Uber die Quantenmechanik der Elek~ronenin Kristallgittern

About the Quantum Mechanics of the Electrons in Crystal Lattices

Felix Bloch

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Abstract: This article aims to review *Felix Bloch* theorem of electron motion in a crystal lattice through his seminal paper that has also acted as his Ph.D. dissertation under *Werner Heisenberg* supervision. Bloch uses the quantum formulation with periodic boundary condition and the Fermi statistics of electrons to resolve many of the unexplained phenomena and contradiction existing the previous free-electron models. The historical context of the problem and Bloch perspective will be addressed first, followed by theory formulation using both the original and modern mathematical notation. We then summarize Bloch utilization of the developed theory in addressing contemporary dilemmas and setting future predictions on electron motion in crystalline lattice. Lastly, we address the shortcoming of this model and the current research trends in generalizing it to disordered and quasicrystal systems.

Historical Background:

After *J. J. Thomson* discovery of the electron by few years [1], *Paul Drude* proposed a simple model that predicts, to a certain degree of accuracy, the thermal, electric, and optical properties of solid-state matter [2]. By applying first-principle kinetic theory of gases to electrons in some type metals, the model provided a good explanation of DC and AC conductivity, Hall-effect and magnetoresistance phenomena, and fortuitously predicting the *Wiedemann-Franz* ratio. However, it greatly overestimated the specific heat of metals which was not observed experimentally. The issue has been rectified by the advent of quantum mechanics where *Arnold Sommerfeld* recognized the need to replace the *Maxwell-Boltzmann* distribution with *Fermi-Dirac* statistics [3]. However, the developed Drude-Sommerfeld free-electron model still makes many quantitative predictions that are quite unambiguously contradicted by observation. For example, the sign of the Hall coefficient and its dependence on the strength of the magnetic field and temperature was inconsistent in certain cases. In addition, The Wiedemann-Franz Law at room temperature was inaccurate in an otherwise alkaline metal [4]. Also, it raised fundamental questions on what determines the number of conduction electrons in the first place and why in some elements it is zero, leading to an insulator. Or more generally why the conduction electrons should be treated as an ideal gas in the first place, as Bloch wrote in his memorial notes [5]:

> *"When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal to avoid a mean free path of the order of atomic distances. Such a distance was much too short to explain the observed resistances,*

*Formulas written in gold color represent the notation used by Flexi Bloch on his original work.

which even demanded that the mean free path become longer and longer with decreasing temperature. But Heitler and London had already shown how electrons could jump between two atoms in a molecule to form a covalent bond, and the main difference between a molecule and a crystal was only that there were many more atoms in a periodic arrangement. To make my life easy, I began by considering wave functions in a one-dimensional periodic potential. By straight Fourier analysis, 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." Well, that wasn't quite it yet, and my calculations were only completed in the summer when I wrote my thesis on "The Quantum Mechanics of Electrons in Crystal Lattices."*

Bloch Wave Theorem:

In principle, electrons moving in a solid is a *many-electron problem (*electron-electron and nuclei-electron interaction). Similar to the independent electron approximation adopted previously by Drude and Sommerfeld, Bloch assumes that such interactions are lumped into an "*effective one-electron potential,"* dramatically reducing the complexity of the model. Therefore, the problem is thus simplified to how an independent electron obeys the one electron Schrodinger equation:

$$\widehat{H}\psi(\boldsymbol{r}) = \left(-\frac{h^2}{2m}\nabla^2 + V(\boldsymbol{r})\right)\psi(\boldsymbol{r}) = \mathrm{E}\psi(\boldsymbol{r}) \tag{1}$$

$$\Delta\psi + \mu(E - V)\psi = 0, \quad \mu = \frac{8\pi^2 m}{h^2}$$

Where $V(\boldsymbol{r})$ is a periodic potential with the lattice periodicity. Such electrons are known as *Bloch electrons,* and it can be noted that it generalizes the *free electron* model when the periodicity is set to zero. Bloch started by assuming an underlaying translation periodicity of lathe ttice by defining the primitive lattice translation wavevector:

$$\boldsymbol{T} = n_1\boldsymbol{a_1} + n_2\boldsymbol{a_2} + n_3\boldsymbol{a_3} \tag{2}$$

$$r_G = g_1\mathfrak{a} + g_2\mathfrak{b} + g_3\mathfrak{c}, \quad g_1g_2g_3 = whole\ number$$

