Quantum Mechanics II

Crystals

Consequences of Periodicity; The Kronig-Penney Model; *E*-Bands and Gaps & the Effective Mass

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Q M II

Crystals

Consequences of Periodicity

- Recall the momentum representation…

$$\widehat{P}_\alpha\,|\vec{p}\rangle = \widehat{P}_\alpha\,|\hbar\vec{k}\rangle = \hbar\,k_\alpha\,\,|\hbar\vec{k}\rangle \qquad \vec{p} \equiv \hbar\vec{k}$$

- Transforming between the coordinate and momentum representation

$$\psi_{\vec{k}}(\vec{r}) = \langle\vec{r}|\hbar\vec{k}\rangle \qquad \frac{\hbar}{i}\frac{\partial}{\partial x^\alpha}\langle\vec{r}|\hbar\vec{k}\rangle = \widehat{P}_\alpha\langle\vec{r}|\hbar\vec{k}\rangle = \hbar k_\alpha\langle\vec{r}|\hbar\vec{k}\rangle \qquad \psi_{\vec{k}}(\vec{r}) = C_{\vec{k}}\,e^{i\vec{k}\cdot\vec{r}}$$

- Normalization

$$\langle\vec{p}|\vec{p}\,'\rangle = \langle\hbar\vec{k}|\hbar\vec{k}'\rangle = \delta^{(3)}(\vec{p}-\vec{p}\,') = \tfrac{1}{\hbar}\delta^{(3)}(\vec{k}-\vec{k}') \qquad C_{\vec{k}} = \frac{1}{(2\pi\hbar)^{3/2}}$$

- …but periodicity in real space

$$\psi_{\vec{k}}(\vec{r}+L\,\hat{\mathrm{e}}_\alpha) = \psi_{\vec{k}}(\vec{r}): \qquad k_\alpha = n_\alpha\frac{2\pi}{L}$$

- …implies discrete linear momenta and

$$\delta(k_\alpha - k'_\alpha) \to \delta_{k_\alpha,k'_a} \qquad \int \mathrm{d}k_\alpha \to \sum_{k_\alpha}$$

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Consequences of Periodicity

- Gaston Floquet (1883)
- Every 1st order ordinary differential system with a periodic system matrix

$$\frac{\mathrm{d}}{\mathrm{d}t}|x(t)\rangle = \mathbb{A}(t)\,|x(t)\rangle \qquad \mathbb{A}(t+T) = \mathbb{A}(t)$$

- has solutions of the form

$$|x(t)\rangle = e^{t\mathbb{B}}\,|\xi(t)\rangle \qquad |\xi(t+T)\rangle = |\xi(t)\rangle$$

- We need this result, but for spatially periodic potentials

$$\widehat{V}(x+a) = \widehat{V}(x) \qquad \frac{\partial}{\partial(x+a)} = \frac{\partial}{\partial x} \qquad \widehat{H}(x+a) = \widehat{H}(x)$$

symmetry

- Then

$$u_1(x),\ u_2(x) \qquad u_1(x+a),\ u_2(x+a) \qquad u_1(x+2a),\ u_2(x+2a) \qquad \cdots$$

- are all solutions
- …which cannot be independent

$$\begin{bmatrix} u_1(x+a) \\ u_2(x+a) \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix} \begin{bmatrix} u_1(x) \\ u_2(x) \end{bmatrix}$$

- Thus: $\boxed{\exists\ \psi_i(x+a) = \lambda_i \psi_i(x) \quad i = 1,2 \qquad \psi(x) := A u_1(x) + B u_2(x)}$

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Consequences of Periodicity

$$\begin{bmatrix} u_1(x+a) \\ u_2(x+a) \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix} \begin{bmatrix} u_1(x) \\ u_2(x) \end{bmatrix}$$

- Felix Bloch (1928) (45 years after Floquet)

$$\begin{aligned} \psi(x+a) &:= Au_1(x+a) + Bu_2(x+a) \\ &= (AC_{11} + BC_{21})u_1(x) + (AC_{12} + BC_{22})u_2(x) \\ &\overset{!}{=} \lambda\psi(x) = \lambda\big(Au_1(x) + Bu_2(x)\big) \qquad \textbf{(by Floquet)} \end{aligned}$$

- This implies

$$\begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = \lambda \begin{bmatrix} A \\ B \end{bmatrix} \quad \lambda_\pm = \frac{C_{11}+C_{22} \pm \sqrt{(C_{11}-C_{22})^2 + 4C_{12}C_{21}}}{2}$$

- This defines the two periodic solutions
- On the other hand

$$-\frac{\hbar^2}{2M}\psi''(x) + V(x)\psi(x) = E\psi(x) \quad \Rightarrow \quad \psi''(x) = \frac{2M}{\hbar^2}[V(x)-E]\psi(x)$$

- is a 2nd order, ordinary linear differential equation
- …that has two linearly independent solutions

