Problem of conductivity: Drude model

$$m\dot{\vec{v}} = -e\vec{E} - m\frac{\vec{v}}{\tau}, \quad \text{(L1)}$$

τ is the relaxation time.

$$\vec{v}(t) = \vec{v}_0 e^{-t/\tau}. \quad \text{(L2)}$$

Steady state, times much longer than τ:

$$\vec{v} = ? \qquad ? \quad \text{(L3)}$$

Current therefore is

$$\vec{j} = ? \qquad ? \quad \text{(L4)}$$

$$\Rightarrow \sigma = ? \qquad ?, \quad \text{(L5)}$$

σ is the electrical conductivity

Problem of conductivity: Drude model

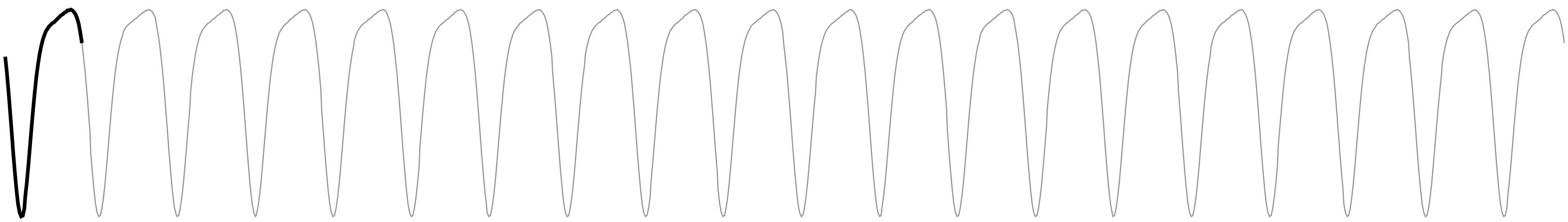
$$\tau = ? \qquad ? = \frac{3.55 \cdot 10^{-13}\,\mathrm{s}}{n/[10^{22}\,\mathrm{cm}^{-3}]\ \rho/[\mu\Omega\,\mathrm{cm}]} \tag{L6}$$

Exercise:

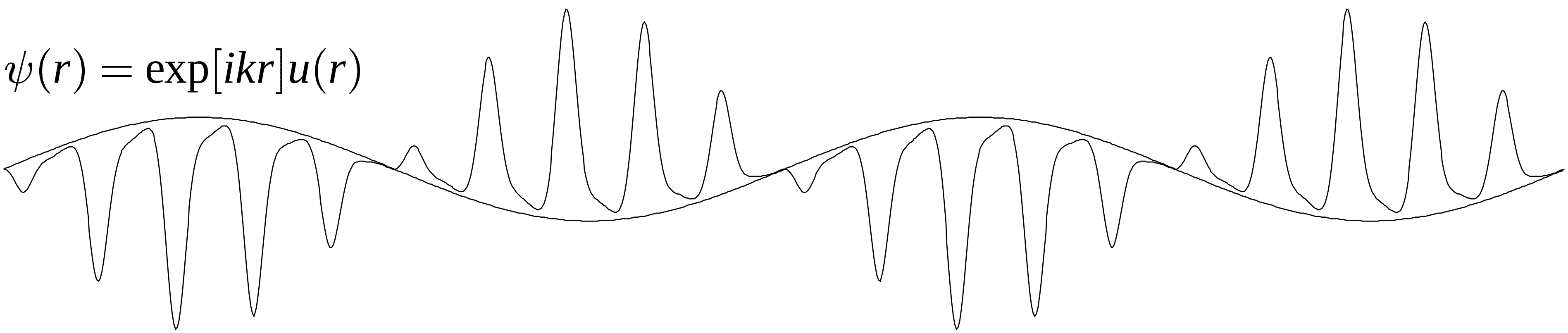
1. Estimate typical value of τ.
2. How does this compare with rate at which classical thermal electrons scatter off nuclei?
3. How does this compare with rate at which electrons at Fermi velocity scatter off nuclei?
4. What happens if one starts over and takes the relaxation time proportional to the electron velocity?

Bloch's solution

Periodic function $u(r)$



$\psi(r) = \exp[ikr]u(r)$



Single particle in periodic potential U:

$$U(\vec{r}+\vec{R}) = U(\vec{r}). \tag{L7}$$

Solve

Bloch's solution

$$\hat{\mathcal{H}} = \frac{\hat{P}^2}{2m} + U(\hat{R}). \tag{L8}$$

WRONG:

$$\psi(\vec{r} + \vec{R}) = \psi(\vec{r}). \tag{L9}$$

Can see this is wrong from case $U = 0$

$$\psi_{\vec{k}}(\vec{r}) \propto e^{i\vec{k}\cdot\vec{r}}. \tag{L10}$$

Translation operators

Let $\hat{T}_{\vec{R}}$ translate wave function by $\vec{R}$

$$\hat{T}_{\vec{R}} = e^{-i\hat{P}\cdot\vec{R}/\hbar}, \tag{L11}$$

Theorem: if one has a collection of Hermitian operators that commute with one another, they can be diagonalized simultaneously

Suppose $\mathcal{O}_2$ has unique eigenvector $|a\rangle$ with eigenvalue a.

$$\mathcal{O}_1\mathcal{O}_2|a\rangle = a\mathcal{O}_1|a\rangle = \mathcal{O}_2\mathcal{O}_1|a\rangle \tag{L12}$$

so $\mathcal{O}_1|a\rangle$ is eigenvector of $\mathcal{O}_2$; by uniqueness, must be some constant times $|a\rangle$.

In case of degenerate eigenvalues, one operator may categorize further states of other; parity.

