Kronig Penney model

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Ralph Kronig was a German-American physicist (March 10, 1904 – November 16, 1995). He is noted for the discovery of particle spin and for his theory of x-ray absorption spectroscopy. His theories include the Kronig–Penney model, the Coster–Kronig transition and the Kramers–Kronig relation.

http://en.wikipedia.org/wiki/Ralph_Kronig

William George Penney, Baron Penney (24 June 1909– 3 March 1991), was an English mathematician and professor of mathematical physics at the Imperial College London as well as the rector of the imperial college. He is widely held responsible for his leading and integral role in the development of Britain's nuclear program, a clandestine programme started following the World war II and the success of Soviet nuclear program.

http://en.wikipedia.org/wiki/William_Penney,_Baron_Penney

1. Kronig-Penney model

The essential features of the behavior of electrons in a periodic potential may be explained by a relatively simple 1D model which was first discussed by Kronig and Penney. We assume that the potential energy of an electron has the form of a periodic array of square wells.

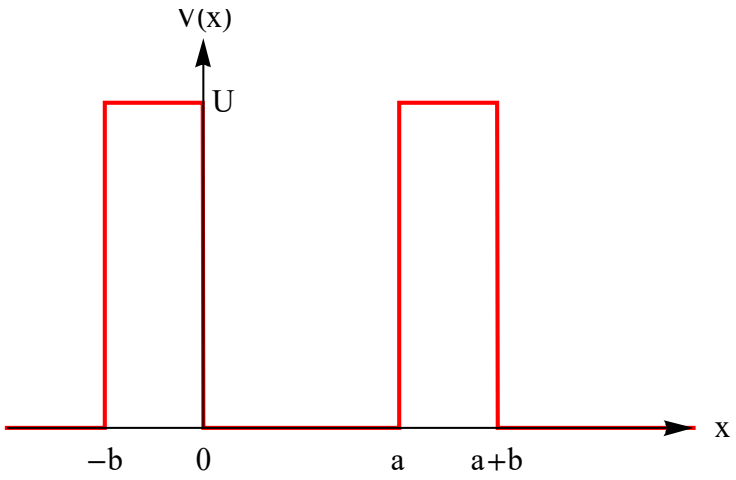

Fig. Periodic potential in the Kronig-Penney model

We now consider a Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)+V(x)\psi(x)=E\psi(x),$$

where E is the energy eigenvalue.

(i) $V(x) = 0$ for $0 \le x \le a$

$$\psi_1(x)=Ae^{iKx}+Be^{-iKx}, \qquad d\psi_1(x)/dx=iK(Ae^{iKx}-Be^{-iKx}),$$

with $E=\hbar^2K^2/2m$.

(ii) $V(x) = U$ for $-b \le x \le 0$

$$\psi_2(x)=Ce^{Qx}+De^{-Qx}, \qquad d\psi_2(x)/dx=Q(Ce^{Qx}-De^{-Qx}),$$

with

$$U - E = \hbar^2 Q^2 / 2m .$$

The Bloch theorem can be applied to the wave function

$$\psi(x + a + b) = e^{ik(a+b)}\psi(x),$$

where k is the wave number. The constants A, B, C, and D are chosen so that ψ and $\mathrm{d}\psi/\mathrm{d}x$ are continuous at $x = 0$ and $x = a$.

(a) At $x = 0$,

$$A + B = C + D,$$

$$iK(A - B) = Q(C - D).$$

Thanks to the Bloch theorem, the boundary condition of the wave function at $x = -b$ is related to that at $x = a$. In other words, we have only to know the knowledge of the wave function in a unit cell (the period is $a + b$).

(b) At $x = -b$,

$$\psi(a) = e^{ik(a+b)}\psi(-b), \qquad \text{or} \qquad \psi_1(a) = e^{ik(a+b)}\psi_2(-b),$$

$$\psi'(a) = e^{ik(a+b)}\psi'(-b), \qquad \text{or} \qquad \psi_1'(a) = e^{ik(a+b)}\psi_2'(-b),$$

or

$$Ae^{iKa} + Be^{-iKa} = e^{ik(a+b)}(Ce^{-Qb} + De^{Qb}),$$

$$iK(Ae^{iKa} - Be^{-iKa}) = Qe^{ik(a+b)}(Ce^{-Qb} - De^{Qb}).$$

The above four equations for A, B, C, and D have a solution only if $det[M]=0$, where the matrix M is given by

$$M = \begin{pmatrix} 1 & 1 & -1 & -1 \\ iK & -iK & -Q & Q \\ e^{iKa} & e^{-iKa} & -e^{-Qb+ik(a+b)} & -e^{Qb+ik(a+b)} \\ iKe^{iKa} & -iKe^{-iKa} & -Qe^{-Qb+ik(a+b)} & Qe^{Qb+ik(a+b)} \end{pmatrix}.$$

The condition of det[M] = 0 leads to

$$\cos[k(a+b)] = \cos(Ka)\cosh(Qb) + \frac{(Q^2 - K^2)}{2KQ}\sin(Ka)\sinh(Qb).$$

where

$$U - E = \hbar^2 Q^2 / 2m, \qquad E = \hbar^2 K^2 / 2m$$

or

$$U = \frac{\hbar^2}{2m}(K^2 + Q^2).$$

The energy dispersion relation (E vs k) can be derived from this equation.