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Consequences of Periodicity

$$\psi''(x) = \frac{2M}{\hbar^2}[V(x) - E]\psi(x)$$

- Consider then the Wronskian

$$W(x) = \psi_1'(x)\psi_2(x) - \psi_1(x)\psi_2'(x)$$

- …and its derivative

$$W'(x) = (\psi_1''\psi_2 + \cancel{\psi_1'\psi_2'}) - (\psi_1\psi_2'' + \cancel{\psi_1'\psi_2'})$$
$$= \cancel{\left(\tfrac{2M}{\hbar^2}[V(x) - E]\psi_1\right)\psi_2} - \cancel{\psi_1\left(\tfrac{2M}{\hbar^2}[V(x) - E]\psi_2\right)} = 0$$

- The Wronskian is thus a constant
- On the other hand,

$$W(x+a) = \psi_1'(x+a)\psi_2(x+a) - \psi_1(x+a)\psi_2'(x+a)$$
$$= (\lambda_1\psi_1'(x))(\lambda_2\psi_2(x)) - (\lambda_1\psi_1(x))(\lambda_2\psi_2'(x))$$
$$= \lambda_1\lambda_2 W(x) \quad \Rightarrow \quad \lambda_1\lambda_2 = 1$$

$$|\lambda_i| > 1 \quad |\psi_i(x+na)| \xrightarrow{n\to\infty} \infty \qquad |\lambda_i| < 1 \quad |\psi_i(x+na)| \xrightarrow{n\to-\infty} \infty$$

- Thus $|\lambda_i| = 1 \quad \lambda_{1,2} = e^{\pm i\phi} = e^{\pm iKa} = e^{\pm i(Ka + 2n\pi)} \qquad -\frac{\pi}{a} \leqslant K \leqslant +\frac{\pi}{a}$

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Consequences of Periodicity

- Thus, solutions of the Schrödinger equation with a periodic potential

$$-\frac{\hbar^2}{2M}\psi''(x)+V(x)\psi(x)=E\psi(x) \qquad V(x+a)=V(x)$$

- are periodic up to a phase

$$\psi(x+na)=e^{iKa}\,\psi(x) \qquad \psi(x)=e^{iKx}u(x) \quad u(x+a)=u(x)$$

$$K=2\pi\frac{n}{Na} \quad n=0,\,1,\,2,\,\dots\,,(N-1)$$

  - …where N is the (very large!) number of lattice sites
  - …and we imposed the (Born-von Karman) periodicity $(n=0)\cong(n=N)$
  - …and K is practically a continuous variable
- For a 3D, rectangular lattice of sizes (a_x, a_y, a_z)

$$\boxed{\psi(\vec{r}+\vec{a})=e^{i\vec{K}\cdot\vec{a}}\,\psi(\vec{r}) \qquad \psi(\vec{r})=e^{i\vec{K}\cdot\vec{r}}\,u(\vec{r}) \quad \vec{K}=2\pi\Big(\frac{n_x}{N_xa_x},\frac{n_y}{N_ya_y},\frac{n_z}{N_za_z}\Big)}$$

reciprocal lattice

Bloch's theorem

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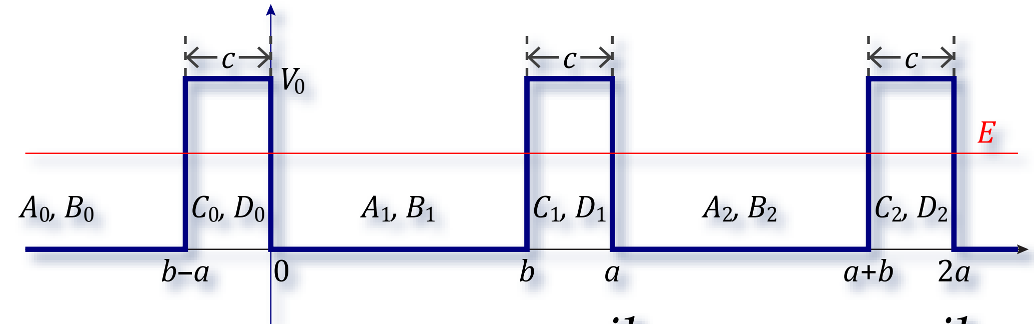
Kronig-Penney Model



$$\psi_1(x) = A_1 e^{ikx} + B_1 e^{-ikx}$$
$$= C_1 e^{-\kappa x} + D_1 e^{\kappa x}$$

- Apply the matching conditions

$$@x = b: \qquad A_1 e^{ikb} + B_1 e^{-ikb} = C_1 e^{-\kappa b} + D_1 e^{\kappa b}$$
$$ikA_1 e^{ikb} - ikB_1 e^{-ikb} = -\kappa C_1 e^{-\kappa b} + \kappa D_1 e^{\kappa b}$$
$$@x = a: \qquad C_1 e^{-\kappa a} + D_1 e^{\kappa a} = e^{iKa}(A_1 + B_1)$$
$$-\kappa C_1 e^{-\kappa b} + \kappa D_1 e^{\kappa b} = e^{iKa}(ikA_1 - ikB_1)$$

