Léon Brillouin and the Brillouin Zone

Review: Les électrons libres dans les métaux et le role des réflexions de Bragg

Zhetao Jia

Abstract

In this report, I followed Brillouin's derivation of energy gap near degeneracy and compared it with contemporary formulation. The previous and follow-up work of the paper is investigated and the implication of the paper on X-ray experiments with alloy is discussed. Recent applications and development of Brillouin Zone in topological insulator, photonic crystal and anisotropic materials are also included with examples.

Introduction

Born in an academic family in France, Léon Brillouin is a great French physicist with his contributions over various aspects. From 1908 to 1912. Brillouin joined École Normale Supérieure where he extracted a new value of Avogadro's number from his measurements of the blue light of the sky under Perrin's supervision. In 1926, the famous Wentzel–Kramers–Brillouin approximation, also known as the WKB method came out and became a well-known tool to find approximate solutions to linear differential equations with spatially varying coefficients.[1] Later, Brillouin proposed a method to calculate the propagation of light in dispersive media guided by Sommerfeld. The Brillouin-Wigner's formula proposed by him was proved useful in many-particle problems, mainly in quantum chemistry and nuclear theory. Besides theoretical contribution, Brillouin also worked on radio transmission in the laboratory of General Ferrié and proposed a new type of amplifier.[2]

Previous work

In 1927, Sommerfeld modified the free electron gas model by replacing the Maxwell-Boltzmann distribution by Fermi-Dirac distribution[3], which successfully explains thermal-electric field and heat capacities, but the mean-free path still exists in his calculation. In 1927, Bloch found the form of eigenfunction in the periodic potential.[4] Shortly afterwards, Rudolf Peierls applied Schrodinger's weak potential approximation to explain the properties of energy band.[5] Phillip Morse also analyzed the band spectrum and total reflection almost at the same time.[6] However, most previous discussions in weak potential approximation were about in one-dimensional case and Peierls' argument about 2D structure limited to the diffraction plane parallel to the coordinate axis. By then, there was no characterization of how Bragg diffraction would affect energy bands in 2D periodic potential system. Moreover, the description of electronic property of periodic lattice is nowhere systematic. [7]

Instead of working in one-dimension, Brillouin proposed a set of mutually intersecting planes in k-space based on Bragg condition close to where the energy bands distorted. [8]It was revealed that the description of the shape of Fermi surface was greatly simplified and easily visualized under this view. The concept of "Brillouin Zone" becomes widely used to describe the electronic property of solids in both 2D and 3D. The Brillouin Zone is also useful in the description of the new emerging field of topological insulators and photonic crystals, where the concepts in solids were borrowed to control the flow of light with periodic structures.

Contents of the paper (Brillouin, 1930)

The paper studies selective reflection (Bragg reflection) and its relationship with the anomalies of propagation of electronic wave in the metal. Brillouin applies the perturbation theory to calculate the first-order and second-order approximation by solving the Schrodinger equation with periodic potential. The main assumptions are that the periodic potential is weak, and the electrons are "nearly free" based on the Sommerfeld's work on free electron gas. Two of the reasons explain why such assumption would work: (1) Conduction electrons are not allowed to get into inner shell of ions due to Pauli principle. (2) The field of ions are shielded by other electrons. Based on the weak-potential and "near free" electron model, Brillouin starts his discussion on the band structure near degeneracy. The original symbols and formalism are kept in the following derivation.

According to the Floquet theorem generalized by Bloch:

$$\psi = A(x,y,z)e^{2\pi i(ax+by+cz)}$$

First, we consider the case of almost free electrons, assuming that the potential inequalities in the crystal are very small, then we apply successive approximations to obtain the solution. Starting from Schrodinger equation

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

The potential P can be separated as constant P0 and lattice potential P'(x,y,z). Because of the periodicity of the lattice potential, it can be expanded as Fourier series

$$P'(x,y,z) = \sum_{\alpha\beta\gamma}{}' P_{\alpha\beta\gamma} e^{-\frac{2\pi i}{d}(\alpha x+\beta y+\gamma z)} \qquad \alpha,\beta,\gamma \text{ are integers}$$

