Electrons in a weak periodic potential

Outline

Electrons in a weak periodic potential

Applicability

Motivation

- Appropriate assumption for metals of I–IV groups
  - *s* and *p* electrons outside a noble gas closed-shell configuration
  - nearly free-electron metals
- Justification:
  - valence electrons are excluded (Pauli exclusion principle) from the core region
  - electron's mobility screen the field due to the ionic cores

General approach to the TISE

Case of a weak periodic potential

Summary: wave function of a Bloch level

- Expand the Block wave function in plane waves:

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

  - sum over all $\boldsymbol{K}$

- Coefficients $c_{\boldsymbol{k}-\boldsymbol{K}}$ and energy ε determined by

$$[\frac{\hbar^2}{2m}(\boldsymbol{k}-\boldsymbol{K})^2 - \varepsilon]c_{\boldsymbol{k}-\boldsymbol{K}} + \sum_{\boldsymbol{K}'} U_{\boldsymbol{K}'-\boldsymbol{K}} c_{\boldsymbol{k}-\boldsymbol{K}'} = 0$$

  - For fixed $\boldsymbol{k}$ there is an equation for every $\boldsymbol{K}$

General approach to the TISE

Case of a weak periodic potential

Free electron case

- $U_{\boldsymbol{K}} = 0$, $\forall \boldsymbol{K}$, therefore:

$$(\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}} - \varepsilon) c_{\boldsymbol{k}-\boldsymbol{K}} = 0 \Longrightarrow \begin{cases} c_{\boldsymbol{k}-\boldsymbol{K}} = & 0 \\ \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}} - \varepsilon = & 0 \end{cases}$$

  - $\varepsilon^0_q = \frac{\hbar^2}{2m} q^2$
- We have two possibilities:
  - $\exists!$ $\boldsymbol{K}$ such that $\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}} = \varepsilon$
  - $\exists$ several $\boldsymbol{K}$, $\boldsymbol{K}_1, \ldots, \boldsymbol{K}_m$ such that $\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_i} = \varepsilon$

General approach to the TISE

Case of a weak periodic potential

Free electron case

- $\exists!\ \boldsymbol{K}$ such that $\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}} = \varepsilon \Longrightarrow \psi_{\boldsymbol{k}} \propto e^{i(\boldsymbol{k}-\boldsymbol{K})\cdot\boldsymbol{r}}$
  - free electron solutions
- $\exists$ several $\boldsymbol{K}$, $\boldsymbol{K}_1, \ldots, \boldsymbol{K}_m$ such that $\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_i} = \varepsilon$
  - m independent plane-wave solutions: $e^{i(\boldsymbol{k}-\boldsymbol{K}_i)\cdot\boldsymbol{r}}$, $i = 1, 2, \ldots, m$
  - complete freedom in chosing the coefficients $c_{\boldsymbol{k}-\boldsymbol{K}_i}$, $i = 1, 2, \ldots, m$
- Two similar situations arise when considering a very weak potential U

General approach to the TISE

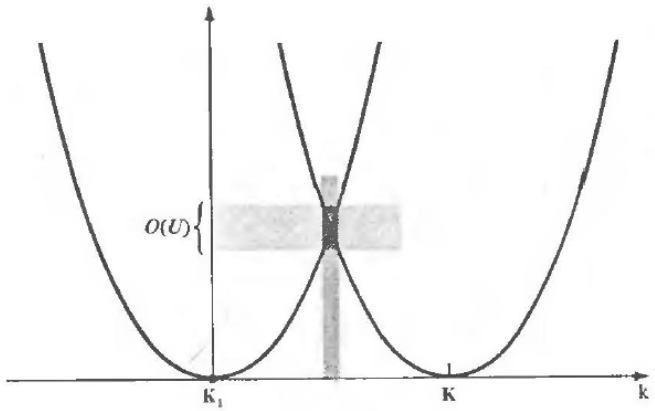
Case of a weak periodic potential

Non-degenerate case

- Fix $\boldsymbol{k}$ and $\boldsymbol{K} = \boldsymbol{K}_1$ such that $\forall \boldsymbol{K} \neq \boldsymbol{K}_1$

$$|\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_1} - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}}| >> U$$

