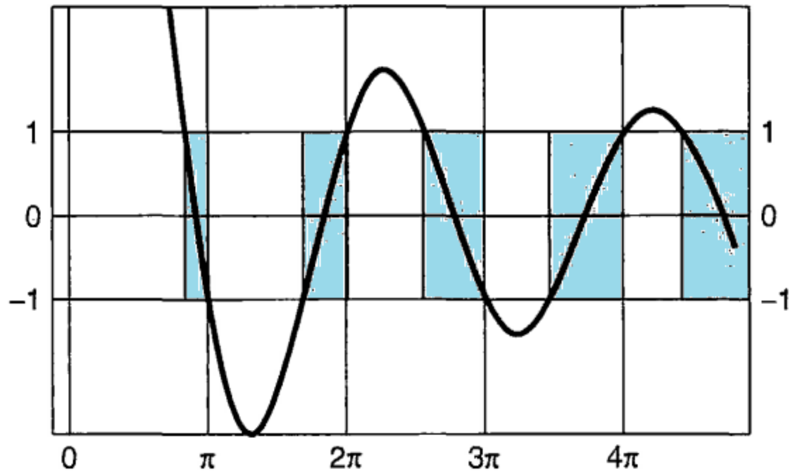

Figure (3.1) II: $\beta = 10$

Credits to: Griffiths Quantum Mechanics (2nd ed.)

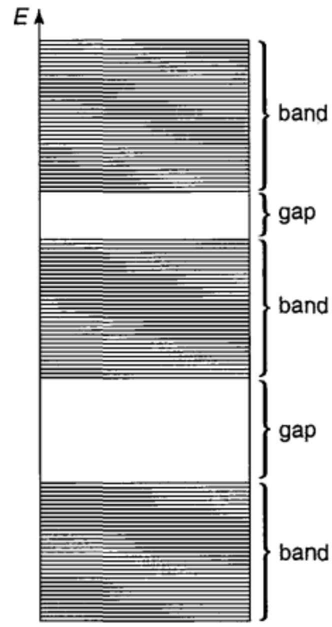

Figure (3.1) III

The shaded areas on the graph, Figure II, represent the allowed energy bands separated by forbidden gaps that, in turn, represent forbidden energies, whereas the intersection points are the solutions that we are after. Therefore, as in Figure III, the allowed energies form a quasi-continuous bands, because we are talking about Avogadro's number of electrons ($N = 6.02 * 10^{23}$), which is so large! Evidently, every band contains N_q states where q is the number of "free" electrons per atom. However, a given spatial state can accommodate only 2 electrons, according to the Pauli Exclusion Principle.

3.2 The Kronig-Penney Model

This model is a little bit more complicated than the 1-D Dirac Comb. However, it is very useful because it is a quite good approximation to that found in reality and it illustrates explicitly many important features of the quantum mechanical behavior of electrons in periodic lattices. The Kornig-Penney model is a treatment for a perfectly periodic potential that consists of infinite 1-D square-well, as in Figure I below. On the top of that, this model admits an exact closed form solution.

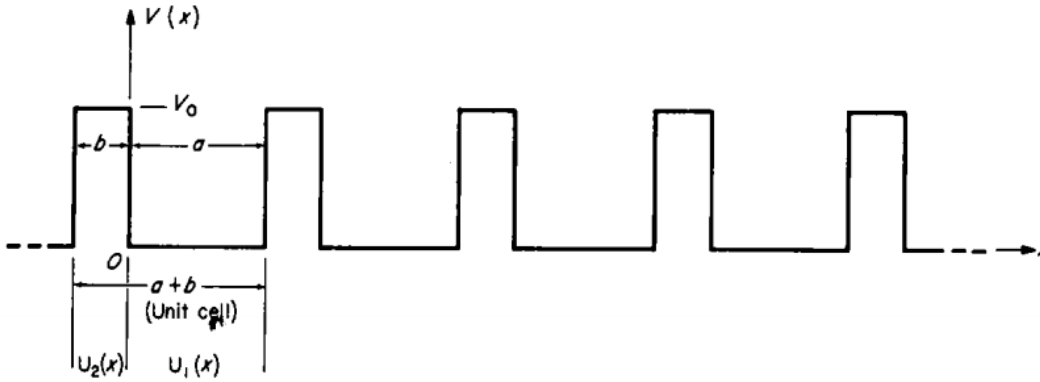

Figure (3.2) I: The 1-D Koring-Penney Model

Credits to: McKelvely Solid State and Semiconductor Physics

Now, we are to use the previous strategy again to find solutions to the Schrödinger equation that reads: $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\big(E - V(x)\big)\psi(x) = 0$. But, according to Bloch's theorem $\psi(x) = e^{ikx}\, u(x)$, which can be substituted back into Schrödinger equation:

$$\therefore \frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - \left(k^2 - \alpha^2 - \frac{2m\,V(x)}{\hbar^2}\right)u(x) = 0, \text{ where } \alpha^2 = \frac{2mE}{\hbar^2}$$

At this moment, we shall insert the square-well potential represented in Figure I. Hence,

$$\frac{d^2u_1}{dx^2} + 2ik\frac{du_1}{dx} - (k^2 - \alpha^2)\, u_1(x) = 0, \quad (0 < x < a)$$

and $$\frac{d^2u_2}{dx^2} + 2ik\frac{du_2}{dx} - (k^2 - \beta^2)\, u_2(x) = 0, \quad (-b < x < 0)$$

where $\beta = \frac{\sqrt{2m(E-V_0)}}{\hbar}$ which is purely imaginary when $0 < E < V_0$

For the above two differential equations of $u_1(x)$ & $u_2(x)$; we can write the general solutions as follows:

$$u_1(x) = A\, e^{i(\alpha-k)x} + B\, e^{-i(\alpha+k)x}, \quad (0 < x < a)$$

$$u_2(x) = C\, e^{i(\beta-k)x} + D\, e^{-i(\beta+k)x}, \quad (-b < x < 0)$$

where $A, B, C,$ and D are arbitrary constants.

Evidently, ψ and ψ' are continuous at the boundaries ($x = a$ & $x = -b$) and of course $u(x)$ exhibits the same periodicity as the lattice (i.e., $u_1(a) = u_2(-b)$). Hence, we find:

$$A + B = C + D$$

$$A\,e^{i(\alpha-k)\boldsymbol{a}} + B\,e^{-i(\alpha+k)\boldsymbol{a}} = C\,e^{-i(\beta-k)\boldsymbol{b}} + D\,e^{i(\beta+k)\boldsymbol{b}}$$

$$i(\alpha-k)A - i(\alpha+k)B = i(\beta-k)C - i(\beta+k)D$$

$$i(\alpha-k)A\,e^{i(\alpha-k)\boldsymbol{a}} - i(\alpha+k)B\,e^{-i(\alpha+k)\boldsymbol{a}} = i(\beta-k)C\,e^{-i(\beta-k)\boldsymbol{b}} - i(\beta+k)D\,e^{i(\beta+k)\boldsymbol{b}}$$

Clearly, if we wish to find non-trivial values for $A, B, C,$ and D, then we must solve this linear homogenous system of these 4 equations simultaneously, which is tedious but straight-forward task.

$$\therefore \begin{vmatrix} 1 & 1 & 1 & 1 \\ e^{i(\alpha-k)\boldsymbol{a}} & e^{-i(\alpha+k)\boldsymbol{a}} & e^{-i(\beta-k)\boldsymbol{b}} & e^{i(\beta+k)\boldsymbol{b}} \\ (\alpha-k) & -(\alpha+k) & (\beta-k) & -(\beta+k) \\ (\alpha-k)\,e^{i(\alpha-k)\boldsymbol{a}} & -(\alpha+k)\,e^{-i(\alpha+k)\boldsymbol{a}} & (\beta-k)\,e^{-i(\beta-k)\boldsymbol{b}} & -(\beta+k)\,e^{i(\beta+k)\boldsymbol{b}} \end{vmatrix} = 0$$

$$\therefore -\frac{\alpha^2+\beta^2}{2\alpha\beta}\sin(\alpha a)\sin(\beta b) + \cos(\alpha a)\cos(\beta b) = \cos k(a+b)$$

A note that worth to be mentioned is that $\alpha^2 - \beta^2 = \frac{2mV_0}{\hbar^2} = \text{const.},$