Use theorem:

$$\hat{T}^{\dagger}_{\vec{R}}|\psi\rangle = e^{i\hat{P}\cdot\vec{R}/\hbar}|\psi\rangle = C_{\vec{R}}|\psi\rangle. \tag{L13}$$

$$\psi(\vec{r}+\vec{R}) = C_{\vec{R}}\psi(\vec{r}). \tag{L14}$$

Translation operators

$$e^{i\vec{k}\cdot\vec{R}}\langle\vec{k}|\psi\rangle = C_{\vec{R}}\langle\vec{k}|\psi\rangle \tag{L15}$$

$$\Rightarrow \text{ either } C_{\vec{R}} = e^{i\vec{k}\cdot\vec{R}} \text{ or } \langle\vec{k}|\psi\rangle = 0. \tag{L16}$$

☞ $\vec{k}$: Bloch wave vector

☞ $\hbar\vec{k}$: Crystal momentum

Bloch's Theorem

$$\hat{\mathcal{H}}|\psi_{n\vec{k}}\rangle = \mathcal{E}_{n\vec{k}}|\psi_{n\vec{k}}\rangle \quad \text{(L17a)}$$

$$\hat{T}^{\dagger}_{\vec{R}}|\psi_{n\vec{k}}\rangle = e^{i\vec{k}\cdot\vec{R}}|\psi_{n\vec{k}}\rangle. \quad \text{(L17b)}$$

Restate as

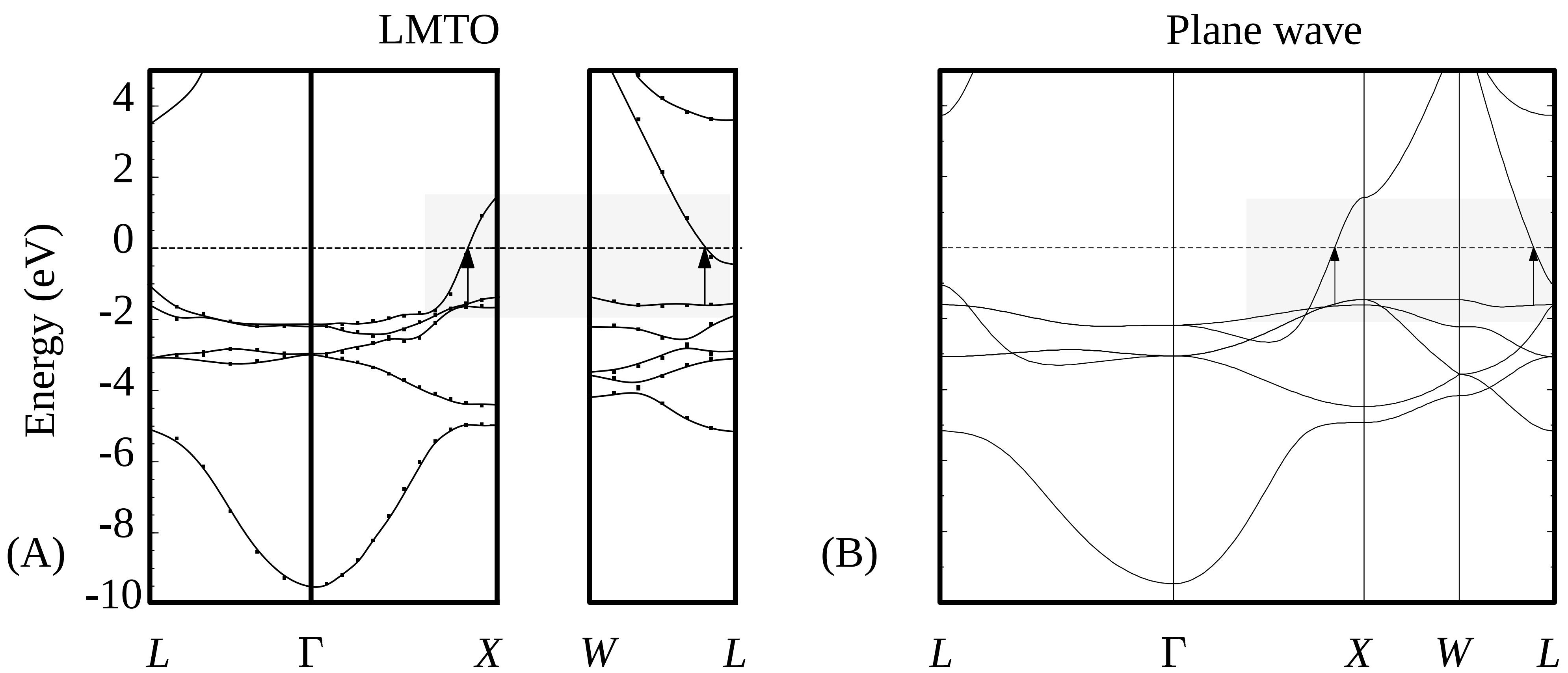
$$\psi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi_{n\vec{k}}(\vec{r}). \quad \text{(L18)}$$

or

$$u_{n\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}}\psi_{n\vec{k}}(\vec{r}). \quad \text{(L19)}$$

$$u(\vec{r}+\vec{R}) = ? \qquad ? \text{ and } \psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r}). \quad \text{(L20)}$$

Energy Bands



$$\hat{\mathcal{H}}_{\vec{k}} u(\vec{r}) = \frac{\hbar^2}{2m}[-\nabla^2 - 2i\vec{k}\cdot\vec{\nabla} + k^2]u(\vec{r}) + U(\vec{r})u(\vec{r}) = \mathcal{E}u(\vec{r}). \quad \text{(L21)}$$

Allowed values of $\vec{k}$

If crystal is periodic with (macroscopic) dimensions $M_1\vec{a}_1, M_2\vec{a}_2, M_3\vec{a}_3$

then requiring $\exp[i\vec{k}\cdot\vec{r}]$ to be periodic constrains $\vec{k}$ to

$$\vec{k} = \sum_{l=1}^{3} \frac{m_l}{M_l}\vec{b}_l,\ 0 \leq m_l < M_l, \tag{L22}$$