- Investigate the effect on the corresponding free-electron level $\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_1}$, $\psi_{\boldsymbol{k}} \propto e^{i(\boldsymbol{k}-\boldsymbol{K}_1)\cdot\boldsymbol{r}}$



$$|\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_1} - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}}| \sim O(U)$$

General approach to the TISE

Case of a weak periodic potential

Non-degenerate case

- Put $\boldsymbol{K} = \boldsymbol{K}_1$:

$$(\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_1}) c_{\boldsymbol{k}-\boldsymbol{K}_1} = \sum_{\boldsymbol{K}} U_{\boldsymbol{K}-\boldsymbol{K}_1} c_{\boldsymbol{k}-\boldsymbol{K}}$$

- The r.h.s. is of order $\mathrm{O}(U^2)$:
  - $\boldsymbol{K} \neq \boldsymbol{K}_1$ on the r.h.s. ($U_{\boldsymbol{0}} = 0$)
  - for $\boldsymbol{K} \neq \boldsymbol{K}_1$, $c_{\boldsymbol{k}-\boldsymbol{K}} \to 0$ when $U \to 0$
- Explicitly:

$$c_{\boldsymbol{k}-\boldsymbol{K}} = \frac{U_{\boldsymbol{K}_1-\boldsymbol{K}} c_{\boldsymbol{k}-\boldsymbol{K}_1}}{\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}}} + \sum_{\boldsymbol{K}' \neq \boldsymbol{K}_1} \frac{U_{\boldsymbol{K}'-\boldsymbol{K}} c_{\boldsymbol{k}-\boldsymbol{K}'}}{\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}}}$$

General approach to the TISE

Case of a weak periodic potential

Non-degenerate case

- Therefore, in case of no degeneracy, for $\boldsymbol{K} \neq \boldsymbol{K}_1$:

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

- The Eq. for $c_{\boldsymbol{k}-\boldsymbol{K}_1}$ becomes:

$$(\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_1}) c_{\boldsymbol{k}-\boldsymbol{K}_1} = \sum_{\boldsymbol{K}} \frac{U_{\boldsymbol{K}-\boldsymbol{K}_1} U_{\boldsymbol{K}_1-\boldsymbol{K}}}{\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}}} c_{\boldsymbol{k}-\boldsymbol{K}_1} + O(U^3)$$

- Finally, to order U^2:

$$\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_1} = \sum_{\boldsymbol{K}} \frac{U_{\boldsymbol{K}-\boldsymbol{K}_1} U_{\boldsymbol{K}_1-\boldsymbol{K}}}{\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_1} - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}}} + O(U^3)$$

General approach to the TISE

Case of a weak periodic potential

Non-degenerate case

$$\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_1} = \sum_{\boldsymbol{K}} \frac{U_{\boldsymbol{K}-\boldsymbol{K}_1} U_{\boldsymbol{K}_1-\boldsymbol{K}}}{\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_1} - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}}} + O(U^3)$$

- Weakly perturbed non-degenerate bands repel each-other
- The perturbation is of order U^2, hence very small
- To order U only nearly-degenerate levels are affected

General approach to the TISE

Case of a weak periodic potential

Degenerate case: $|\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_i} - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_j}| \sim O(U)$, $i,j = 1,\dots,m$

- $\forall \boldsymbol{K} \neq \boldsymbol{K}_i$, $i = 1,\dots,m$

$$|\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_i} - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}}| >> U$$

- Coefficients $c_{\boldsymbol{k}-\boldsymbol{K}_i}$ do not necessarily vanish in the limit $U \to 0$
- For all other coefficients $c_{\boldsymbol{k}-\boldsymbol{K}} \to 0$
- For $c_{\boldsymbol{k}-\boldsymbol{K}_i}$, $i = 1,2,\dots,m$ we can write:

$$(\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_i}) c_{\boldsymbol{k}-\boldsymbol{K}_i} = \sum_{j=1}^{m} U_{\boldsymbol{K}_j-\boldsymbol{K}_i} c_{\boldsymbol{k}-\boldsymbol{K}_j} + \sum_{\boldsymbol{K}\neq\boldsymbol{K}_1,\dots,\boldsymbol{K}_m} U_{\boldsymbol{K}-\boldsymbol{K}_i} c_{\boldsymbol{k}-\boldsymbol{K}}$$