Where $\boldsymbol{a_1} \perp \boldsymbol{a_2} \perp \boldsymbol{a_3}$ $and\ n_1, n_2, n_3 \in \mathbb{Z}$. Therefore, the lattice potential should also follow the same periodicity:

$$V(\boldsymbol{r} + \boldsymbol{T}) = V(\boldsymbol{r}) \tag{3}$$

$$V(\mathfrak{r}) = V(\mathfrak{r} + g_1\mathfrak{a} + g_2\mathfrak{b} + g_3\mathfrak{c})$$

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Because the potential is periodic, Bloch followed the approach taken by *Max Born* and *Theodore von Kármán* in 1912 in their study of the specific heat of solid based on crystalline material [6]. By applying a cyclic *Born-von Karman* boundary conditions, Bloch reasoned that such an approach would lead to eigenfunctions with three-fold symmetry, permitting the study of the whole lattice behavior by considering its unit cell only. The question that follows naturally is the kind of constraints that such boundary condition will imply on the wavefunction in Eq. (1). The theorem will be derived first by Bloch approach and notation and then by Ashcroft/Mermin [7]:

Bloch's original derivation:

For the sake of derivation simplicity, Bloch assumed that the bravais vectors of $r(\mathfrak{g})$ are all orthogonal to each other. However, the derivation is still valid for any triclinic crystals. Based on the assumption, three translation operators on each vector is defined as follow:

$$\begin{array}{lll} R\colon \acute{x} = x + a, & \acute{y} = y, & \acute{z} = z \\ S\colon \acute{x} = x, & \acute{y} = y + b, & \acute{z} = z \\ T\colon \acute{x} = x, & \acute{y} = y, & \acute{z} = z + c \end{array} \tag{4}$$

Where a, b, c, are the magnitude of the bravais vectors respectively. The eigenfunctions after an R, S, T translations can be decomposed to a linear combination of the eigenfunctions at the frame of reference as:

$$\begin{aligned} \psi_\lambda(x + a, y, z, E) &= \sum_{x=1}^{l} a_{x\lambda}\, \psi_x(x, y, z, E) \\ \psi_\lambda(x, y + b, z, E) &= \sum_{x=1}^{l} b_{x\lambda}\, \psi_x(x, y, z, E) \\ \psi_\lambda(x, y, z + c, E) &= \sum_{x=1}^{l} c_{x\lambda}\, \psi_x(x, y, z, E) \end{aligned} \tag{5}$$

We also note that applying the R, S, T translation operators g_1, g_2, g_3 times, the eigenvalues of the decomposition in Eq. (5) will correspond to $(a_{x\lambda})^{g1}, (b_{x\lambda})^{g2}, (c_{x\lambda})^{g3}$. Since the eigenfunction exhibit three-fold symmetry when (Born-Von Karmen boundary conditions), we expect the eigenvalue to be periodic where after a translation of G_1, G_2, G_3, the wavefunction will be the same as the one in the frame of reference and the eigenvalue are:

$$(a_{x\lambda})^{G1} = (b_{x\lambda})^{G2} = (c_{x\lambda})^{G3} = \delta_{x\lambda} \tag{6}$$

Where $\delta_{x\lambda}$ is the identity matrix. Therefore, the eigenvalues are periodic and can be expressed as:

$$\acute{a}_{\lambda\lambda} = e^{\frac{2\pi i}{G_1} k_\lambda}, \acute{b}_{\lambda\lambda} = e^{\frac{2\pi i}{G_2} l_\lambda}, \acute{c}_{\lambda\lambda} = e^{\frac{2\pi i}{G_3} m_\lambda} \tag{7}$$

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Substituting Eq. (7) back into Eq. (5), we have:

$$\begin{aligned}
\grave{\psi}_\lambda(x+a,y,z,E) &= \sum_{x=1}^{l} \grave{a}_{x\lambda}\,\grave{\psi}_x(x,y,z,E) = \grave{a}_{\lambda\lambda}\grave{\psi}_\lambda(x,y,z,E) = e^{\frac{2\pi i}{G_1}k_\lambda}\,\grave{\psi}_\lambda(x,y,z,E)\\
\grave{\psi}_\lambda(x,y+b,z,E) &= \sum_{x=1}^{l} \grave{b}_{x\lambda}\,\grave{\psi}_x(x,y,z,E) = \grave{b}_{\lambda\lambda}\grave{\psi}_\lambda(x,y,z,E) = e^{\frac{2\pi i}{G_2}l_\lambda}\,\grave{\psi}_\lambda(x,y,z,E)\\
\grave{\psi}_\lambda(x,y,z+c,E) &= \sum_{x=1}^{l} \grave{c}_{x\lambda}\,\grave{\psi}_x(x,y,z,E) = \grave{c}_{\lambda\lambda}\grave{\psi}_\lambda(x,y,z,E) = e^{\frac{2\pi i}{G_3}m_\lambda}\,\grave{\psi}_\lambda(x,y,z,E)
\end{aligned} \tag{8}$$