$\vec{b}_1 \ldots \vec{b}_3$

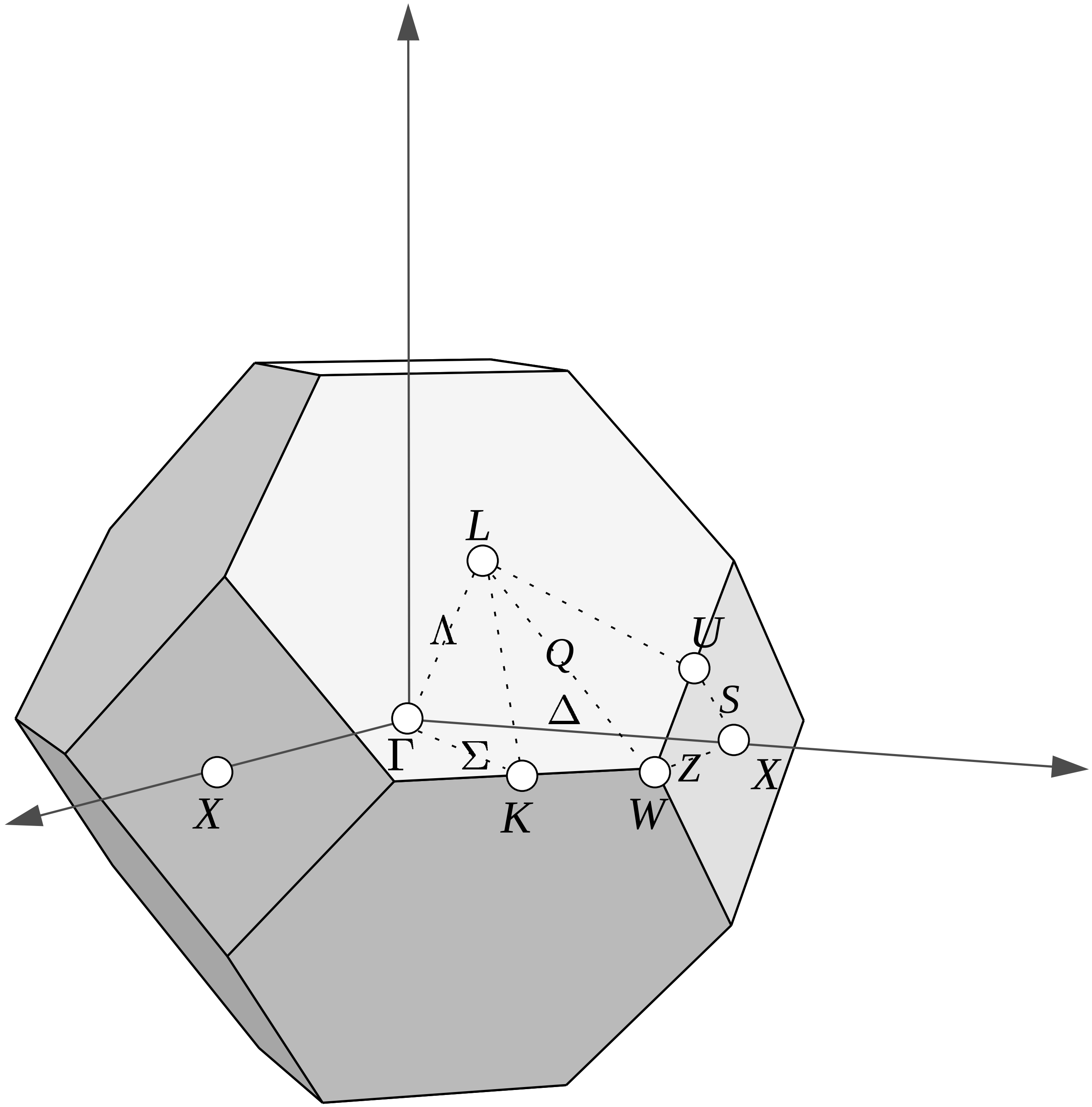
$$\vec{b}_l \cdot \vec{a}_{l'} = 2\pi\delta_{ll'}. \tag{L23}$$

Periodic boundary conditions place a condition on how small k can be.

Demanding that $C_{\vec{R}} = \exp[i\vec{k}\cdot\vec{R}]$ be unique places conditions on how big k can be.

Number of points in crystal equals number of unique Bloch wave vectors.

Brillouin Zone



$$\frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{M_1 M_2 M_3} \tag{L24}$$

$$= \frac{2\pi}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)} \frac{\vec{b}_1 \cdot (\vec{b}_2 \times (\vec{a}_1 \times \vec{a}_2))}{M_1 M_2 M_3} \tag{L25}$$

$$= \frac{(2\pi)^3}{M_1 M_2 M_3 \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \tag{L26}$$

$$= \frac{(2\pi)^3}{\mathcal{V}} \tag{L27}$$

$$\sum_{\vec{k}\sigma} F_{\vec{k}} = \mathcal{V} \int [d\vec{k}]\, F_{\vec{k}}, \tag{L28}$$

Define $D_{\vec{k}}$ as before:

$$D_n(\mathcal{E}) = \int [d\vec{k}]\, \delta(\mathcal{E} - \mathcal{E}_{n\vec{k}}). \tag{L29}$$

Dynamical importance of energy bands

$$\vec{v}_{n\vec{k}} = \frac{1}{\hbar}\vec{\nabla}_{\vec{k}}\mathcal{E}_{n\vec{k}}. \tag{L30}$$

$v = \partial\omega/\partial k$

Wave packet:

$$W(\vec{r},\vec{k},t) = \int [d\vec{k}']\, w(\vec{k}'-\vec{k})\, e^{i\vec{k}'\cdot\vec{r}-i\mathcal{E}_{\vec{k}'}t/\hbar}\psi_{\vec{k}'}e^{-i\vec{k}'\cdot\vec{r}}, \tag{L31}$$

$$\approx e^{i\vec{k}\cdot\vec{r}-i\mathcal{E}_{\vec{k}}t/\hbar}\int [d\vec{k}'']\, w(\vec{k}'')? \qquad ? \tag{L32}$$

$$\approx ? \qquad ? \tag{L33}$$

Van Hove Singularities

$$D(\mathcal{E}) = \int dk\,(2/2\pi)\delta\,(\mathcal{E}-\mathcal{E}_k) \quad \text{(L34)}$$

$$= \frac{2}{\pi}\int \frac{d\mathcal{E}_k}{|d\mathcal{E}_k/dk|}\delta\,(\mathcal{E}-\mathcal{E}_k) \quad \text{(L35)}$$

$$= \frac{2}{\pi}\frac{1}{|d\mathcal{E}_k/dk|}. \quad \text{(L36)}$$

$$D(\mathcal{E}) \sim \frac{1}{k-\pi/a} \sim \frac{1}{\sqrt{\mathcal{E}_{\max}-\mathcal{E}}} \quad \text{(L37)}$$