- Rearrange

$$\begin{bmatrix} e^{ikb} & e^{-ikb} & e^{-\kappa b} & e^{\kappa b} \\ ike^{ikb} & -ike^{-ikb} & -\kappa e^{-\kappa b} & \kappa e^{\kappa b} \\ e^{iKa} & e^{iKa} & e^{-\kappa a} & e^{\kappa a} \\ ike^{iKa} & -ike^{iKa} & -\kappa e^{-\kappa a} & \kappa e^{\kappa a} \end{bmatrix} \begin{bmatrix} A_1 \\ B_1 \\ C_1 \\ D_1 \end{bmatrix} = 0$$

The determinant of the system must vanish

$$0 \stackrel{!}{=} \begin{vmatrix} e^{ikb} & e^{-ikb} & e^{-\kappa b} & e^{\kappa b} \\ ike^{ikb} & -ike^{-ikb} & -\kappa e^{-\kappa b} & \kappa e^{\kappa b} \\ e^{iKa} & e^{iKa} & e^{-\kappa a} & e^{\kappa a} \\ ike^{iKa} & -ike^{iKa} & -\kappa e^{-\kappa a} & \kappa e^{\kappa a} \end{vmatrix} = \begin{vmatrix} e^{ikb} & e^{-ikb} & 1 & 1 \\ ike^{ikb} & -ike^{-ikb} & -\kappa & \kappa \\ e^{iKa} & e^{iKa} & e^{-\kappa c} & e^{\kappa c} \\ ike^{iKa} & -ike^{iKa} & -\kappa e^{-\kappa c} & \kappa e^{\kappa c} \end{vmatrix}$$

$e^{\kappa b}$ $\quad$ $e^{-\kappa b}$

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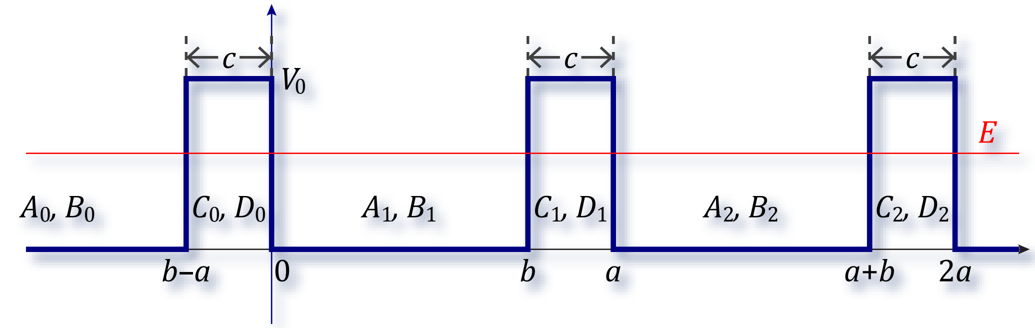
Kronig-Penney Model



- Expand the determinant and set to zero

$$\cos(Ka) = \cos(kb)\cosh(\kappa c) - \frac{k^2-\kappa^2}{2k\kappa}\sin(kb)\sinh(\kappa c) \qquad 0 \leqslant E \leqslant V_0$$

$$\cos(Ka) = \cos(kb)\cos(k'c) - \frac{k^2-k'^2}{2kk'}\sin(kb)\sin(k'c) \qquad V_0 \leqslant E$$

- This excludes some values of energy

$$kb \approx n\pi \qquad \sin(kb) \approx 0 \quad \cos(kb) \approx (-1)^n$$

$$\cos(Ka) \cancel{\approx} (-1)^n \cosh(\kappa c) \qquad |\cosh(z)| \geqslant 1 \ \ \& \ \ |\cos(\varphi)| \leqslant 1$$

$$n\pi \not\approx kb = \frac{\sqrt{2ME}}{\hbar}\, b \qquad E \not\approx \frac{n^2\pi^2\hbar^2}{2Mb^2}$$

(standing waves trapped in the "valleys")

- In particular $E \to 0$

$$\kappa \to 0 \quad \kappa \to \kappa_0 := \frac{\sqrt{2MV_0}}{\hbar}$$

$$\cos(kb) \to 1 \quad \frac{1}{k}\sin kb \to b$$

$$\text{r.h.s.} \to \cosh(\kappa_0 c) + \frac{\kappa_0 b}{2}\sinh(\kappa_0 c) > 1$$

(the minimal energy must be strictly positive)