2. Numerical claculation

The essential features of the behavior of electrons in a periodic potential may be explained by a relatively simple 1D model which was first discussed by Kronig and Penney. We assume that the potential energy of an electron has the form of a periodic array of square wells.

Here we show only the result of the Kronig-Penny model:

((**Mathematica**))
Using the Mathematica, one can derive the fundamentak equation for the energy diagram in the Kronig-Penney model.

```
M = {{1, 1, -1, -1}, {i K, -i K, -Q, Q},
   {Exp[i K a], Exp[-i K a], -Exp[i k (a + b) - Q b], -Exp[i k (a + b) + Q b]},
   {i K Exp[i K a], -i K Exp[-i K a], -Q Exp[i k (a + b) - Q b],
    Q Exp[i k (a + b) + Q b]}}; M2 = Det[M];
Simplify[ExpToTrig[M2]]
```

```
4 i (Cos[(a + b) k] + i Sin[(a + b) k])
 (2 K Q Cos[(a + b) k] - 2 K Q Cos[a K] Cosh[b Q] + (K^2 - Q^2) Sin[a K] Sinh[b Q])
```

$$2KQ\cos[k(a+b)]-2KQ\cos(aK)\cosh(bQ)+(K^2-Q^2)\sin(aK)\sinh(bQ)=0$$

or

$$\cos[k(a+b)]=\cos(aK)\cosh(bQ)+\frac{(Q^2-K^2)}{2KQ}\sin(aK)\sinh(bQ)$$

where

$$K=\sqrt{\frac{2mE}{\hbar^2}}, \qquad Q=\sqrt{\frac{2m(U-E)}{\hbar^2}}$$

$$K^2+Q^2=\frac{2mU}{\hbar^2},$$

E is the energy of electron and U is the potential height.

((**Note**))

We check to see whether this energy dispersion relation coincides with that of the free particle. To this end, we assume that $U\rightarrow 0$ and $b\rightarrow 0$. This gives a particle in a quantum box (with the wall of infinity potential).

$$K=\sqrt{\frac{2mE}{\hbar^2}}, \qquad Q=\sqrt{\frac{2m(-E)}{\hbar^2}}=iK$$

Then we get the Kronig-Penney expression.

$$\cos[k(a)]=\cos(aK)$$

or

$$K = \sqrt{\frac{2mE}{\hbar^2}} = k \qquad \text{or} \qquad E = \frac{\hbar^2 k^2}{2m}$$

3. Dimensionless expression

The mass of electron and the Dirac constant are given by

m = 9.10938215 x 10^{-28} g
$\hbar$ = 1.054571628 x 10^{-27} erg s

(a+b) is the repeat distance. The reciprocal lattice is

$$G = \frac{2\pi}{a+b}$$

Here we introduce the dimensionless-quantities ε, u, and κ as follows.

(i) ε

$$K^2(a+b)^2 = \frac{2mE(a+b)^2}{\hbar^2} = 0.262468\ E_0(a_0+b_0)^2 = \varepsilon$$

or

$$K(a+b) = \sqrt{\varepsilon}\,, \qquad K = \frac{\sqrt{\varepsilon}}{a+b}$$

(ii) u

$$Q^2(a+b)^2 = \frac{2m(U-E)(a+b)^2}{\hbar^2} = 0.262468\ (U_0-E_0)(a_0+b_0)^2 = u-\varepsilon$$

or

$$Q(a+b) = \sqrt{u-\varepsilon}\,, \qquad Q = \frac{\sqrt{u-\varepsilon}}{a+b}$$

where

$$\frac{2mU(a+b)^2}{\hbar^2} = 0.262468\ U_0(a_0+b_0)^2 = u$$

(iii) κ

$$k(a+b) = k_0(a_0+b_0) = \kappa \qquad\qquad k = \frac{\kappa}{a+b}$$

((Note)) That a and b are in the units of Å, k is in the unit of Å^{-1}, and E and U is the unit of eV. In other words, a_0, b_0, k_0, E_0, and U_0 are dimensionless.