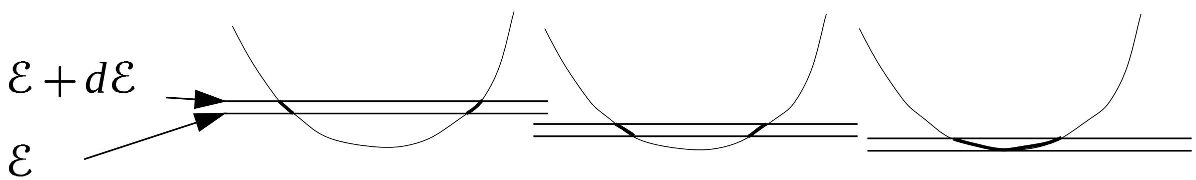
$d\mathcal{E}/dk$

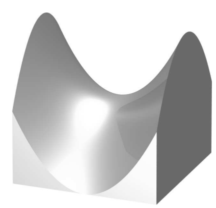
$$D(\mathcal{E}) = \int d\vec{k}\,2\frac{L^d}{(2\pi)^d}\delta(\mathcal{E}-\mathcal{E}_{\vec{k}}). \quad \text{(L38)}$$

$$D(\mathcal{E}) \sim \ln|\mathcal{E}/\mathcal{E}_0-1| \quad \text{or} \quad \theta(\pm\mathcal{E}) \quad \text{(L39)}$$

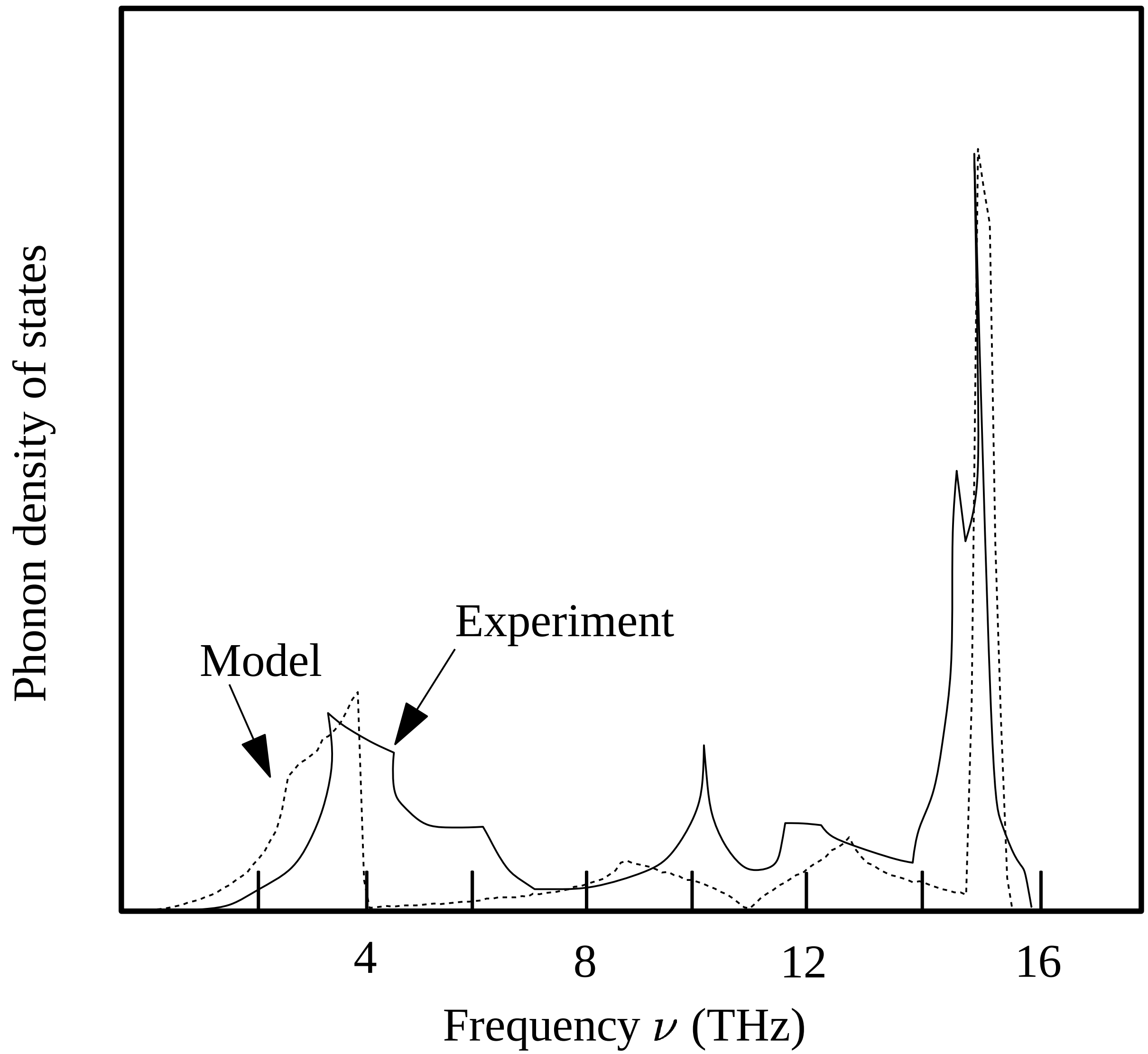
Van Hove Singularities

$$D(\mathcal{E}) \sim \begin{cases} \sqrt{\mathcal{E}} & \text{for} \quad \mathcal{E} > 0,\ 0 \text{ else}, \\ & \text{or} \\ \sqrt{-\mathcal{E}} & \text{for} \quad \mathcal{E} < 0,\ 0 \text{ else}, \end{cases} \tag{L40}$$