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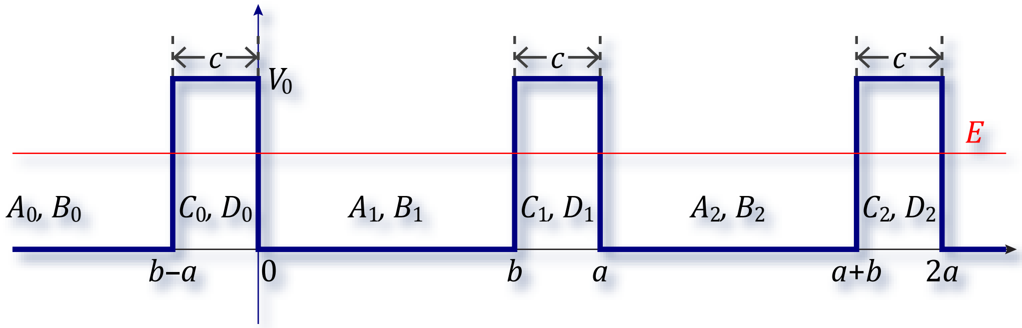
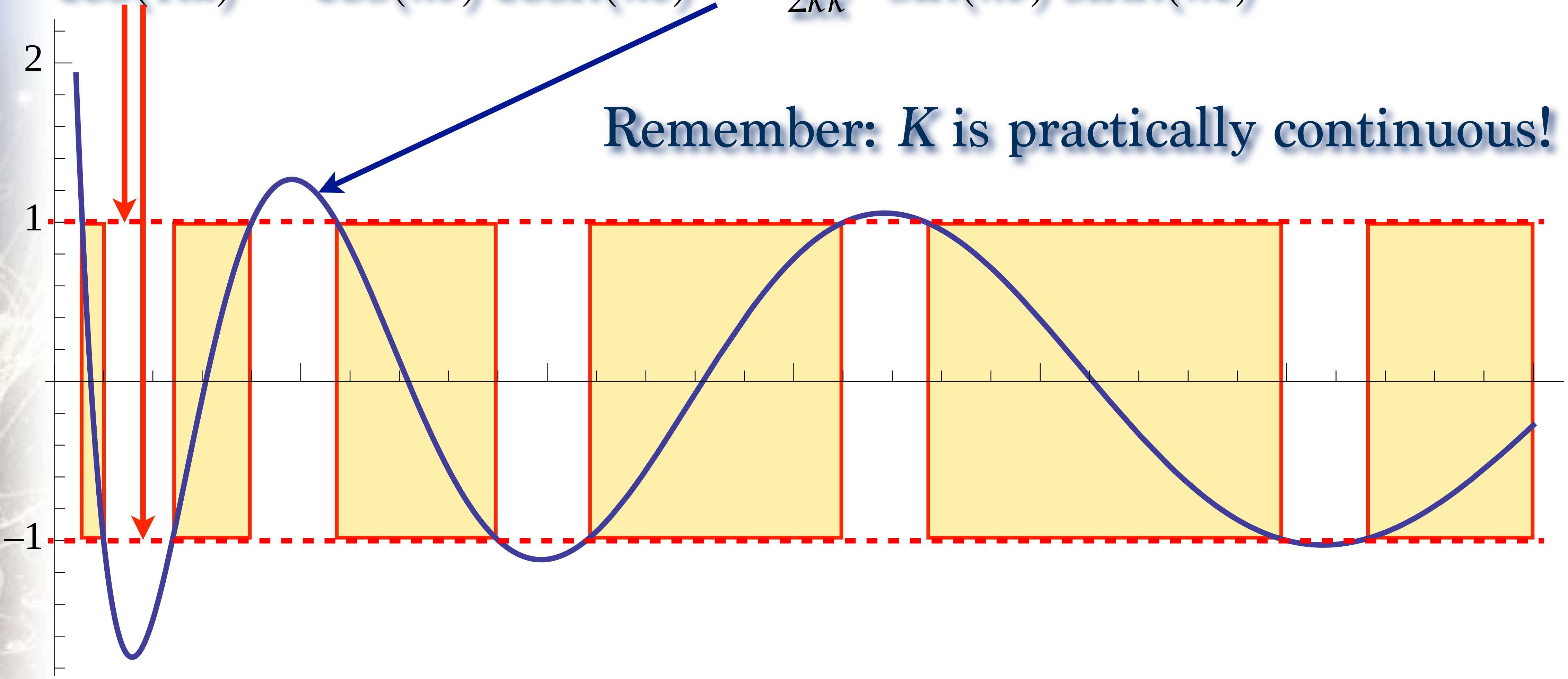
Kronig-Penney Model



- The allowed energies thus form bands

$$\cos(Ka) = \cos(kb)\cosh(\kappa c) - \frac{k^2-\kappa^2}{2k\kappa}\sin(kb)\sinh(\kappa c)$$



- …as do the “forbidden” gaps between them
- In every band, there are $N(\ggg 1)$ states, virtually a continuum