$$a = a_0\,(\text{Å}), \qquad b = b_0\,(\text{Å}), \qquad k = k_0\,(\text{Å}^{-1}),$$

$$E = E_0\ (\text{eV}), \text{ and} \qquad U = U_0\ (\text{eV}),$$

Then we get

$$aK = \frac{a}{a+b}\sqrt{\varepsilon} = \frac{1}{1+\alpha}\sqrt{\varepsilon}$$

$$bQ = \frac{b}{a+b}\sqrt{u-\varepsilon} = \frac{\alpha}{1+\alpha}\sqrt{u-\varepsilon}$$

$$k(a+b) = \kappa$$

where

$$\alpha = \frac{b}{a} = \frac{b_0}{a_0}.$$

Using the above parameters, the Kronig-Penney expression can be rewritten as

$$2\sqrt{u-\varepsilon}\sqrt{\varepsilon}\cos[\kappa] = 2\sqrt{u-\varepsilon}\sqrt{\varepsilon}\cos[\frac{\sqrt{\varepsilon}}{1+\alpha}]\cosh(\frac{\alpha\sqrt{u-\varepsilon}}{1+\alpha}]$$
$$+(u-2\varepsilon)\sin(\frac{\sqrt{\varepsilon}}{1+\alpha})\sinh[\frac{\alpha\sqrt{u-\varepsilon}}{1+\alpha}]$$

or

$$\cos[\kappa]=\cos[\frac{\sqrt{\varepsilon}}{1+\alpha}]\cosh(\frac{\alpha\sqrt{u-\varepsilon}}{1+\alpha}]+\frac{(u-2\varepsilon)}{2\sqrt{u-\varepsilon}\sqrt{\varepsilon}}\sin(\frac{\sqrt{\varepsilon}}{1+\alpha})\sinh[\frac{\alpha\sqrt{u-\varepsilon}}{1+\alpha}]$$

which means that the energy dispersion relation is dependent only on the values of α and u.

4. Energy gap regions

Here we put the right hand side of the above equation as $H(\varepsilon)$,

$$H(\varepsilon)=\cos[\frac{\sqrt{\varepsilon}}{1+\alpha}]\cosh(\frac{\alpha\sqrt{u-\varepsilon}}{1+\alpha}]+\frac{(u-2\varepsilon)}{2\sqrt{u-\varepsilon}\sqrt{\varepsilon}}\sin(\frac{\sqrt{\varepsilon}}{1+\alpha})\sinh[\frac{\alpha\sqrt{u-\varepsilon}}{1+\alpha}]$$

The left-hand side $\cos(\kappa)$ oscillates between -1 and 1. We make a plot of $H(\varepsilon)$ as a function of ε, where u is given as a parameter. The energy gap occurs in the energy range where $|H(\varepsilon)|>1$.

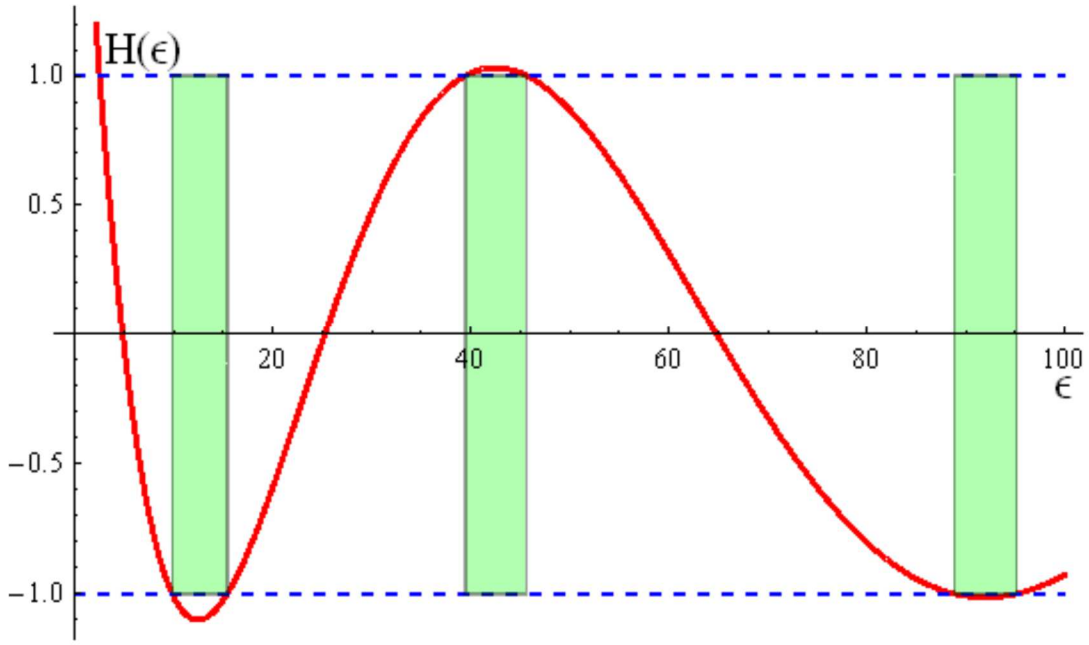

Fig. The right hand side of the Kronig-Penney expression, $H(\varepsilon)$ as a function of ε, where $u = 100$. $\alpha = b/a = 0.1/3$. The energy gap exists in the green zone where $|H(\varepsilon)|>1$. ε = (9.87507 - 15.4575). ε = (39.5002 - 45.6691), ε = (88.8754 - 95.1686), and ε = (158.0 - 164.288). The energy gap width ($\Delta\varepsilon$) is the same