General approach to the TISE

Case of a weak periodic potential

Degenerate case: $|\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_i} - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_j}| \sim O(U)$, $i,j = 1,\dots,m$

- $\forall \boldsymbol{K} \neq \boldsymbol{K}_i$, $i = 1,\dots,m$

$$c_{\boldsymbol{k}-\boldsymbol{K}} = \frac{1}{\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}}} \left(\sum_{j=1}^{m} U_{\boldsymbol{K}_j-\boldsymbol{K}} c_{\boldsymbol{k}-\boldsymbol{K}_j} + \sum_{\boldsymbol{K}' \neq \boldsymbol{K}_1,\dots,\boldsymbol{K}_m} U_{\boldsymbol{K}'-\boldsymbol{K}} c_{\boldsymbol{k}-\boldsymbol{K}'} \right)$$

- Since $c_{\boldsymbol{k}-\boldsymbol{K}} \sim O(U)$ we have:

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

General approach to the TISE

Case of a weak periodic potential

Degenerate case: $|\varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_i} - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_j}| \sim O(U)$, $i,j = 1,\dots,m$

- Putting everything together:

$$\begin{aligned}(\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_i})c_{\boldsymbol{k}-\boldsymbol{K}_i} &= \sum_{j=1}^{m} U_{\boldsymbol{K}_j-\boldsymbol{K}_i} c_{\boldsymbol{k}-\boldsymbol{K}_j} \\ &+ \sum_{j=1}^{m} \left(\sum_{\boldsymbol{K}\neq\boldsymbol{K}_1,\dots,\boldsymbol{K}_m} \frac{U_{\boldsymbol{K}-\boldsymbol{K}_i} U_{\boldsymbol{K}_j-\boldsymbol{K}}}{\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}}} \right) c_{\boldsymbol{k}-\boldsymbol{K}_j} + O(U^3)\end{aligned}$$

- For leading order corrections in U we have:

$$(\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_i})c_{\boldsymbol{k}-\boldsymbol{K}_i} = \sum_{j=1}^{m} U_{\boldsymbol{K}_j-\boldsymbol{K}_i} c_{\boldsymbol{k}-\boldsymbol{K}_j}$$

Energy levels near a single Bragg plane

Degenerate case with $m = 2$

Mathematical treatment

- For $m = 2$ the equations (to leading order U) are

$$\begin{cases} (\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_1}) c_{\boldsymbol{k}-\boldsymbol{K}_1} & = U_{\boldsymbol{K}_2-\boldsymbol{K}_1} c_{\boldsymbol{k}-\boldsymbol{K}_2} \\ (\varepsilon - \varepsilon^0_{\boldsymbol{k}-\boldsymbol{K}_2}) c_{\boldsymbol{k}-\boldsymbol{K}_2} & = U_{\boldsymbol{K}_1-\boldsymbol{K}_2} c_{\boldsymbol{k}-\boldsymbol{K}_1} \end{cases}$$

- Put $\boldsymbol{q} = \boldsymbol{k} - \boldsymbol{K}_1$, $\boldsymbol{K} = \boldsymbol{K}_2 - \boldsymbol{K}_1$:

$$\begin{cases} (\varepsilon - \varepsilon^0_{\boldsymbol{q}}) c_{\boldsymbol{q}} & = U_{\boldsymbol{K}} c_{\boldsymbol{q}-\boldsymbol{K}} \\ (\varepsilon - \varepsilon^0_{\boldsymbol{q}-\boldsymbol{K}}) c_{\boldsymbol{q}-\boldsymbol{K}} & = U_{-\boldsymbol{K}} c_{\boldsymbol{q}} = U^*_{\boldsymbol{K}} c_{\boldsymbol{q}} \end{cases}$$

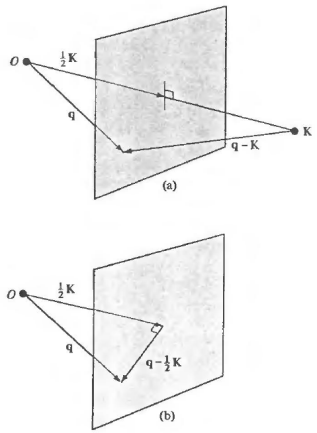
- With the assumption that $\varepsilon^0_{\boldsymbol{q}} \sim \varepsilon^0_{\boldsymbol{q}-\boldsymbol{K}}$, $|\varepsilon^0_{\boldsymbol{q}} - \varepsilon^0_{\boldsymbol{q}-\boldsymbol{K}'}| >> U$ for $\boldsymbol{K}' \neq \boldsymbol{K}, \boldsymbol{0}$