Van Hove Singularities



Uniqueness of Bloch vectors

$$e^{i(\vec{k}+\vec{K})\cdot\vec{R}} = e^{i\vec{k}\cdot\vec{R}}, \tag{L41}$$

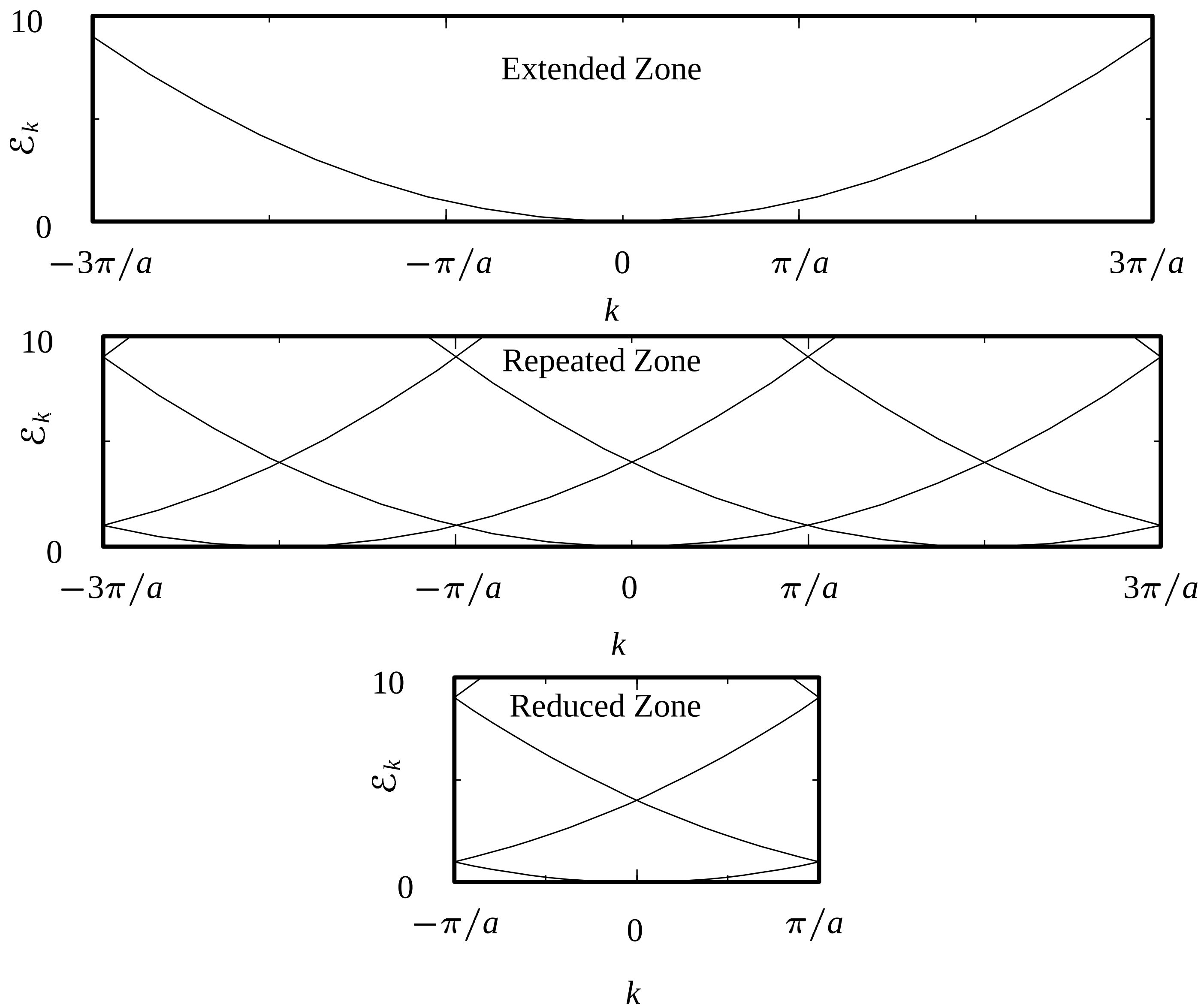
it follows that

$$\psi_{n,\vec{k}+\vec{K}} = \psi_{n',\vec{k}}. \tag{L42}$$

$$\psi_{nk} = e^{ikr}e^{inKr}, \tag{L43}$$

- ☞ Reduced zone scheme
- ☞ Extended zone scheme

Uniqueness of Bloch vectors



Explicit construction of Bloch functions

$$e^{i\vec{k}\cdot(\vec{r}+\vec{R})} = e^{i\vec{k}\cdot\vec{r}}. \tag{L44}$$

$$\int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} U(\vec{r}) = \sum_{\vec{R}} \int_{\substack{\text{unit}\\ \text{cell}}} d\vec{r}\, e^{-i\vec{q}\cdot\vec{R}} U(\vec{r}+\vec{R}) e^{-i\vec{q}\cdot\vec{r}} \tag{L45}$$

$$= \Omega \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} U_{\vec{q}}, \tag{L46}$$

where Ω is the volume of the unit cell, and

$$U_{\vec{q}} \equiv ? \qquad\qquad ?. \tag{L47}$$

Ω is volume of unit cell

$$\sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} = N \sum_{\vec{K}} \delta_{\vec{q}\vec{K}} \tag{L48}$$

Explicit construction of Bloch functions

$$\Rightarrow \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} U(\vec{r}) \quad = \quad \mathcal{V} \sum_{\vec{K}} \delta_{\vec{q}\vec{K}} U_{\vec{K}}. \tag{L49}$$

$$U(\vec{r}) = ? \qquad ? \sum_{\vec{K}} e^{i\vec{K}\cdot\vec{r}} U_{\vec{K}}. \tag{L50}$$

Periodic boundary conditions imply

$$\psi(\vec{r}) = \frac{1}{\mathcal{V}} \sum_{\vec{q}} \psi(\vec{q}) e^{i\vec{q}\cdot\vec{r}}. \tag{L51}$$

$$\int d\vec{r} e^{i\vec{q}\cdot\vec{r}} = \mathcal{V}\delta_{\vec{q}\vec{0}}. \tag{L52}$$

$$0 \quad = \quad \frac{1}{\mathcal{V}} \sum_{\vec{q}'} \left[\mathcal{E}^0_{\vec{q}'} - \mathcal{E} + U(\vec{r})\right] \psi(\vec{q}') e^{i\vec{q}'\cdot\vec{r}} \tag{L53}$$

$$= \quad ?$$

Explicit construction of Bloch functions

$$? \Rightarrow 0 \quad = \quad ?$$

$$? \quad = \quad ?$$

$$? \Rightarrow 0 \quad = \quad (\mathcal{E}^0_{\vec{q}} - \mathcal{E})\psi(\vec{q}) + \sum_{\vec{K}} U_{\vec{K}}\psi(\vec{q}-\vec{K}). \tag{L57}$$

$$\psi(\vec{r}) = \frac{1}{\mathcal{V}} \sum_{\vec{K}} \psi(\vec{k}-\vec{K}) e^{i(\vec{k}-\vec{K})\cdot\vec{r}}. \tag{L58}$$

$$\hat{\mathcal{H}} = \sum_{\vec{q}'} |\vec{q}'\rangle \mathcal{E}^0_{\vec{q}'} \langle \vec{q}'| + \sum_{\vec{q}'\vec{K}'} |\vec{q}'\rangle U_{\vec{K}'} \langle \vec{q}' - \vec{K}'|. \tag{L59}$$