5. Energy dispersion relation (numerical calculation)

The energy dispersion relation (ε vs k) can be determined the ContourPlot of the Mathematica, where u and α are given as parameters.

((**Parameters**))

$$u = 0.262468\ U_0 a_0^{\,2}$$

$$\alpha = \frac{b}{a} = \frac{b_0}{a_0}$$

(i) units of horizontal and vertical axes for the energy dispersion relation

$$k_0 = \frac{\kappa}{a_0 + b_0} \qquad \text{(given in the unit of Å}^{-1}\text{)}$$

$$E_0 = \frac{\varepsilon}{0.262468 a_0^{\,2}} \qquad \text{(given in the unit of eV)}$$

Note that k_0 and E_0 are dimension-less.

(ii) Brillouin zone boundary of the first Brillouin zone

$$\kappa_B = \pi\ .$$

(iii) Empty lattice approximation: Free electron model

$$(\kappa - 2n\kappa_B)^2$$

where n = 0, ±1, ±2, ...

((**Example**))

$\alpha = b/a$ = 0.1/3. u = 100.

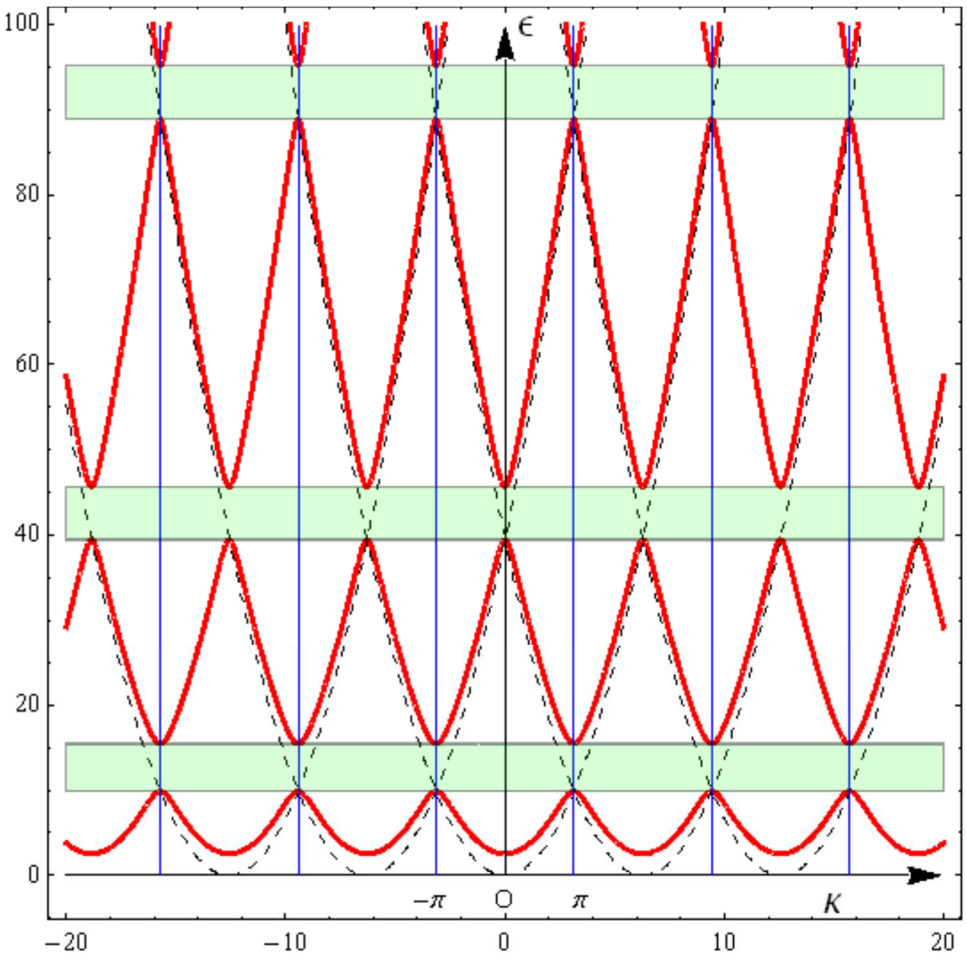

Fig. Kronig-Penney energy band in the extended zone scheme. $b/a = 0.1/3$. $u = 100$. When $a_0 = 5$ (Å), $E_0 = \varepsilon/6.5617$ (eV). It means that $E_0 = 15.24$ eV for $\varepsilon = 100$.