Substituting $aG_1 = K, bG_2 = L, cG_3 = M$, Eq. (8) can be combined to:

$$\psi_{klm}(x,y,z) = e^{2\pi i\left(\frac{kx}{K}+\frac{ky}{L}+\frac{mz}{M}\right)}.u_{klm}(x,y,z) \qquad Q.E.D \tag{9}$$

where u_{klm} is a periodic function with the lattice periodicity.

Alternative derivation (Ashcroft):

The periodic nature implies that the potential can be expanded by the Fourier series:

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{K}} V_{\boldsymbol{K}}\, e^{i\boldsymbol{K}.\boldsymbol{r}} \tag{10}$$

$$V_{\boldsymbol{K}} = \frac{1}{v}\int V(\boldsymbol{r}) e^{-i\boldsymbol{K}.\boldsymbol{r}}\, d\boldsymbol{r} \tag{11}$$

Two important notes to be taken here. First, since the potential $V(\boldsymbol{r})$ is real and symmetric for a suitable choice of origin, the Fourier coefficients should also be symmetric and real $U_{-\boldsymbol{k}} = U_{\boldsymbol{k}} = U_{\boldsymbol{k}}^*$. Second, because the effective potential follows the periodicity of the lattice, we expect it Fourier dual to be related to the Fourier dual of the Braves lattice; which is the reciprocal lattice. This can be seen by substituting Eq. (10) into Eq. (3), we get:

$$e^{i\boldsymbol{K}.\boldsymbol{T}} = 1 \rightarrow \boldsymbol{K}.\boldsymbol{T} = 2n\pi \tag{12}$$

Such a perspective has extraordinary consequences of determining the motions of electrons in the crystalline material. Thus, all the concepts and mathematics of the reciprocal geometry (Brillion zone) will prove to be important in studying the electron motion in crystals [8].

Next, applying *Born-von Karman* periodic boundary condition implies a periodic wavevector that can also be expanded using Fourier series:

$$\psi(\boldsymbol{r}) = \sum_{\boldsymbol{q}} c_{\boldsymbol{q}}\, e^{i\boldsymbol{q}.\boldsymbol{r}} \tag{10}$$

Substituting both, effective potential Eq. (10) and wavefunction expansion Eq. (13) in the time-independent Schrodinger in Eq. (1), we get:

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$$\left(-\frac{h^2}{2m}\nabla^2 + \sum_{\boldsymbol{K}} V_{\boldsymbol{K}}\, e^{i\boldsymbol{K}.\boldsymbol{r}} - E\right)\sum_{\boldsymbol{q}} c_{\boldsymbol{q}}\, e^{i\boldsymbol{q}.\boldsymbol{r}} = 0 \tag{14}$$

$$\sum_{\boldsymbol{q}}\left(\frac{h^2 q^2}{2m} - E\right) c_{\boldsymbol{q}}\, e^{i\boldsymbol{q}.\boldsymbol{r}} + \sum_{\boldsymbol{K},\boldsymbol{q}} V_{\boldsymbol{K}}\, c_{\boldsymbol{q}}\, e^{i(\boldsymbol{K}+\boldsymbol{q}).\boldsymbol{r}} = 0 \tag{15}$$

Changing the index in the second term $\boldsymbol{K} + \boldsymbol{q} \rightarrow \grave{\boldsymbol{q}}$:

$$\sum_{\boldsymbol{q}} e^{i\boldsymbol{q}.\boldsymbol{r}}\left\{\left(\frac{h^2 q^2}{2m} - E\right) c_{\boldsymbol{q}} + \sum_{\boldsymbol{K}} V_{\boldsymbol{K}}\, c_{\boldsymbol{q}-\boldsymbol{K}}\right\} = 0 \tag{16}$$

Since Eq. (16) form orthogonal set, all the coefficients must vanish. This can also be represented in the following form by changing the indexes again:

$$\left(\frac{h^2}{2m}(\boldsymbol{k}-\boldsymbol{K})^2 - E\right) c_{\boldsymbol{k}-\boldsymbol{K}} + \sum_{\grave{\boldsymbol{K}}} V_{\grave{\boldsymbol{K}}-\boldsymbol{K}}\, c_{\boldsymbol{k}-\grave{\boldsymbol{K}}} = 0 \tag{17}$$