In order to make things look nicer on the graph and to simplify the calculations a bit; the last equation can be divided and written into two parts according to the energy intervals {($0 < E < V_0$) and ($V_0 < E < \infty$)}, including some change of variables.

$$\left[1 + \frac{(\alpha^2+\gamma^2)^2}{4\alpha^2\gamma^2}\sinh^2\gamma b\right]^{\frac{1}{2}}\cos(\alpha a - \delta') = \cos k(a+b)$$

Where $\gamma = i\beta$, and $\tan\delta' = \frac{\alpha^2+\gamma^2}{2\alpha\gamma}\tanh\gamma b \quad \ldots \quad (0 < E < V_0)$

$$\left[1+\frac{\left(\alpha^2-\beta^2\right)^2}{4\alpha^2\beta^2}\sin^2\beta b\right]^{\frac{1}{2}}\cos(\alpha a-\delta)=\cos k(a+b)$$

Where $\tan\delta=-\frac{\alpha^2+\beta^2}{2\alpha\beta}\tan\beta b \quad \ldots \quad (V_0 < E < \infty)$

Since α and β were defined initially as functions of the energy, then we can plot the last two equations as functions of energy, as shown in Figure II below.

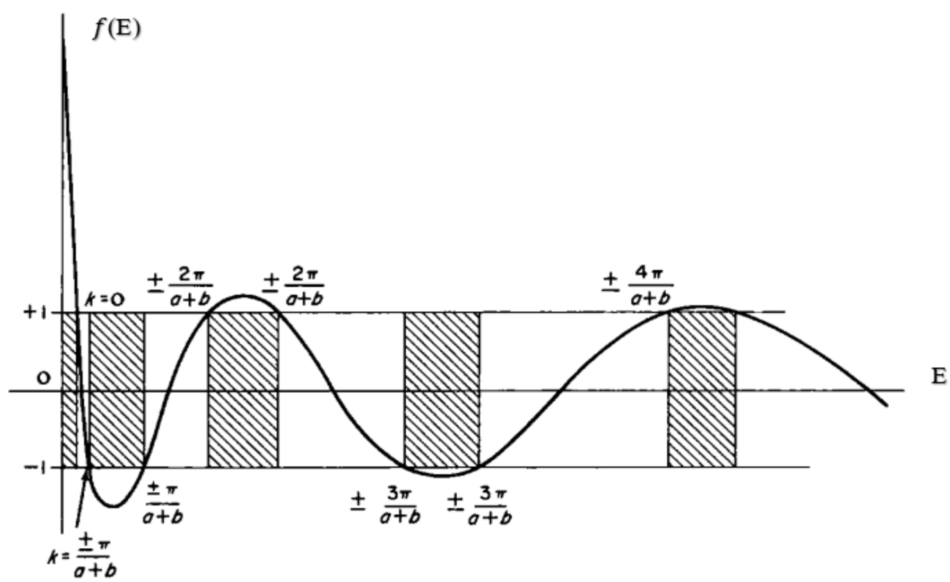

Figure (3.2) II

Credits to: McKelvely Solid State and Semiconductor Physics

The unshaded areas on the graph, Figure II, represent the allowed energy bands (corresponding to real *k*-values) separated by forbidden gaps that, in turn, represent forbidden energies (corresponding to complex *k*-values). This result is the opposite of that found in the 1-D Comb because essentially they are two entirely different models! However, the solutions still live in $(-1,+1)$, where a real value of *k* corresponds to physically possible wave-functions. Meanwhile outside these limits, a complex value of *k* can never lead to any physically possible wave-functions.

4. Conclusion

We see, the energy bands admit the same qualitative characteristics no matter what the explicit form of the potential is! as long as it is periodic. This is the interesting common fact that Bloch's theorem revels. Of course, K is the crystal momentum which makes sense that the eigenstates in such periodic potentials are labeled by the crystal momenta.

Once we have a periodic potential, Bloch's theorem stands as a holy tool in our hands. This is mainly because of the behaviors of the electrons in potentials, which is to say they are nearly free electrons! Again, electrons behave almost as if they do not see any atoms. This is derived by the periodicity regardless how strong the potential is. This is also an essential key to calculate the band structure in more realistic situations, alongside with some other helping tools like the tight binding model and the perturbation theories.

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