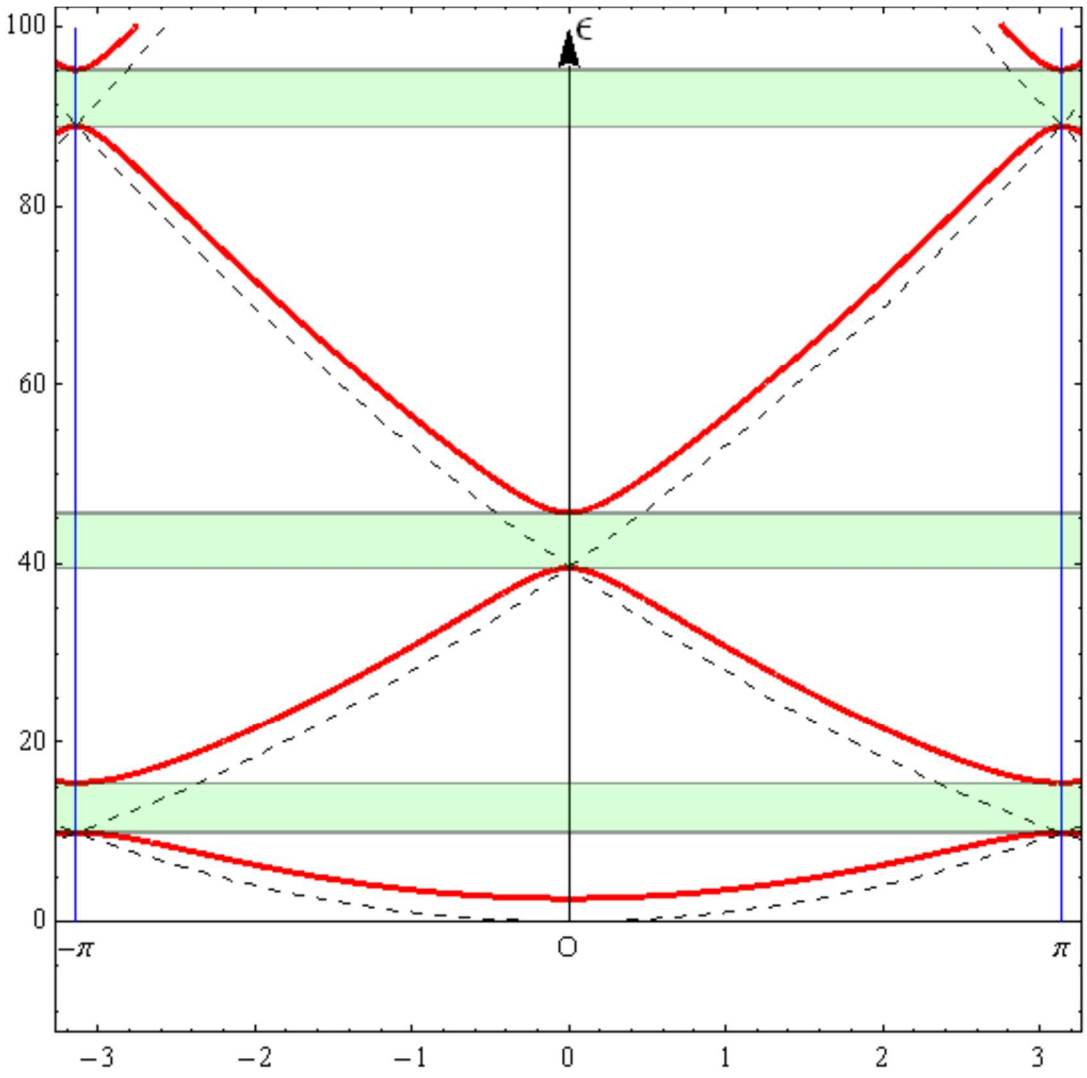

Fig. Kronig-Penney energy band in the reduced zone scheme. $b/a = 0.1/3$. $u = 100$.

5. Dirac delta function

The Result of Kronig-Penney can be simplified if we represent the potential by the periodic delta function.