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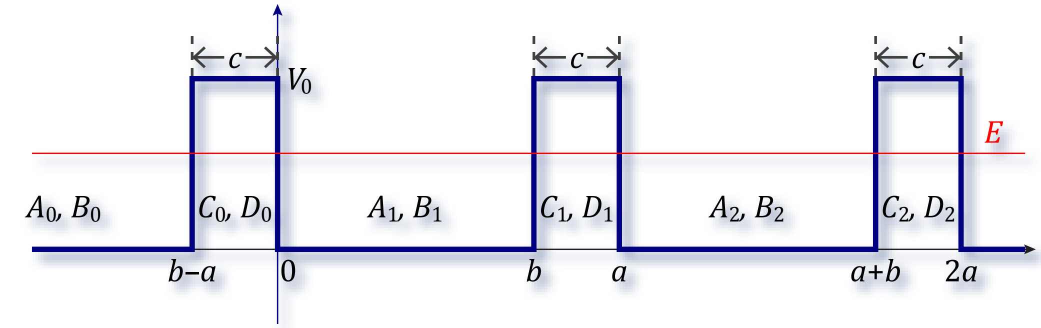
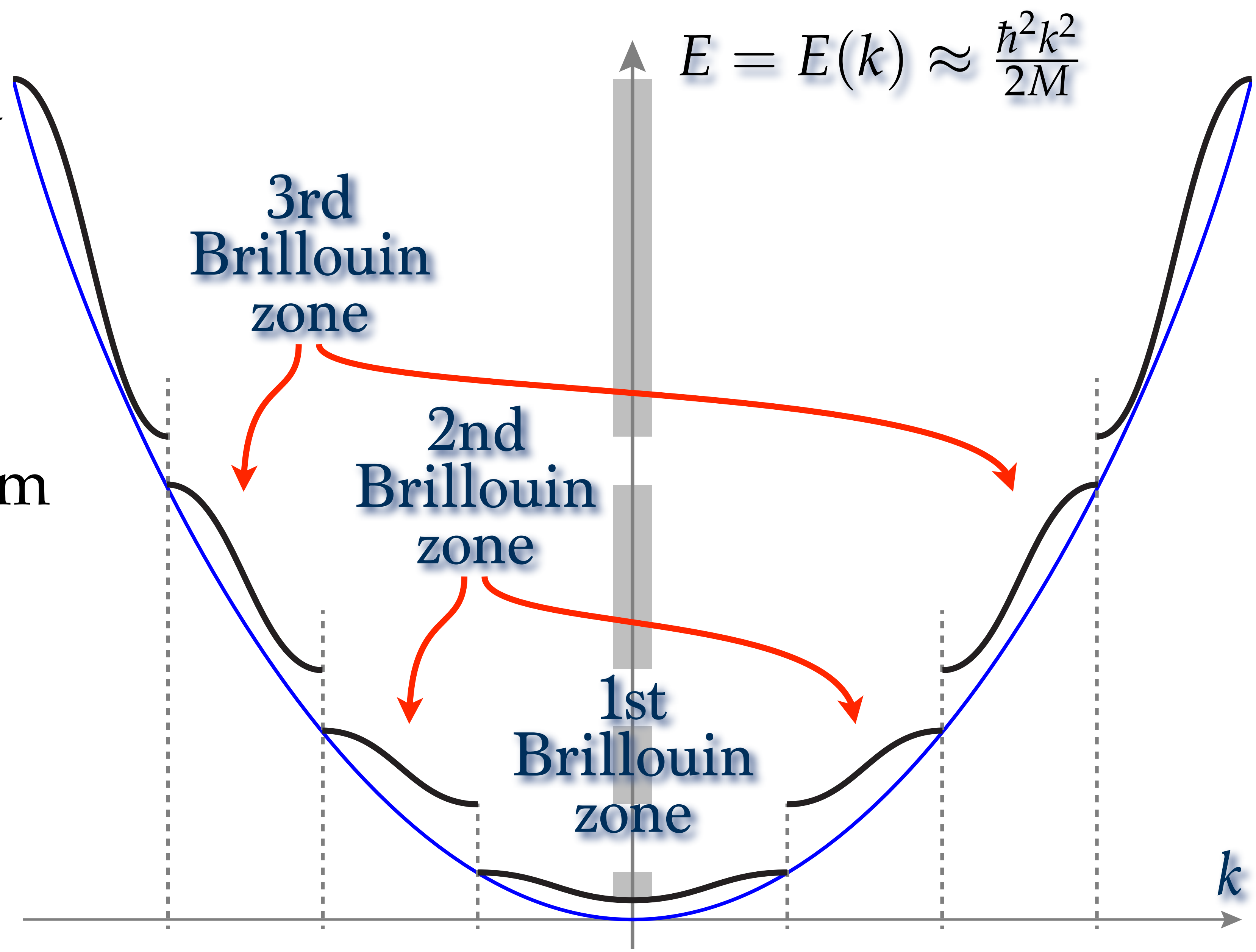
Kronig-Penney Model



- Energy varies within the bands, skipping the gaps
- Linear momentum varies continuously
- Regions where both E and k are continuous are (Léon) Brillouin zones (in momentum space!)
- $E(k)$ has both
  - discontinuities
  - inflections



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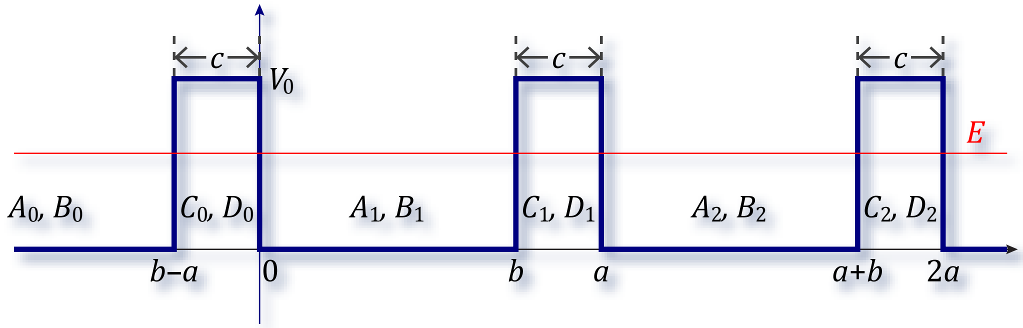