The perturbed eigenfunctions and eigenvalues are

$$\psi_{abc} = \psi^{o}_{abc} + \psi'_{abc} + \cdots \qquad E_{abc} = E^{o}_{abc} + E'_{abc}$$

By introducing the coupling, the original eigenstates couples if (for small e)

$$a'^2 + b'^2 + c'^2 = a^2 + b^2 + c^2 + e$$

The coupling induced by the perturbed potential can be represented by the matrix element:

$$P'(abc;a'b'c') = \int_v P' e^{2\pi i(a-a')r} d\tau = \sum_{\alpha\beta\gamma} P_{\alpha\beta\gamma} \frac{1}{v} \int_r e^{2\pi i(a-a'-\frac{\alpha}{d})\cdot r} d\tau$$

We have a degeneracy problem when the following equations are satisfied:

$$a - a' - \frac{\alpha}{d} = 0 \qquad b - b' - \frac{\alpha}{d} = 0 \qquad c - c' - \frac{\gamma}{d} = 0$$

The Bragg condition is approximately satisfied when

$$\lambda - 2\delta \cos\theta = \varepsilon\lambda\delta^2$$

We need to find a linear combination of the original eigenfunction to make the next order calculation possible. The intermediate energy is defined by

$$E = \frac{E^o_{abc} + E^o_{a'b'c'}}{2} + \eta \quad \text{or} \quad E = \eta \pm \frac{h^2}{2m}\varepsilon$$

The combined wave function needs to satisfy the Schrodinger equation with energy E.

$$\psi = B\psi^o_{abc} + B'\psi^o_{a'b'c'} + \psi' \cdots$$

Insert into Schrodinger equation, we obtain

$$\Delta\psi' + \frac{8\pi^2 m}{h^2}(E - P_0)\psi' = B\psi^o_{abc}\left[\frac{8\pi^2 m}{h^2}(\eta + P') - 2\pi^2\varepsilon\right] + B'\psi^o_{a'b'c'}\left[\frac{8\pi^2 m}{h^2}(\eta + P') + 2\pi^2\varepsilon\right]$$

The first order perturbation term in wavefunction should be orthogonal to both original wavefunction. Hence, the above equation times the $\Psi_{abc}, \Psi_{a'b'c'}$ and integrate respectively, we have

$$B\left(\eta - \frac{h^2}{4m}\varepsilon\right) + B'P'(abc;a'b'c') = 0$$

$$BP'(abc;a'b'c') + B'\left(\eta + \frac{h^2}{4m}\varepsilon\right) = 0$$

It has solution only when the determinant is zero, which gives the results of η as

$$\eta = \pm\sqrt{P^2(abc;a'b'c') + \frac{h^4\varepsilon^2}{16m^2}}$$

An example of the abnormal energy variation caused by degeneracy is demonstrated in Figure 1(a). The region is selected for $\alpha = \pm 1, \beta = 0, \gamma = 0$. In the Figure 1(a), the curves split into a series of separate branches and Brillouin pointed out that the curve branch

should with vertical tangent. At the degeneracy point, the curve shows a discontinuity of energy and such discontinuity happens in the vicinity of all these planes in 2D. Brillouin also pointed out that the waves of each zone were obtained by the coupling of the waves corresponding to oscillations of the electron in each valley of potential.