Structure of equations

$$
\begin{pmatrix}
\begin{pmatrix}
\mathcal{O}^{(1)}_{11} & \mathcal{O}^{(1)}_{12} & \mathcal{O}^{(1)}_{13}\cdots & \mathcal{O}^{(1)}_{1M} \\
\mathcal{O}^{(1)}_{21} & \mathcal{O}^{(1)}_{22} & \mathcal{O}^{(1)}_{23}\cdots & \mathcal{O}^{(1)}_{2M} \\
\mathcal{O}^{(1)}_{31} & \mathcal{O}^{(1)}_{32} & \mathcal{O}^{(1)}_{33}\cdots & \mathcal{O}^{(1)}_{3M} \\
 & . & & \\
 & . & & \\
 & . & & \\
 & & & \mathcal{O}^{(1)}_{MM}
\end{pmatrix} & 0 \\
0 & \begin{pmatrix}
\mathcal{O}^{(2)}_{11} & \mathcal{O}^{(2)}_{12} & \mathcal{O}^{(2)}_{13}\cdots & \mathcal{O}^{(2)}_{1M} \\
\mathcal{O}^{(2)}_{21} & \mathcal{O}^{(2)}_{22} & \mathcal{O}^{(2)}_{23}\cdots & \mathcal{O}^{(2)}_{2M} \\
\mathcal{O}^{(2)}_{31} & \mathcal{O}^{(2)}_{32} & \mathcal{O}^{(2)}_{33}\cdots & \mathcal{O}^{(2)}_{3M} \\
 & . & & \\
 & . & & \\
 & . & & \\
 & & & \mathcal{O}^{(2)}_{MM}
\end{pmatrix}
\end{pmatrix}
\begin{pmatrix}
\psi(\vec{q}_1-\vec{K}_1) \\
\psi(\vec{q}_1-\vec{K}_2) \\
\psi(\vec{q}_1-\vec{K}_3) \\
. \\
. \\
. \\
\underline{\psi(\vec{q}_1-\vec{K}_M)} \\
\psi(\vec{q}_2-\vec{K}_1) \\
\psi(\vec{q}_2-\vec{K}_2) \\
\psi(\vec{q}_2-\vec{K}_3) \\
. \\
. \\
\underline{\psi(\vec{q}_2-\vec{K}_M)} \\
. \\
.
\end{pmatrix}
$$