Energy levels near a single Bragg plane

Degenerate case with $m = 2$

Mathematical treatment

- $\varepsilon^0_{\boldsymbol{q}} = \varepsilon^0_{\boldsymbol{q}-\boldsymbol{K}} \Longrightarrow |\boldsymbol{q}| = |\boldsymbol{q} - \boldsymbol{K}|$:
  - $\boldsymbol{q}$ must lie on a Bragg plane
- If $\varepsilon^0_{\boldsymbol{q}} = \varepsilon^0_{\boldsymbol{q}-\boldsymbol{K}'}$ only for $\boldsymbol{K}' = \boldsymbol{K}$:
  - $\boldsymbol{q}$ must lie only on this Bragg plane
- Therefore $\boldsymbol{q}$ is close to only one Bragg plane



(a) $\boldsymbol{q}$ lie in the Bragg plane determined by $\boldsymbol{K}$

(b) $\boldsymbol{q} - \frac{1}{2}\boldsymbol{K}$ is parallel to the plane

Energy levels near a single Bragg plane

Degenerate case with $m = 2$

Mathematical treatment

- For two nearly degenerate levels, the electron's wave vector (nearly) satisfy the condition for a single Bragg scattering
- For m nearly degenerate levels, $\boldsymbol{q}$ lies nearby the intersection with m different Bragg planes
- As a general rule:
  - a weak periodic potential has its major effects on only those free electron levels whose wave vectors are close to ones at which Bragg reflections can occur

Energy levels near a single Bragg plane

Degenerate case with $m = 2$

Mathematical treatment

- The linear system has non-trivial solutions only if:

$$\begin{vmatrix} \varepsilon - \varepsilon^0_{\boldsymbol{q}} & -U_{\boldsymbol{K}} \\ -U^*_{\boldsymbol{K}} & \varepsilon - \varepsilon^0_{\boldsymbol{q}-\boldsymbol{K}} \end{vmatrix} = 0$$

- Leading to a quadratic equation

$$(\varepsilon - \varepsilon^0_{\boldsymbol{q}})(\varepsilon - \varepsilon^0_{\boldsymbol{q}-\boldsymbol{K}}) - |U_{\boldsymbol{K}}|^2 = 0$$

- With roots:

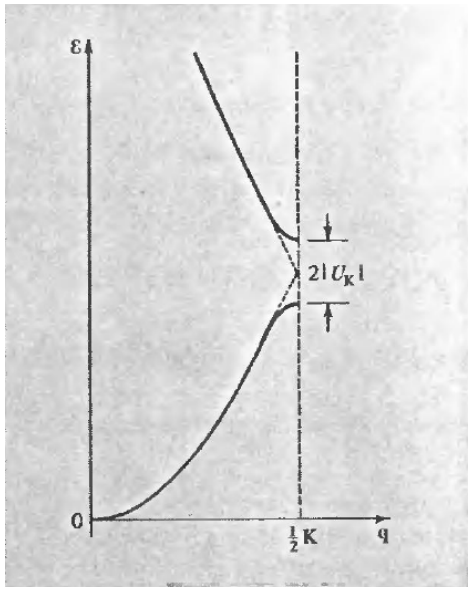
$$\varepsilon = \frac{1}{2}(\varepsilon^0_{\boldsymbol{q}} + \varepsilon^0_{\boldsymbol{q}-\boldsymbol{K}}) \pm \left[\left(\frac{\varepsilon^0_{\boldsymbol{q}} - \varepsilon^0_{\boldsymbol{q}-\boldsymbol{K}}}{2} \right)^2 + |U_{\boldsymbol{K}}|^2 \right]^{1/2}$$