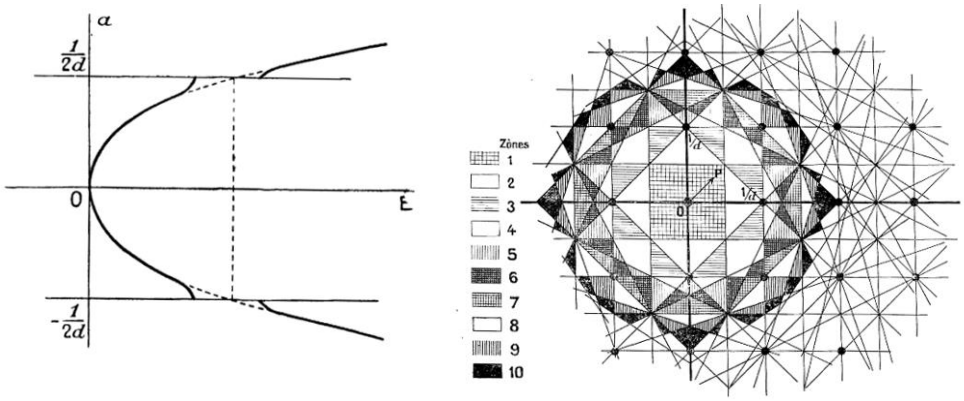

Fig. 1 (from Brillouin, 1930) (a) 1D energy variation near degeneracy. Energy gap opens near the degeneracy points according to Brillouin's derivation. (b) 2D Brillouin Zone in reciprocal lattice. The lines indicate Bragg planes and each zone is colored differently.

From the intriguing Figure 1(b) plotted by Brillouin, it can be concluded that long waves propagate without anomalies but when wavelength decreases, the proportion of waves propagation freely without affected by Bragg diffraction decreases dramatically. After simply derivation, Brillouin shows that the area in reciprocal space affected by Bragg diffraction at distance p from the origin increases as p^3. In the paper, Brillouin also discussed about average electric current of wave-guided electrons and the high order Brillouin Zone in 3D structure (for example, body-centered cubic) along with its representations.

It is interesting to compare the section of derivation in contemporary textbook with the Brillouin's original work. To solve similar degeneracy problem near the Bragg plane, the Ashcroft textbook describes it in a more general way by dividing the problem into non-degenerate and nearly degenerate cases and the derivation is clearer. Consider the Bloch wave function

$$\psi_{\mathrm{k}}(\mathrm{r}) = \sum_{\mathrm{K}} c_{\mathrm{k}-\mathrm{K}} e^{i(\mathrm{k}-\mathrm{K})-\mathrm{r}}$$

, where K points from one lattice in reciprocal space to another. The Schrodinger equation leads to

$$\left[\frac{h^2}{2m}(\mathrm{k}-\mathrm{K})^2 - \varepsilon\right] c_{\mathrm{k}-\mathrm{K}} + \sum_{\mathrm{K}} U_{\mathrm{K}'-\mathrm{K}} c_{\mathrm{k}-\mathrm{K}'} = 0 \quad .$$

Conceptually, in the free space, the translational symmetry makes the wave with momentum k-K a non-degenerate eigenfunction. After the system is perturbed by weak

periodic potential, mode k-K are perturbed by other modes, hence introducing perturbation terms.

To solve the coefficient and energy, the textbook considers the following two cases:

Non-degenerate Case: the mode considered is non-degeneracy, as U is too small to couple it to other modes

$$\left|\varepsilon^0_{\text{k-K}_1} - \varepsilon^0_{\text{k-K}}\right| \gg U$$

By applying the nondegenerate perturbation theory, the first order perturbation would give

$$c_{\text{k-K}} = \frac{U_{\text{K}_1-\text{K}} c_{\text{k-K}_1}}{\varepsilon - \varepsilon^0_{\text{k-K}}} + O\left(U^2\right)$$

Plug the first order perturbed wave function into the Schrodinger equation, we obtain the second order perturbation of energy

$$\varepsilon = \varepsilon^0_{\text{k-K}_1} + \sum_{\text{K}} \frac{\left|U_{\text{k-K}_1}\right|^2}{\varepsilon^0_{\text{k-K}_1} - \varepsilon^0_{\text{k-K}}} + O\left(U^3\right)$$

Nearly-degenerate Case: the mode considered is nearly-degeneracy, as the perturbed potential manages to couple it to other modes

$$\left|\varepsilon^0_{\text{k-K}} - \varepsilon^0_{\text{k-K}_i}\right| \gg U, i = 1,\ldots,m, \text{K} \neq \text{K}_1,\ldots,\text{K}_m$$

Similarly, to the first order perturbation

$$\left(\varepsilon - \varepsilon^0_{\text{k-K}_i}\right) c_{\text{k-K}_i} = \sum_{j=1}^{m} U_{\text{K}_j\text{-K}_i} c_{\text{k-K}_j} + \sum_{\text{K} \neq \text{K}_1,\ldots,\text{K}_m} U_{\text{K-K}_i} c_{\text{k-K}}, i = 1,\ldots,m.$$