$$U_0 a\delta(x), \tag{L60}$$

$$U_K = U_0, \tag{L61}$$

$$0 = (\mathcal{E}_q^0 - \mathcal{E})\psi(q) + \sum_K U_0 \psi(q-K). \tag{L62}$$

$$Q_q = \sum_K \psi(q-K). \tag{L63}$$

Then Eq. (L62) becomes

$$\psi(q) + \frac{U_0}{\mathcal{E}_q^0 - \mathcal{E}} Q_q = 0. \tag{L64}$$

Note from its definition (63) that

$$Q_q = Q_{q-K} \tag{L65}$$

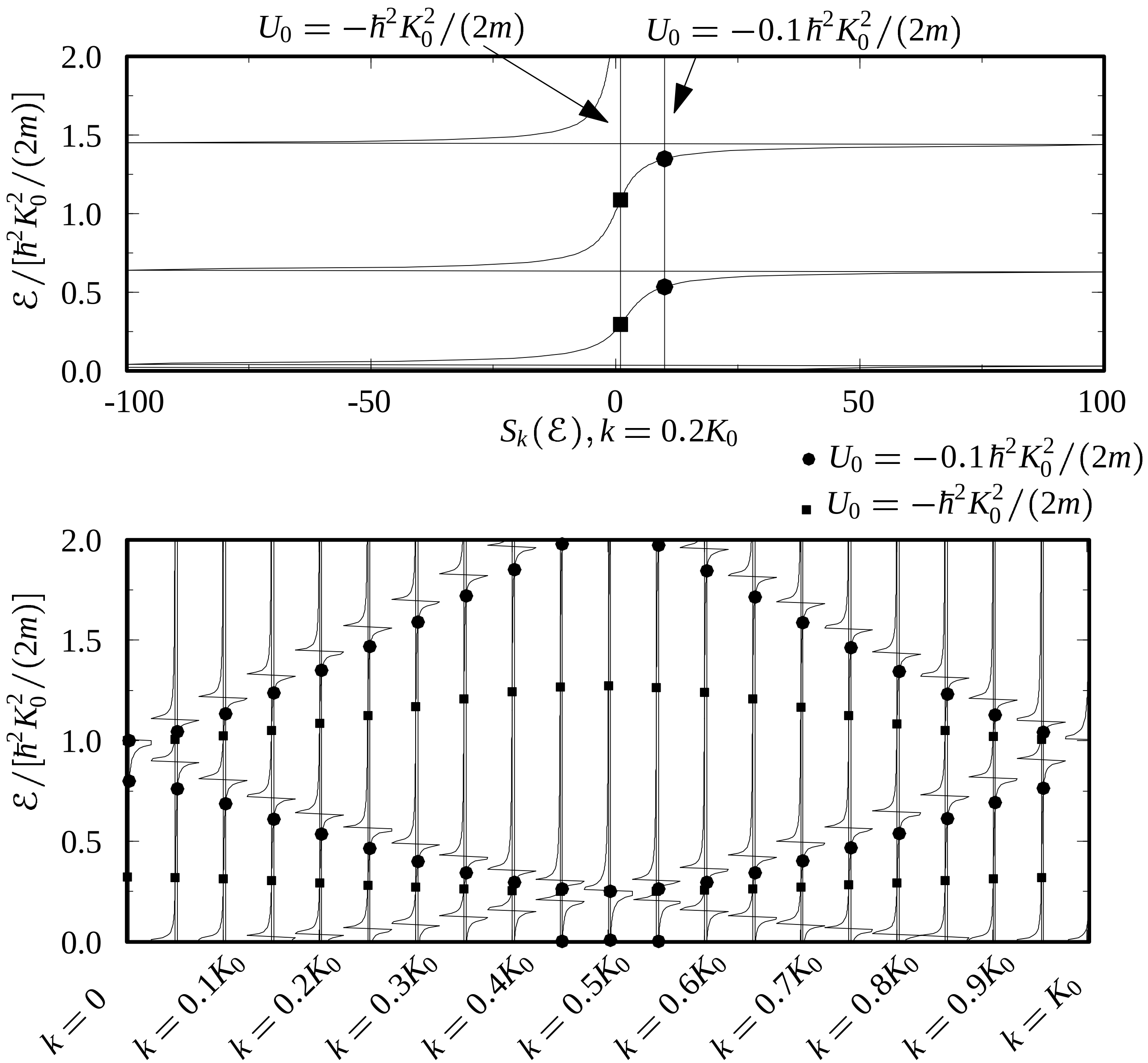
$$? \qquad ? = 0 \tag{L66}$$

$$? \qquad ? = 0 \tag{L67}$$

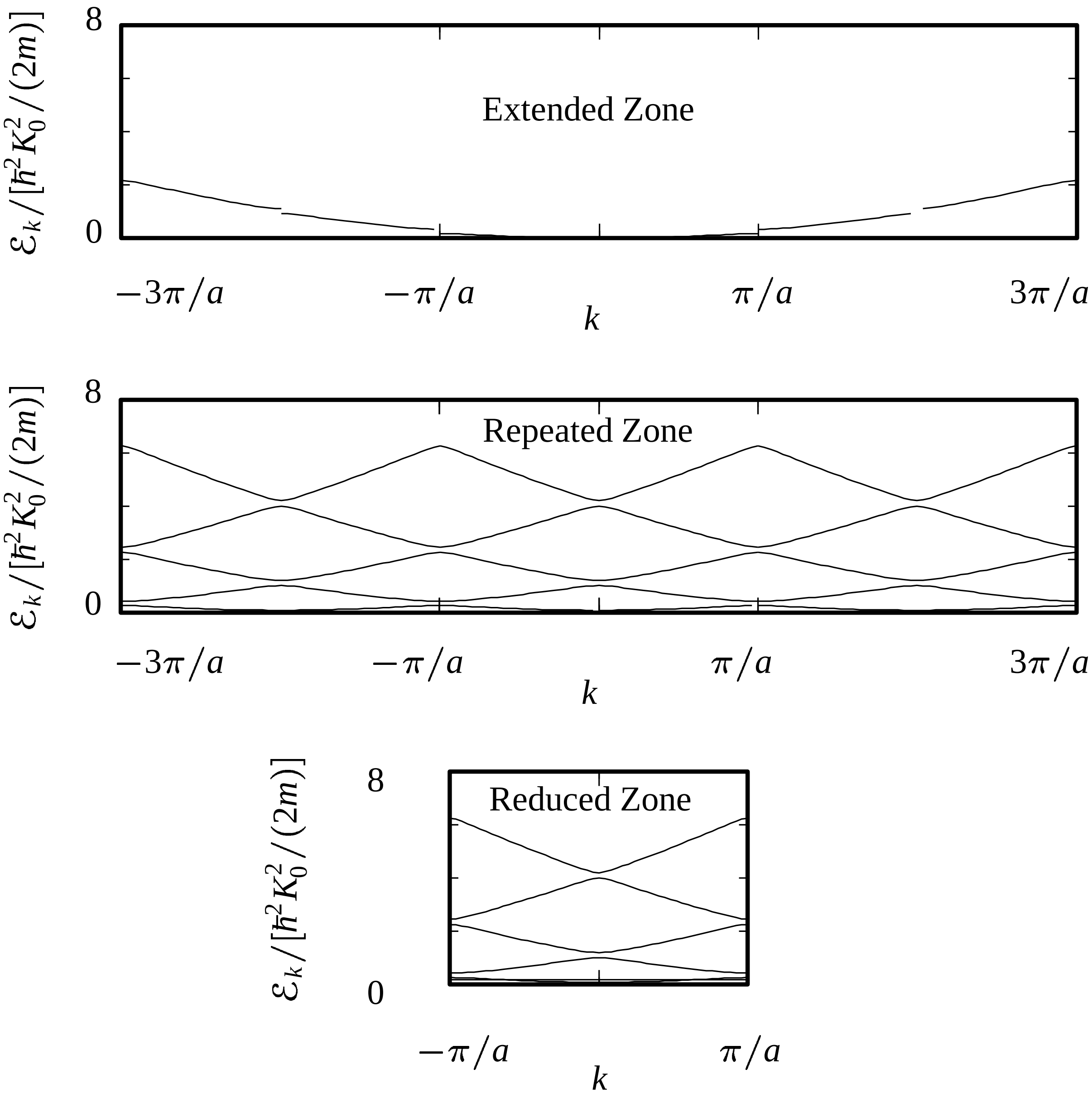
$$\Rightarrow \qquad Q_k + ? \qquad ? 0. \tag{L68}$$

$$-\frac{1}{U_0} = \sum_K \frac{1}{\mathcal{E}^0_{k-K} - \mathcal{E}} \equiv S_k(\mathcal{E}). \tag{L69}$$