Energy levels near a single Bragg plane

Degenerate case with $m = 2$

Mathematical treatment

- For $\boldsymbol{q}$ on the Bragg plane, the two roots are $\varepsilon = \varepsilon^0_{\boldsymbol{q}} \pm |U_{\boldsymbol{K}}|^2$
- Also $\frac{\partial \varepsilon}{\partial \boldsymbol{q}} = \frac{\hbar^2}{m}(\boldsymbol{q} - \frac{1}{2}\boldsymbol{K})$
  - the gradient is parallel to the plane
  - constant energy surfaces at Bragg's planes are $\perp$ to the plane



plot of the two roots for $\boldsymbol{q}$ parallel to $\boldsymbol{K}$

Energy levels near a single Bragg plane

Degenerate case with $m = 2$

Mathematical treatment

- For $\boldsymbol{q}$ on the Bragg plane $c_{\boldsymbol{q}} = \pm \mathrm{sgn}(U_{\boldsymbol{K}}) c_{\boldsymbol{q}-\boldsymbol{K}}$
- If $U_{\boldsymbol{K}} > 0$:

$$\begin{cases} |\psi(\boldsymbol{r})|^2 \propto (\cos \frac{1}{2}\boldsymbol{K} \cdot \boldsymbol{r})^2 & \varepsilon = \varepsilon^0_{\boldsymbol{q}} + |U_{\boldsymbol{K}}| \\ |\psi(\boldsymbol{r})|^2 \propto (\sin \frac{1}{2}\boldsymbol{K} \cdot \boldsymbol{r})^2 & \varepsilon = \varepsilon^0_{\boldsymbol{q}} - |U_{\boldsymbol{K}}| \end{cases}$$

- If $U_{\boldsymbol{K}} < 0$:

$$\begin{cases} |\psi(\boldsymbol{r})|^2 \propto (\sin \frac{1}{2}\boldsymbol{K} \cdot \boldsymbol{r})^2 & \varepsilon = \varepsilon^0_{\boldsymbol{q}} + |U_{\boldsymbol{K}}| \\ |\psi(\boldsymbol{r})|^2 \propto (\cos \frac{1}{2}\boldsymbol{K} \cdot \boldsymbol{r})^2 & \varepsilon = \varepsilon^0_{\boldsymbol{q}} - |U_{\boldsymbol{K}}| \end{cases}$$

  - *p*-like solutions: $|\psi(\boldsymbol{r})|^2 \propto (\sin \frac{1}{2}\boldsymbol{K} \cdot \boldsymbol{r})^2$
  - *s*-like solutions: $|\psi(\boldsymbol{r})|^2 \propto (\cos \frac{1}{2}\boldsymbol{K} \cdot \boldsymbol{r})^2$