We start with the equation given by

$$\cos[k(a+b)] = \cos(aK)\cosh(bQ) + \frac{(Q^2 - K^2)}{2KQ}\sin(aK)\sinh(bQ)$$

We assume the limit $b = 0$ and $U = \infty$ such a way that

$$Ub = 1\,.$$

In this limit,

$$Q >> K \qquad \text{and} \qquad Qb<<1.$$

We note that

$$\cosh(bQ) \approx 1$$

$$\frac{(Q^2 - K^2)}{2KQ}\sinh(bQ) \approx \frac{Q^2}{2KQ}bQ = \frac{Q^2}{2Ka}ab = \frac{P}{Ka}$$

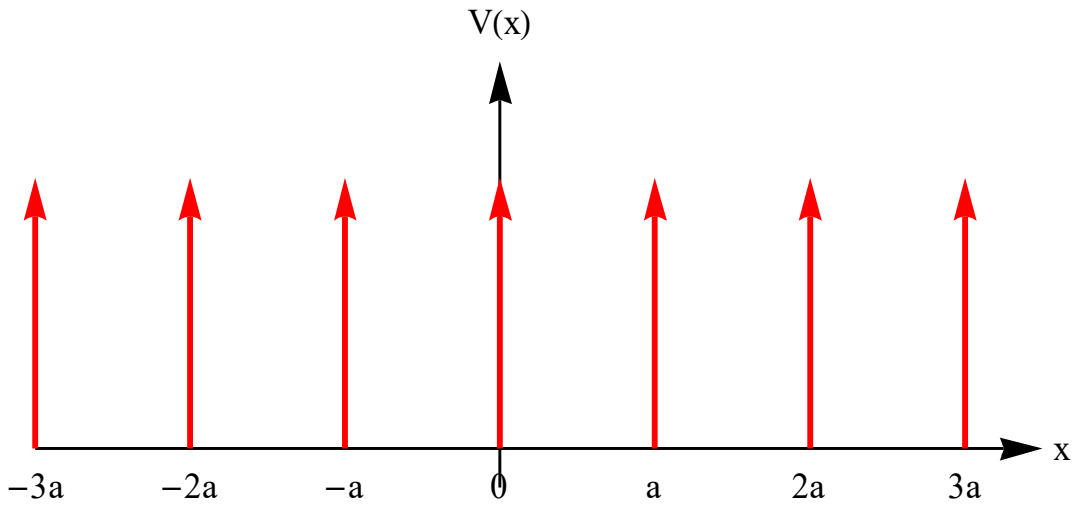

Fig. Dirac-comb type potential energy with the separation distance *a*.

Then we have

$$\cos(ka) = \cos(aK) + P\frac{\sin(aK)}{aK}$$

with

$$P = \frac{abQ^2}{2}$$

where *P* remains constant as a fixed parameter.

((**Note**)) Why is P constant?

Since $Ub = 1$,

$$b(K^2 + Q^2) = \frac{2mUb}{\hbar^2} = \frac{2m}{\hbar^2}$$

Since

$$K = \sqrt{\frac{2mE}{\hbar^2}}, \qquad Q = \sqrt{\frac{2m(U-E)}{\hbar^2}}$$

the ratio is given by

$$\frac{K}{Q} = \sqrt{\frac{E}{U-E}}$$

In the limit of $U \to \infty$, we have $Q \gg K$, leading to the relation

$$bQ^2 \approx \frac{2m}{\hbar^2} Ub = \frac{2m}{\hbar^2} = \text{constant}$$

leading to the parameter $P = \frac{abQ^2}{2} \approx \frac{ma}{\hbar^2}$, which is constant.

6. Numerical calculation

We use the same notion,

$$aK = \sqrt{\varepsilon}$$

$$ak = \kappa$$

Then we have

$$\cos(\kappa) = \cos(\sqrt{\varepsilon}) + P\frac{\sin(\sqrt{\varepsilon})}{\sqrt{\varepsilon}} = f(\varepsilon)$$

We make a plot of $f(\varepsilon)$ as a function of ε. P is a parameter. When $\sin(\sqrt{\varepsilon})=0$ ($\sqrt{\varepsilon}=\pi$, 2π, 3π), the value of $f(\varepsilon)$ is independent of P.