Consider only the leading term where modes are coupled by O(U)

$$c_{\text{k-K}} = \frac{1}{\varepsilon - \varepsilon^0_{\text{k-K}}} \sum_{j=1}^{m} U_{\text{K}_j\text{-K}} c_{\text{k-K}_j} + O\left(U^2\right)$$

Consider the simplest example, where only two free electron levels are with order U of each other, we have

$$\left(\varepsilon - \varepsilon^0_q\right) c_q = U_{\text{K}} c_{\text{q-K}},$$

$$\left(\varepsilon - \varepsilon^0_{\text{q-K}}\right) c_{\text{q-K}} = U_{\text{-K}} c_{\text{q}} = U^*_{\text{K}} c_{\text{q}}$$

It is solvable only when the determinant is zero, which gives

$$\varepsilon = \frac{1}{2}\left(\varepsilon_{\mathrm{q}}^{0} + \varepsilon_{\mathrm{q\text{-}K}}^{0}\right) \pm \left[\left(\frac{\varepsilon_{\mathrm{q}}^{0} + \varepsilon_{\mathrm{q\text{-}K}}^{0}}{2}\right)^{2} + \left|U_{\mathrm{K}}\right|^{2}\right]^{1/2}$$

which is of the same form as the result in paper.

Follow-up work

At the time solid state is fast developing theoretically, experimentalists have been using X-rays to examine the structure of alloy. However, not all the observations are well-explained, and difficulties remain in understanding some results. In this case, Brillouin's work become a useful tool to analyze and understand the experiment data. In 1934, H. Johns applied the Brillouin Zone and the energy gap calculation in understanding alloy in gamma-phase.[11] Based on Bradley and Thewlis' experimental results of brass with X-ray[12], Johns calculated the energy gap near the Bragg plane explicitly, following Brillouin's derivation. He also pointed out that the change of Hall coefficient, from large positive to large negative, is due to the distortion of Fermi surface close to the boundary of Brillouin Zone and the large diamagnetic susceptibilities can also be expected for alloys in this phase. Published in the same year, Johns' another paper[10] explained the difference of intensity difference in bands beryllium and magnesium[9], which has similar structure with two valence electrons, also based on the distortion of Fermi surface near the boundary of Brillouin Zone.

Besides its application in explaining X-ray experiments, the analysis of Brillouin Zone is developed further by L. Bouckaert under the view of group theory in 1936.[13] In the case of Brillouin Zone, the representations of a space group forms a continuous manifold, characterizing by continuous parameters. The analysis leads to the conclusion that the energy is a continuous function of the reduced wave vector.

Recent work

Since its development, the concept of Brillouin Zone has been widely used in describing the properties of electronic system with band diagram. Even after eighty-years, the investigation and application of Brillouin Zone is still active and open.

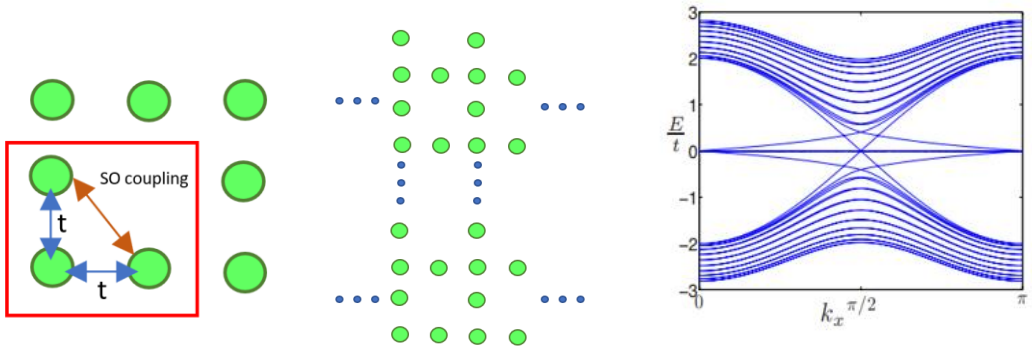

Fig. 2 (a) A tight-binding model with Lieb lattice. A unit cell is enclosed by the red rectangle. Nearest Neighbor hopping, and Next-Nearest Neighbor spin-orbital coupling is considered in this model (b) A supercell with 10 unit cells in y-direction and infinity cells in x-direction (c) Band diagram for structure in (b) with spin-orbital coupling amplitude $\lambda = 0.2t$. Four conducting edge states inside the topological bandgap is observed.