Energy levels near a single Bragg plane

Degenerate case with $m = 2$

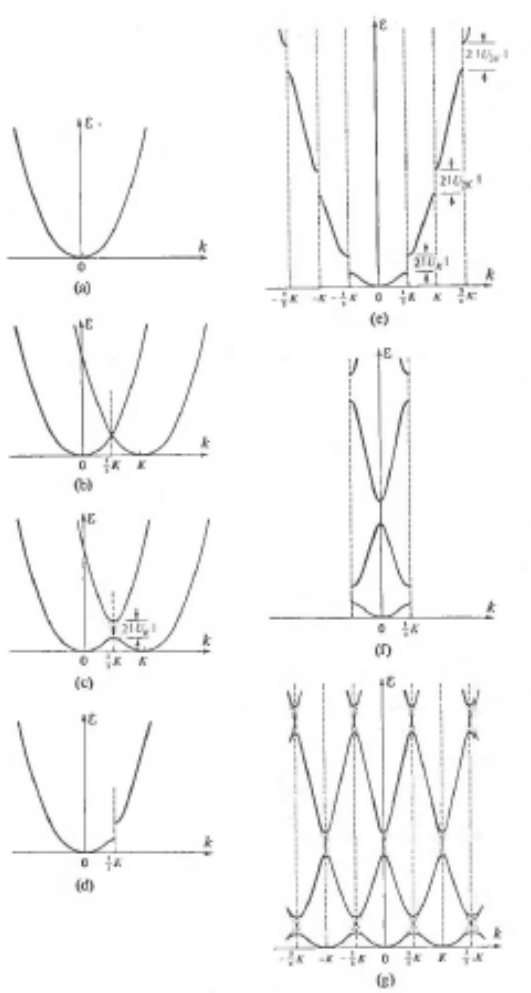
Energy bands in one dimension

- Free electron case: electronic levels are a parabola in k
  - limit of no interaction
  - to $O(U)$ the levels are correct in the presence of U, except near Bragg points
- Nearby the point $\frac{1}{2}K$ the degeneracy is split by $2U_K$
  - the slope of the two curves must be zero at $\frac{1}{2}K$
  - the free electron curve is modified as Fig. (d)
- Extended-zone scheme: repeat the procedure near every Bragg point
  - for the corresponding Fourier component (Fig. (e))
  - emphasises continuity with the free electron levels
- Reduced-zone scheme: all levels are specified by $k \in$ 1st BZ
  - translate all pieces through the appropriate K to stay in the 1st BZ (Fig. (f))
- Repeated-zone scheme: shows the periodicity of labelling in k-space

Energy levels near a single Bragg plane

Degenerate case with $m = 2$

Energy bands in one dimension

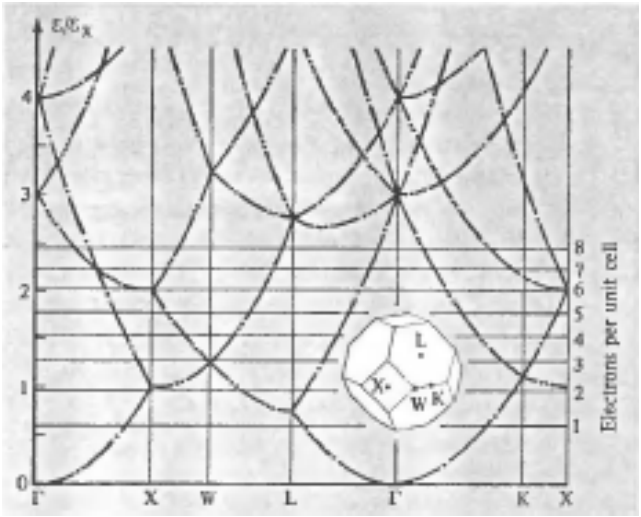


Energy levels near a single Bragg plane

Degenerate case with $m > 2$

Energy-wave-vector curves in three dimensions

- Plot ε vs $\boldsymbol{k}$ along straight lines in k-space
  - Uses a reduced-zone scheme
  - Most curves are highly degenerate
  - Introduction of a periodic potential lowers the degeneracy
  - Very complex curves also in the free-electron approximation



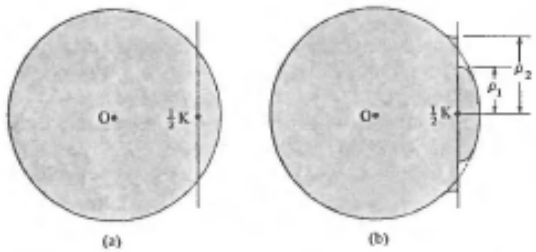
free-electron energy levels for a fcc Bravais lattice

Brillouin zones

Procedures used to draw the Fermi surface

Drawing the Fermi surface

- Draw the free-electron Fermi sphere centered at $\boldsymbol{k} = 0$
- It will be deformed in a simple manner when it crosses Bragg planes
  - constant energy surfaces are $\perp$ to Bragg planes
- Consider the effect of all Bragg planes intersecting the sphere
  - fractured sphere in the extended-zone scheme



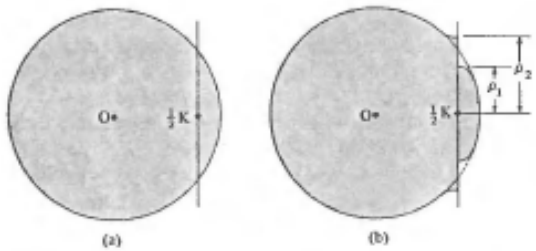
deformation of the free-electron sphere near the Bragg plane when $U_{\boldsymbol{k}} \neq 0$

Brillouin zones

Procedures used to draw the Fermi surface

Drawing the Fermi surface

- Similar construction with spheres centered on each lattice point to get the repeated-zone scheme
- Translate all pieces back into the first zone to get the surface in the reduced-zone scheme