Kronig-Penney Model

- In a simple superposition

$$\psi(x) = u_k(x)\, e^{i[kx-\omega t]} + u_{k+\triangle k}(x)\, e^{i[(k+\triangle k)x-(\omega+\triangle\omega)t]}$$

$$\approx 2u_k(x)e^{i[(k+\frac{\triangle k}{2})x-(\omega+\frac{\triangle\omega}{2})t]}\cos\left(\frac{\triangle k}{2}x-\frac{\triangle\omega}{2}t\right) \qquad u_{k+\triangle k}(x)\approx u_k(x)$$

$$\left|\psi(x)\right|^2 \approx 4\left|u_k(x)\right|^2\cos^2\left(\frac{\triangle k}{2}x-\frac{\triangle\omega}{2}t\right)$$

- The "amplitude modulation" train-wave travels with

$$v_g := \frac{\partial\omega}{\partial k} = \frac{1}{\hbar}\frac{\partial\hbar\omega}{\partial k} = \frac{1}{\hbar}\frac{\partial E}{\partial k} \qquad \frac{\partial E}{\partial k} = \hbar v_g$$

- Require

$$\frac{\mathrm{d}E}{\mathrm{d}t} \overset{!}{=} e\mathscr{E}v_g = \frac{\partial E}{\partial k}\frac{\mathrm{d}k}{\mathrm{d}t} = (\hbar v_g)\frac{\mathrm{d}k}{\mathrm{d}t} \qquad \left(\hbar\frac{\mathrm{d}k}{\mathrm{d}t} = \frac{\mathrm{d}p}{\mathrm{d}t}\right) = e\mathscr{E} = F_{\mathrm{el.}}$$

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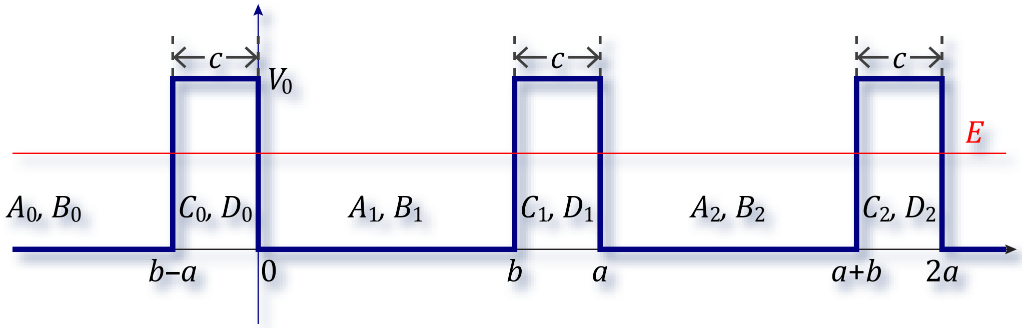

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- Then

$$\frac{\mathrm{d}v_g}{\mathrm{d}t} = \frac{\partial v_g}{\partial k}\frac{\mathrm{d}k}{\mathrm{d}t} = \left(\frac{\partial}{\partial k}\frac{1}{\hbar}\frac{\partial E}{\partial k}\right)\left(\frac{1}{\hbar}e\mathscr{E}\right)$$

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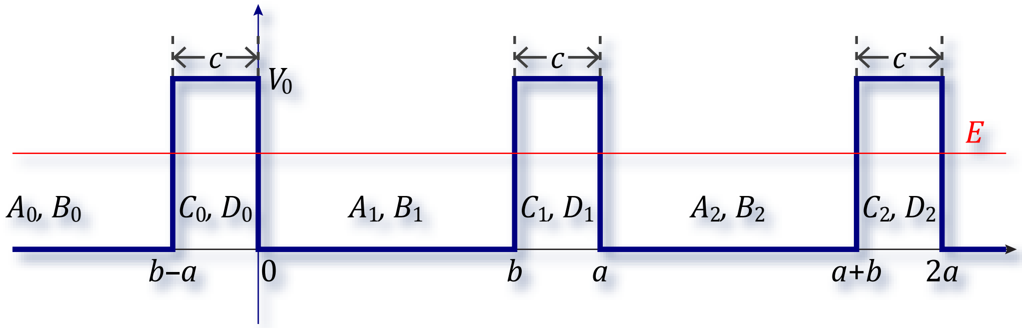
Kronig-Penney Model



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- Then

$$\frac{\mathrm{d}v_g}{\mathrm{d}t} = \frac{\partial v_g}{\partial k}\frac{\mathrm{d}k}{\mathrm{d}t} = \left(\frac{\partial}{\partial k}\frac{1}{\hbar}\frac{\partial E}{\partial k}\right)\left(\frac{1}{\hbar}e\mathscr{E}\right) = \left[\frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}\right] e\mathscr{E}$$