In the recent research of topological insulator, which is material with symmetry-protected topological order, behaving as insulator in bulk but conductor along the edge (surface), the topological invariant can be identified by studying the first Brillouin Zone. As an example, a simple tight-binding model with similar structure as the homework problem of planar CuO_2 is analyzed following Ref. [14] The Bravais unit consists of three sites, with nearest neighbor hopping amplitude t. The Quantum Spin Hall effect appears by introducing an additional spin-orbital Next-Nearest Neighbor(NNN) coupling term to the Hamiltonian and the momentum-space Hamiltonian now becomes

$$H_k = H_k^0 + H_k^{SO} = -2t\begin{pmatrix} 0 & \cos k_x & \cos k_y \\ \cos k_x & 0 & 0 \\ \cos k_y & 0 & 0 \end{pmatrix} \pm 4\lambda \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i\sin k_x \sin k_y \\ 0 & i\sin k_x \sin k_y & 0 \end{pmatrix}$$

In the following discussion, the Hamiltonian is considered for spin-up electrons only, corresponding to the plus sign for the spin-orbital Hamiltonian.

The topological property embedded in the additional as $2\pi C$ Berry phase as the system adiabatically changes along the band. C is an invariant integer under perturbation if the symmetry is not broken and the bandgap is not closed. Following the TKNN invariant calculation proposed in Ref.[15],

$$C = \frac{1}{2\pi}\int_{band} d^2k \int d^2r \left(\frac{\partial u^*}{\partial k_y}\frac{\partial u}{\partial k_x} - \frac{\partial u^*}{\partial k_x}\frac{\partial u}{\partial k_y}\right)$$

, where the integration is over the first Brillouin Zone for specific band and u is the eigenmode corresponding to (kx, ky) in the BZ. I calculate the topological number for the upper band and obtain C = 4. The details of the numerical calculation is provided in

Supplementary Material with Mathematica following Ref. [16] The topological invariant obtained indicates the existence of four different conducting modes propagating along the edge with their energy inside the topological bandgap. To verify this, the band structure for strip of Ny = 10 unit cells with open boundary conditions along the y direction and periodic along x is simulated in Figure 2(c). Four modes with positive dE/dk for spin-up electrons is predicted by C = 4. Two of them are clearly shown within the topological bandgap while the other two is in range $kx \in [-\pi, 0]$ by symmetry. In sum, the topological property of the material can be obtained by studying the band structure inside the first Brillouin Zone.

Beside solid-state physics, Brillouin Zone has been transplanted into other fields, for example, photonic crystal. The concept of photonic crystal, a periodic nanostructure designed to manipulate the propagation of light, was proposed in 1987, based on the similar behavior as electrons in solids. Shortly afterwards, Eli Yablonovitch draw the band diagram in Brillouin Zone of a fcc dielectric photonic crystal for the first time in history, with its photonic band gap indicating a forbidden band of energy in any incident directions.[17] With the development of nanofabrication technology, the material properties and geometric structure of such photonic crystals have more options, hence researchers are trying to extend the concept of Brillouin to make it useful in more scenarios. For example, the definition of Brillouin Zone has also been extended for anisotropic material, where the material's optical properties are different along different axis. For anisotropic material, the Brillouin Zone no longer conforms the original definition as bounded by Bragg planes.[18] The new Brillouin Zone can be obtained by applying Wigner-Seitz method to a stretched or compressed reciprocal lattice for material without dispersion and its boundary becomes curved for dispersive material. The theoretically proposed Brillouin Zone boundary is also confirmed experimentally by sending femtosecond laser pulses to excite polaritons and image their propagation in lithium niobate. In this method, the band diagram can be observed and the BZ boundary is identified at the lowest bandgap, following the similar idea in Brillouin's derivation.