What needs to be emphasized here that this Eq. (17) is nothing put the *Schrodinger* equation in the momentum space under a periodic potential. This approach of mathematical analysis has been used before by *Gaston Floquet* to relate the class of solutions to periodic differential equations [9]. What it means qualitatively is that any specific value of $\boldsymbol{k}$, only the coefficients $c_{\boldsymbol{k}}$ that are different by a reciporical lattice $\boldsymbol{K}$ vector will sustain. This means that our wavefunction with a specific value of $\boldsymbol{k}$ can be written as:

$$\psi_k(\boldsymbol{r}) = \sum_{\boldsymbol{K}} c_{\boldsymbol{k}-\boldsymbol{K}}\, e^{i(\boldsymbol{k}-\boldsymbol{K}).\boldsymbol{r}} = e^{i\boldsymbol{k}.\boldsymbol{r}} \sum_{\boldsymbol{K}} c_{\boldsymbol{k}-\boldsymbol{K}}\, e^{i\boldsymbol{K}.\boldsymbol{r}} \tag{18}$$

$$\psi_k(\boldsymbol{r}) = e^{i\boldsymbol{k}.\boldsymbol{r}}\, u_{\boldsymbol{n},\boldsymbol{k}}(\boldsymbol{r}) \qquad Q.E.D \tag{19}$$

Bloch Wave Characteristics:

From the previous derivation, we note that in a periodic lattice, as the one shown in Fig. 1(a), Bloch theorem does not give an explicit solution of the wavefunction $\psi(r)$. Nonetheless, it confine it to a class of solutions that can be described by a plane waves $e^{i\boldsymbol{k}.\boldsymbol{r}}$ modulated by periodic functions $u_{\boldsymbol{n},\boldsymbol{k}}(\boldsymbol{r})$ with lattice periodicity, as shown in Fig. 1(b).

- From Eq. (6) and Eq. (12), the Bloch vector (k) can be always confined in a reciporical lattice primitive cell (e.g. ,Brillouin zone) and will be periodic thereafter.

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- We note from Eq. (9) or Eq. (19) that at a fixed value of $\boldsymbol{k}$, there are infinite solutions generated from the many periodic functions $u_{\boldsymbol{n},\boldsymbol{k}}(\boldsymbol{r})$ that satisfy the lattice. Thus, we need two quantum numbers ($n\ and\ k$) to fully specify a Bloch state.
- The previous two points lead to the description of the *band structure*, which is a plot of the Hamiltonian eigenvalues (E_{kn}) of Bloch waves (usually along a symmetry line in the first Brillion zone) as can be seen in Fig. 1(c). Various information can be inferred from this dispersion relation such as the effective mass, bandgap formation, and material electronic and thermal behavior.
- One of the important constant energy surfaces is *Fermi-surface* which contain the k vectors with energies equal to that of the chemical potential at zero temperature. In a constant potential (as the free-electron model) the fermi-surface take the form of a sphere where in than the periodic one (Bloch model) it is severly deformed, as shown in Fig. 1(d).
- We also note that the electron momentum is not simply proportional to $\frac{p}{h}$ as the case in Sommerfeld theory. This is expected since the Hamiltonian does not have complete translation invariance under a non-constant lattice potential. Thus, the momentum of a Bloch electron, known as the *crystal momentum,* restrict the allowed energies that an electron can have under the application of an external electric field. This has consequently lead to the concept of the *effective mass,* which shown importance in calculating many of the electron thermal and electrical properties.