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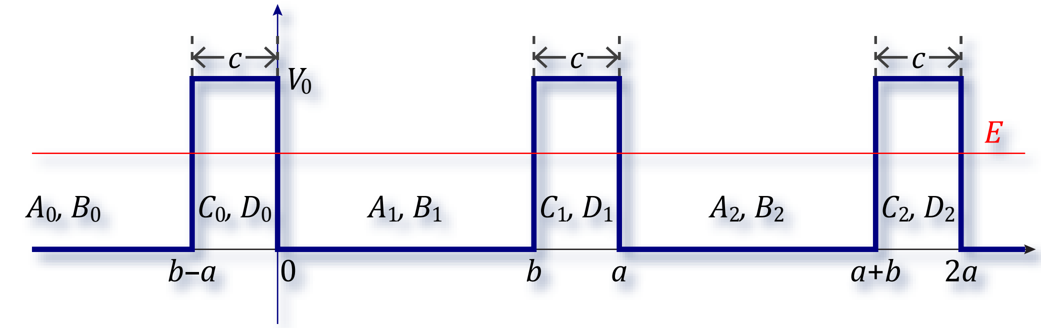
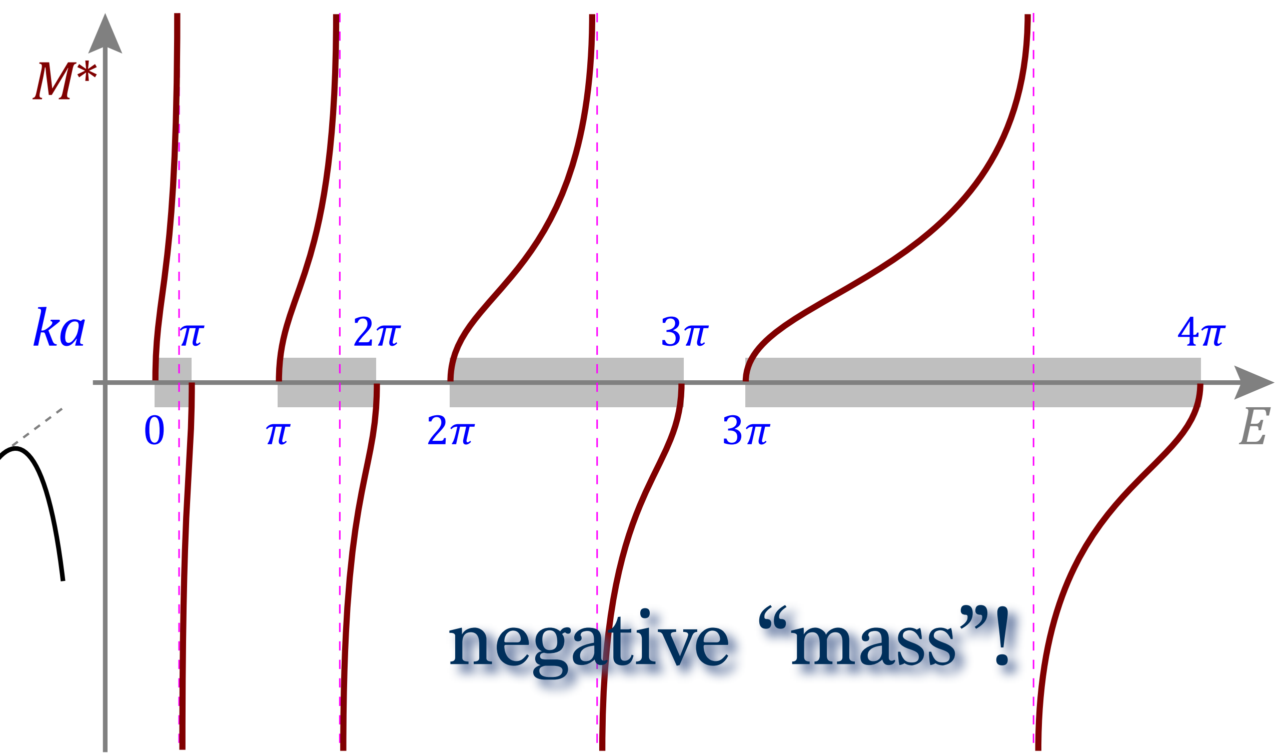
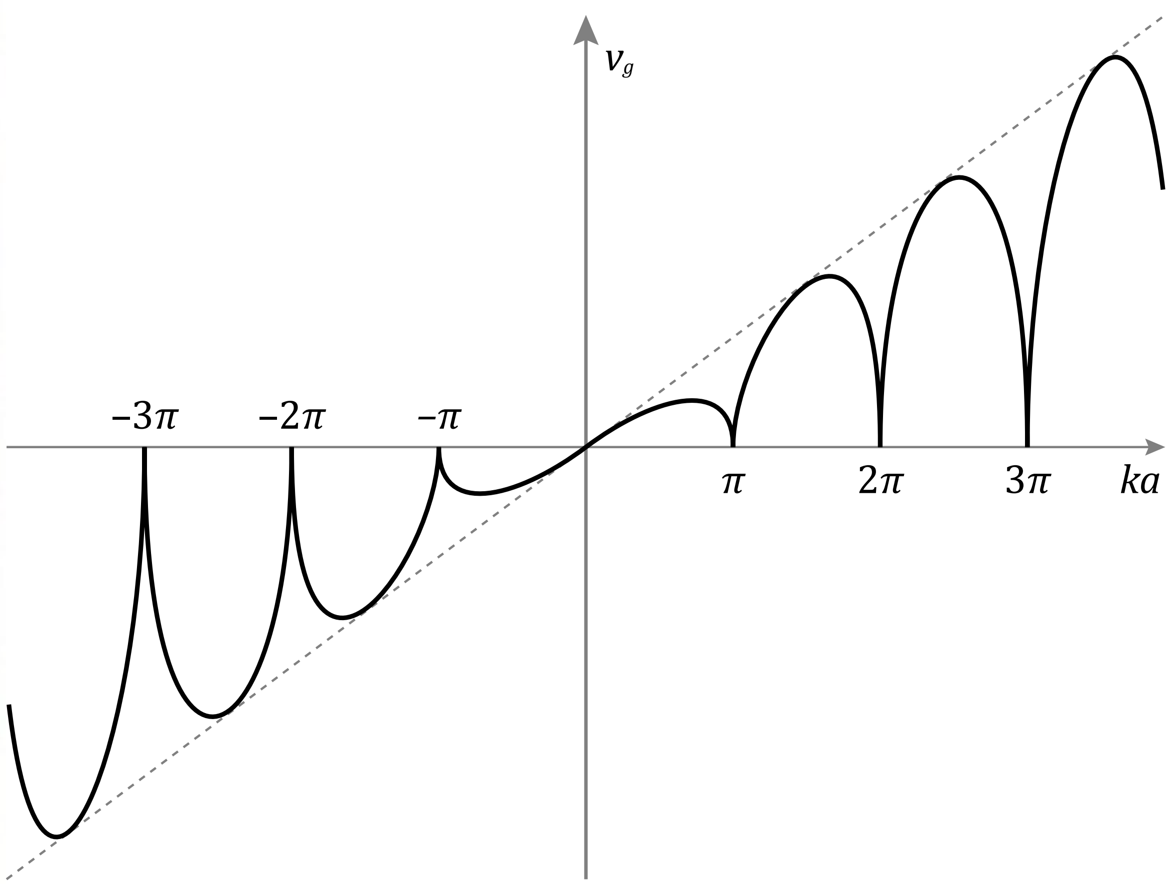
Kronig-Penney Model