In conclusion, Brillouin's derivation of energy gap and his visualization of Brillouin Zone is a significant step in understanding the properties of solid. Researchers successfully applied Brillouin's work to explain the observation from X-ray experiments of alloy in 1930s. Brillouin Zone also remains a developmental tool over time. The analysis inside the first Brillouin Zone can be used to classify the Hamiltonian with topological invariants and predict the number of edge modes. Brillouin Zone can be applied to other periodic structures like photonic crystals and/or anisotropic materials, which proves it as a simple and adaptable tool in analyzing different kinds of periodic structures.

Reference

1. WKB approximation - Wikipedia. Available at:

   https://en.wikipedia.org/wiki/WKB_approximation (Accessed: 28th November

2018)

2. Brillouin, Léon Nicolas | Encyclopedia.com. Available at: https://www.encyclopedia.com/science/dictionaries-thesauruses-pictures-and-press-releases/brillouin-leon-nicolas. (Accessed: 28th November 2018)
3. Sommerfeld, A. Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik. *Zeitschrift fur Physik* **47,** 1–32 (1928).
4. Bloch, F. Uber die Quantenmechanik der Elektronen in Kristallgittern. *Zeitschrift fur Physik* **52,** 555–600 (1929).
5. Peierls, R. Zur Theorie der elektrischen und thermischen Leitfähigkeit von Metallen. *Ann. Phys.* **396,** 121–148 (1930).
6. Morse, P. M. The Quantum Mechanics of Electrons in Crystals. *Physical Review* **35,** 1310–1324 (1930).
7. Hoddeson, L., Baym, G. & Eckert, M. The development of the quantum-mechanical electron theory of metals: 1928—1933. *Rev. Mod. Phys.* **59,** 287–327 (1987).
8. Brillouin, L. Les électrons libres dans les métaux et le role des réflexions de Bragg. *J. Phys. Radium* **1,** 377–400 (1930).
9. O'Bryan, H. M. & Skinner, H. W. B. Characteristic X-Rays from Metals in the Extreme Ultraviolet. *Physical Review* **45,** 370–378 (1934).
10. Jones, H., Mott, N. F. & Skinner, H. W. B. A Theory of the Form of the X-Ray Emission Bands of Metals. *Physical Review* **45,** 379–384 (1934).
11. Jones, H. The theory of alloys in the γ-phase. *Proc. R. Soc. Lond. A Math. Phys. Sci.* **144,** 225–234 (1934).
12. Bradley, A. J. & Thewlis, J. The structure of γ-brass. *Proc. R. Soc. Lond. A Math.*

Phys. Sci. **112,** 678–692 (1926).

13. Bouckaert, L. P., Smoluchowski, R. & Wigner, E. Theory of Brillouin Zones and Symmetry Properties of Wave Functions in Crystals. *Physical Review* **50,** 58–67 (1936).
14. Weeks, C. & Franz, M. Topological insulators on the Lieb and perovskite lattices. *Phys. Rev. B: Condens. Matter Mater. Phys.* **82,** (2010).
15. Thouless, D. J., Kohmoto, M., Nightingale, M. P. & den Nijs, M. Quantized Hall Conductance in a Two-Dimensional Periodic Potential. *Phys. Rev. Lett.* **49,** 405–408 (1982).
16. Fukui, T., Hatsugai, Y. & Suzuki, H. Chern Numbers in Discretized Brillouin Zone: Efficient Method of Computing (Spin) Hall Conductances. *J. Phys. Soc. Jpn.* **74,** 1674–1677 (2005).
17. Yablonovitch, E. & Gmitter, T. J. Photonic band structure: The face-centered-cubic case. *Phys. Rev. Lett.* **63,** 1950–1953 (1989).
18. Sivarajah, P., Maznev, A. A., Ofori-Okai, B. K. & Nelson, K. A. What is the Brillouin zone of an anisotropic photonic crystal? *Phys. Rev. B: Condens. Matter Mater. Phys.* **93,** (2016).