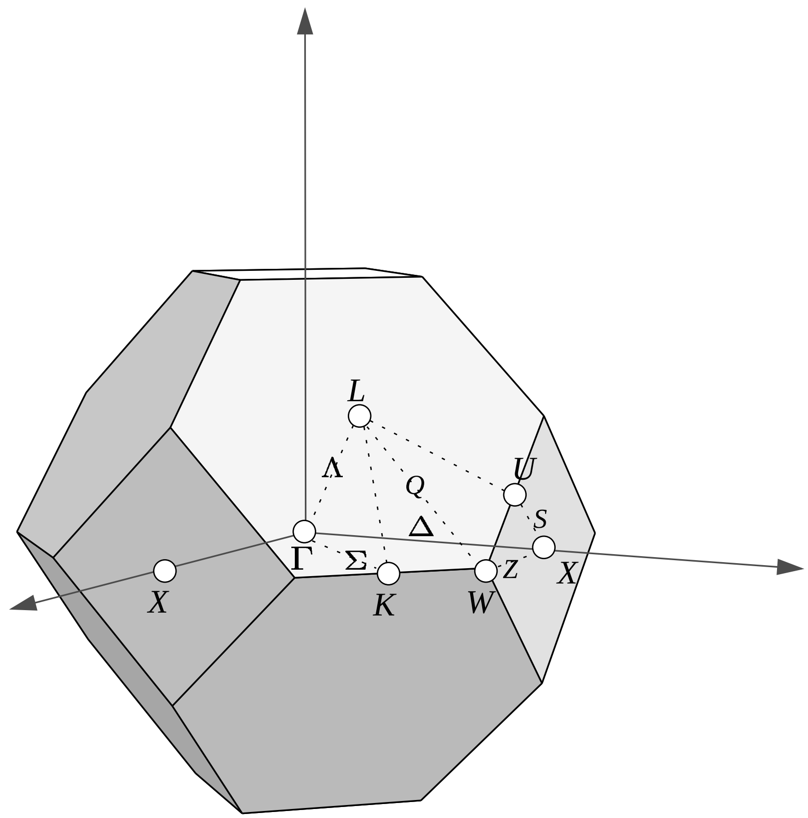
Kronig–Penney model



Kronig–Penney model

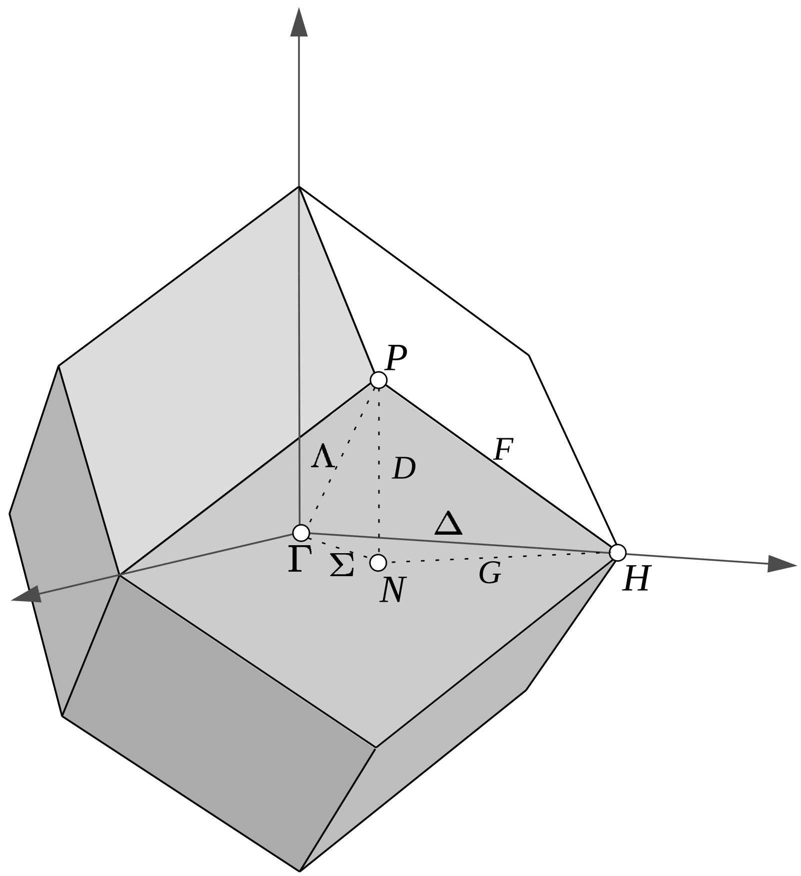


Brillouin zones and rotational symmetry



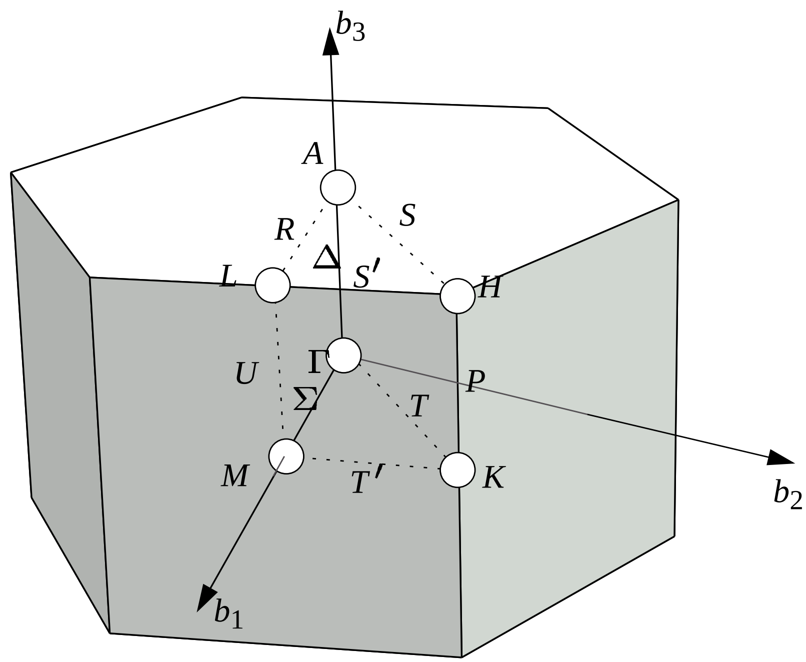
In units of $2\pi/a$, $\Gamma = (0\ 0\ 0)$, $X = (0\ 1\ 0)$, $L = (1/2\ 1/2\ 1/2)$, $W = (1/2\ 1\ 0)$, $K = (3/4\ 3/4\ 0)$, and $U = (1/4\ 1\ 1/4)$.

Brillouin zones and rotational symmetry



In units of $2\pi/a$, $\Gamma = (0\ 0\ 0)$, $H = (0\ 1\ 0)$, $N = (1/2\ 1/2\ 0)$, and $P = (1/2\ 1/2\ 1/2)$.

Brillouin zones and rotational symmetry



In units of $4\pi/a\sqrt{3}$, $4\pi/a\sqrt{3}$, and $2\pi/c$, along the three primitive vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$; $\Gamma = (0\ 0\ 0)$, $A = (0\ 0\ 1/2)$, $M = (1/2\ 0\ 0)$, $K = (1/3\ 1/3\ 0)$, $H = (1/3\ 1/3\ 1/2)$, and $L = (1/2\ 0\ 1/2)$.