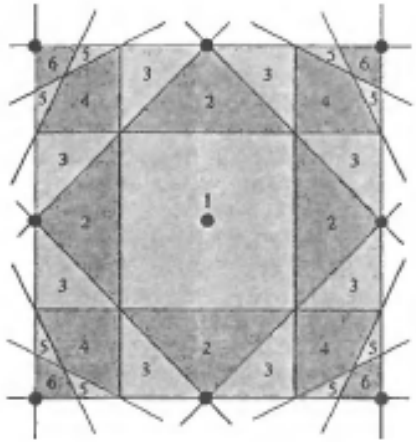
deformation of the free-electron sphere near the Bragg plane when $U_k \neq 0$

Brillouin zones

Procedures used to draw the Fermi surface

Brillouin zones

- All are set of points in k-space that can be reached:
  - 1st BZ: from the origin without crossing any Bragg plane
  - 2nd BZ: from the 1st BZ crossing one Bragg plane
  - $n+1$ BZ: from the n BZ crossing one Bragg plane (not in the $n-1$ BZ)
- Each BZ is a primitive cell

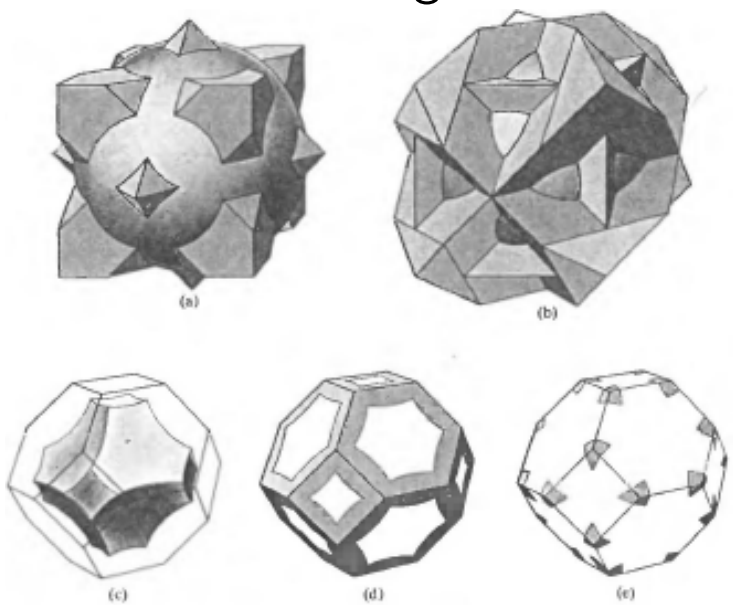


BZs for a 2D square Bravais lattice of sice b. Only BZs 1 2 3 are entirely contained in the square of side $2b$

Brillouin zones

Branches of the Fermi surface in the repeated-zone scheme

- Draw the free-electron Fermi sphere
- Deform it in the vicinity of every Bragg plane
- Translate the portion within the n-th BZ through all $\boldsymbol{K}$
  - Branch of the Fermi surface assigned to the nth band



free-electron Fermi sphere for a fcc metal of valence 4. (c) 2nd zone Fermi surface.

(d) 3rd zone Fermi surface. (e) 4th zone Fermi surface.

Geometrical structure factor

Monoatomic lattice with a basis

- For a basis of identical ions at positions $\boldsymbol{d}_j$: $U(\boldsymbol{r}) = \sum_{\boldsymbol{R}} \sum_j \phi(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{d}_j)$:
  - atomic potentials $\phi(\boldsymbol{r})$ centered at the ions positions
- Then we have:

$$\begin{aligned} U_{\boldsymbol{K}} &= \frac{1}{v} \int_C d\boldsymbol{r} e^{-i\boldsymbol{K}\cdot\boldsymbol{r}} U(\boldsymbol{r}) \\ &= \frac{1}{v} \int_V d\boldsymbol{r} e^{-i\boldsymbol{K}\cdot\boldsymbol{r}} \sum_j \phi(\boldsymbol{r} - \boldsymbol{d}_j) \\ &= \frac{1}{v} \phi(\boldsymbol{K}) S^*_{\boldsymbol{K}} \end{aligned}$$

- If $S_{\boldsymbol{K}} = 0 \Longrightarrow U_{\boldsymbol{K}} = 0$
  - lowest-order splitting of free-electron levels disappears