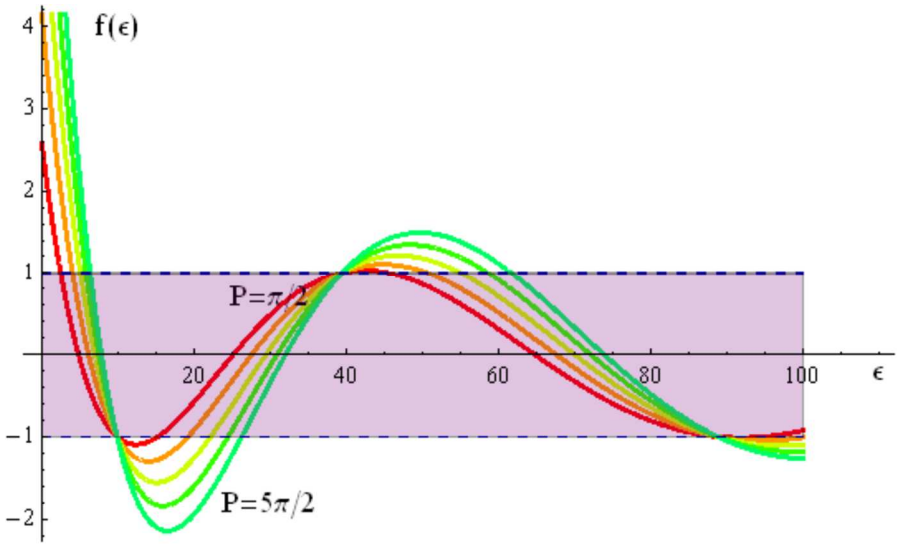

Fig. Plot of $f(\varepsilon)$ as a function of ε, where P is changed as a parameter. $P = \pi/2$ (red), π (orange), $3\pi/2$ (green), 2π (dark green), and $5\pi/2$ (blue). Allowed state in the region where $|f(\varepsilon)|<1$ (the purple zone). The forbidden states in the region where $|f(\varepsilon)|>1$. The energy gap increases with increasing P.

Using the ContourPlot of the Mathematica, we can draw the ε vs κ diagram for each P.

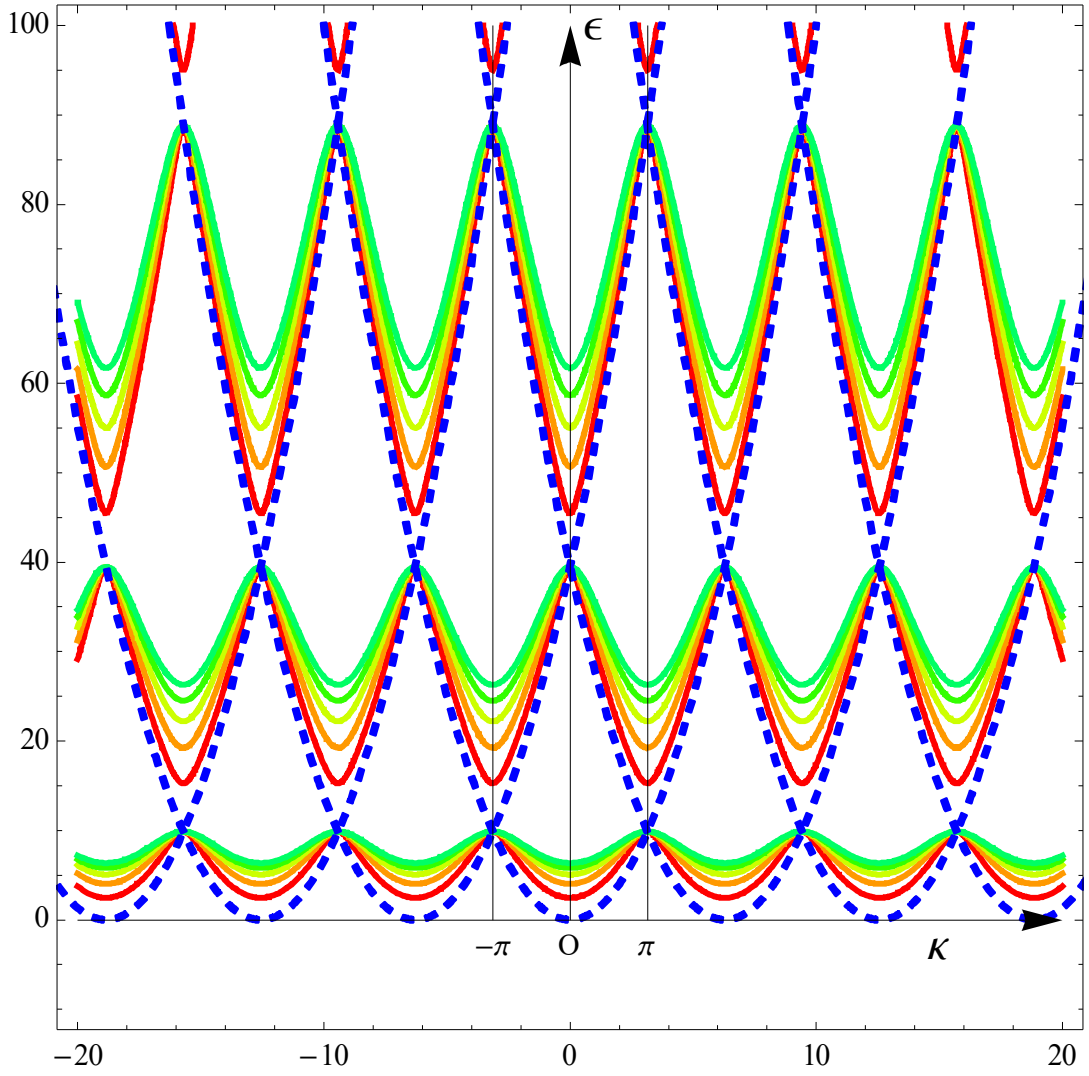

Fig. Energy band in the expended Brillouin zone. $P = \pi/2$ (red), π, $3\pi/2$, 2π, $5\pi/2$ (green). The dashed lines (blue) are described by $(\kappa - 2n\pi)^2$.