- In response to external (electrostatic force), the electrons in the Kronig-Penney model accelerate

$$e\mathscr{E} = \underbrace{\hbar^2\left(\frac{\partial^2 E}{\partial k^2}\right)^{-1}}_{M^*}\frac{\mathrm{d}v_g}{\mathrm{d}t}$$





- The group velocity vanishes at the edges of the Brillouin zones ($E(k)$ discontinuities)

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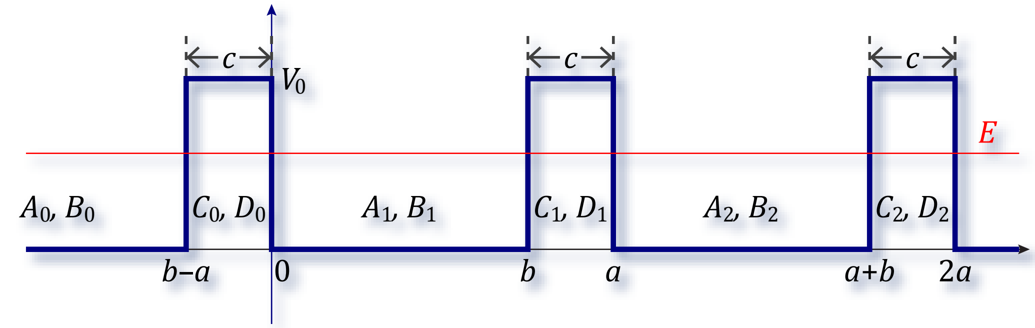
Kronig-Penney Model



- Expanding $E(k)$ near an edge of a band/gap

$$E(k) \approx E_e + \left(\frac{\partial E}{\partial k}\right)_{k_e}(k-k_e) + \frac{1}{2}\left(\frac{\partial^2 E}{\partial k^2}\right)_{k_e}(k-k_e)^2 + \dots$$

$$\approx E_e + \hbar\left(\cancel{v_g}\big|_e\right)(k-k_e) + \frac{\hbar^2}{2\,M^*(k_e)}(k-k_e)^2 + \dots$$

$$\approx E_e + \frac{M^*(k_e)}{2}\left(v_g(k_e)\right)^2 + \dots$$

- …so

$$\left(M^* v_g\right)\big|_{k_e} \approx \hbar(k-k_e)$$

and M^* is ***<u>negative</u>*** when $k < k_e$ at the top of a band, just below a gap

- Collective behavior is radically different from that of a simple free particle
- The qualitative results: E-bands, gaps, discontinuous $E(k)$, Brillouin zones, nonlinear M^* & v_g are general features

Quantum Mechanics II

Now, go forth and calculate!!

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Quantum Mechanics II

Now, go forth and calculate!!

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