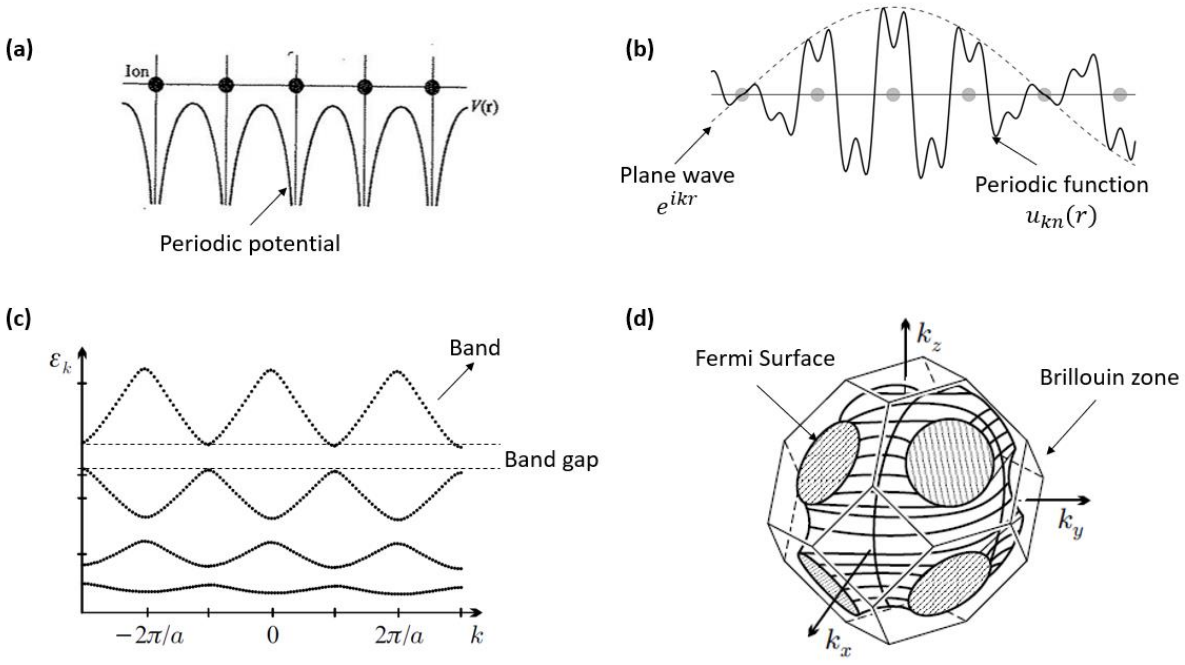

Figure. 1 Bloch Theorem: (a) Periodic lattice and the effective potential, (b) Bloch wave, (c) band structure, (d) Brillouin zone and Fermi Surface.

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Bloch follow-up work and theorem predictions:

Right after his derivation, Bloch applied his theory, attempting to resolve the inconsistency in the free-electron model:

- In the Drude model, the resistivity stems from the collisions of electrons with the lattice atoms. However, Bloch theorem treats electrons as states, excluding the collision per se from its theoretical grounds and include the interaction only as an effective potential. Despite the existence of such interaction, once the Bloch wave has a non-vanishing mean velocity, it will persist forever. The material resistivity arises only due to lattice defects and thermal vibrations. Bloch wrote, "*The greatest effort in my thesis was spent on calculating the resistivity. Since a perfectly periodic lattice had been understood to present no impediment to the current, it was clear that a finite resistance could arise only from irregularities and that its temperature-dependence would have to be explained by the thermal motion of the ions."* [10].
- Bloch has also been able to address the specific heat problem at room temperature. He has been able to resolve the inconsistency of the specific heat with experimental results and showing that it is consistent with *Wilson* as well as *Wiedemann-Franz* ratios.
- Bloch has also evaluated his theorem for two opposite limiting cases; strongly bound and weekly bound electrons. He developed the method of Linear Combination of Atomic Orbitals (LCAO) in solids, concurrently with Robert Mullikan on monocular orbitals in 1929 where a simpler version has been developed later by *Slater* and *Kosteon* on their *"SK tight-binding approximation"* [11].
- Later work of Bloch and Zener attempt to describe the oscillatory motion of Bloch electrons in a lattice under a constant external force acting on it. However, it was hard to be observed due to the electron scattering with lattice defects. However, it has been later predicted by *Leo Esaki* in 1970, and experimentally observed for the first time in a superlattice by *Jochen Feldmann* and *Karl Leo* in 1992 [12].

Bloch Theorem and Light:

Lawrence and William Braggs analyzed crystal structure using x-ray diffraction in 1913 and observed an electromagnetic bandgap where certain photonic k-vectors are prohibited due to distractive interference. *Kogelnik* and *Shank* suggested later building a laser mirror by utilizing such a phenomenon and alternating different refractive index materials [13]. *Eli Yablonovittch* has suggested then that if such a photonic bandgap of a laser cavity overlaps with the electronic bandgap of the gain material, the spontaneous emission can be completely inhibited, a milestone on matter-light interaction and acted as the birth of the photonic crystal field that has been subject to rigorous research in the last few decades [14]. Bloch theorem is a general-wave theorem that applies similarly to photonic structure and has acted as a powerful tool in analyzing and engineering various photonic devices and systems.

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Biography

Flexi Bloch (1905~1983) is a Swiss physicist and Nobel laureates. After his PhD dissertation on the study of electron in a periodic lattice, he worked on ferromagnetism, superconductors, and nuclear magnetic resonance. Bloch went on to become the first professor for theoretical physics at Stanford and the first Director General of CERN in Geneva.

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