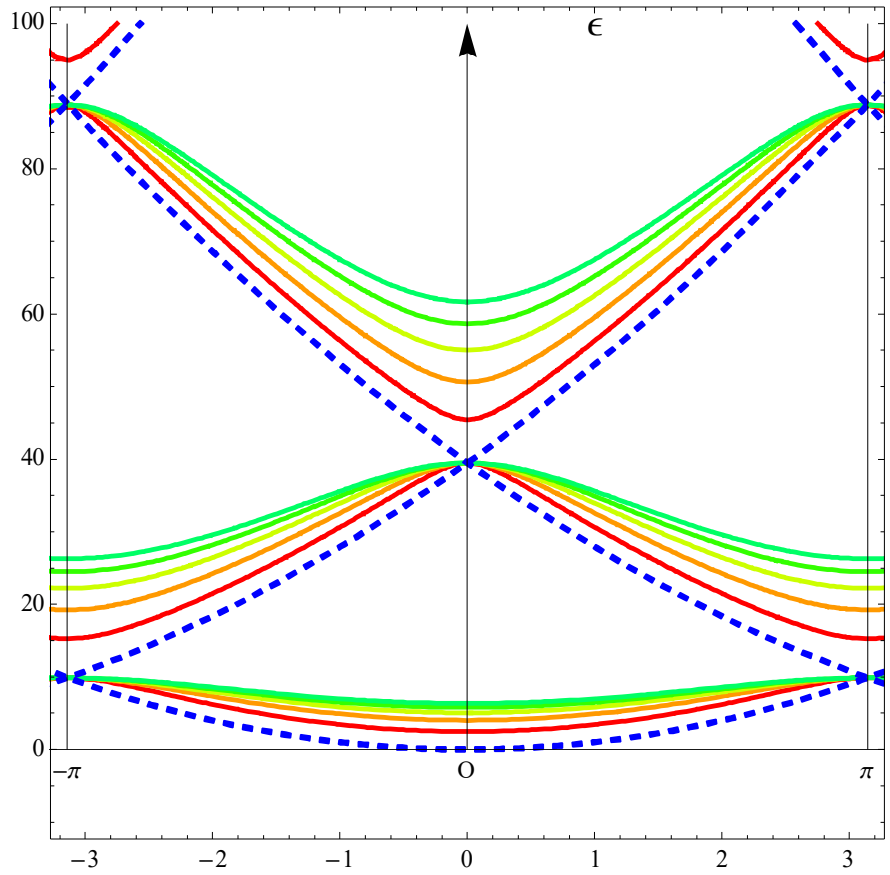

Fig. Energy band in the reduced Brillouin zone.

8. Summary

The following interesting conclusions may be derived from the above figures.

(a) The energy spectrum of the electrons consists of a number of allowed energy bands separated by energy gaps.

(b) The discontinuities in the energy spectrum, occur for the zone boundaries.

APPENDIX

Mathematica program for the Kronig-Penney model with Dirac-comb type potential

```
Clear["Global`*"]; eq1 = Cos[κ] == P Sin[Sqrt[ϵ]]/Sqrt[ϵ] + Cos[Sqrt[ϵ]];
p11 = ContourPlot[Evaluate[Table[eq1, {P, π/2, 5π/2, π/2}]],
  {κ, -20, 20}, {ϵ, 1, 100}, PlotPoints → 100,
  ContourStyle → Table[{Hue[0.1 i], Thick}, {i, 0, 5}]];
g1 = Plot[Evaluate[Table[(κ - 2 n π)^2, {n, -3, 3}]], {κ, -50, 50},
  PlotStyle → Table[{Blue, Dashed, Thick}, {n, 0, 5}],
  PlotRange → {{-30, 30}, {0, 100}}];
g2 = Graphics[{Black, Thin, Arrow[{{0, 0}, {0, 100}}],
   Arrow[{{-20, 0}, {20, 0}}], Text[Style["κ", Black, 15], {15, -3}],
   Text[Style["ϵ", Black, 15], {1, 100}],
   Text[Style["O", Black, 10], {0, -3}],
   Text[Style["π", Black, 10], {π, -3}],
   Text[Style["-π", Black, 10], {-π, -3}], Line[{{-π, 0}, {-π, 100}}],
   Line[{{π, 0}, {π, 100}}]}];
Show[p11, g1, g2, PlotRange → {{-π, π}, {-10, 100}}]
```

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