Lectures 8-9

Electrons in a periodic potential and NFE approximation: Band gaps, Bragg Planes and Zone Edges

Bloch's Theorem (review)

Form 1

$$\psi_{nk}(x) = e^{ikx} u_{nk}(x),$$

$$u_{nk}(x+R) = u_{nk}(x)$$

Form 2

$$\psi_{nk}(x+R) = e^{ikR} \psi_{nk}(x)$$

Expand Bloch state in a plane-wave basis set

$$|\psi\rangle = \sum_{\vec{G}} c\left(\vec{k}+\vec{G}\right)\left|\vec{k}+\vec{G}\right\rangle \qquad \text{where} \qquad \left\langle \vec{r}\,\middle|\,\vec{k}+\vec{G}\right\rangle = \frac{1}{V^{1/2}} e^{i\left(\vec{k}+\vec{G}\right)\vec{r}}$$

Schrödinger equation becomes

$$\left\langle \vec{k}+\vec{G}\middle|H\middle|\psi\right\rangle = \sum_{\vec{G}'}\left[\frac{\hbar^2\left(\vec{k}+\vec{G}\right)^2}{2m}\delta\left(\vec{G},\vec{G}'\right) + \left\langle \vec{k}+\vec{G}\middle|V\middle|\vec{k}+\vec{G}'\right\rangle\right] c\left(\vec{k}+\vec{G}'\right)$$

$$= \varepsilon_n\left(\vec{k}\right)\left\langle \vec{k}+\vec{G}\middle|\psi\right\rangle = \varepsilon_n\left(\vec{k}\right) c\left(\vec{k}+\vec{G}\right)$$

Matrix version of Schrödinger equation

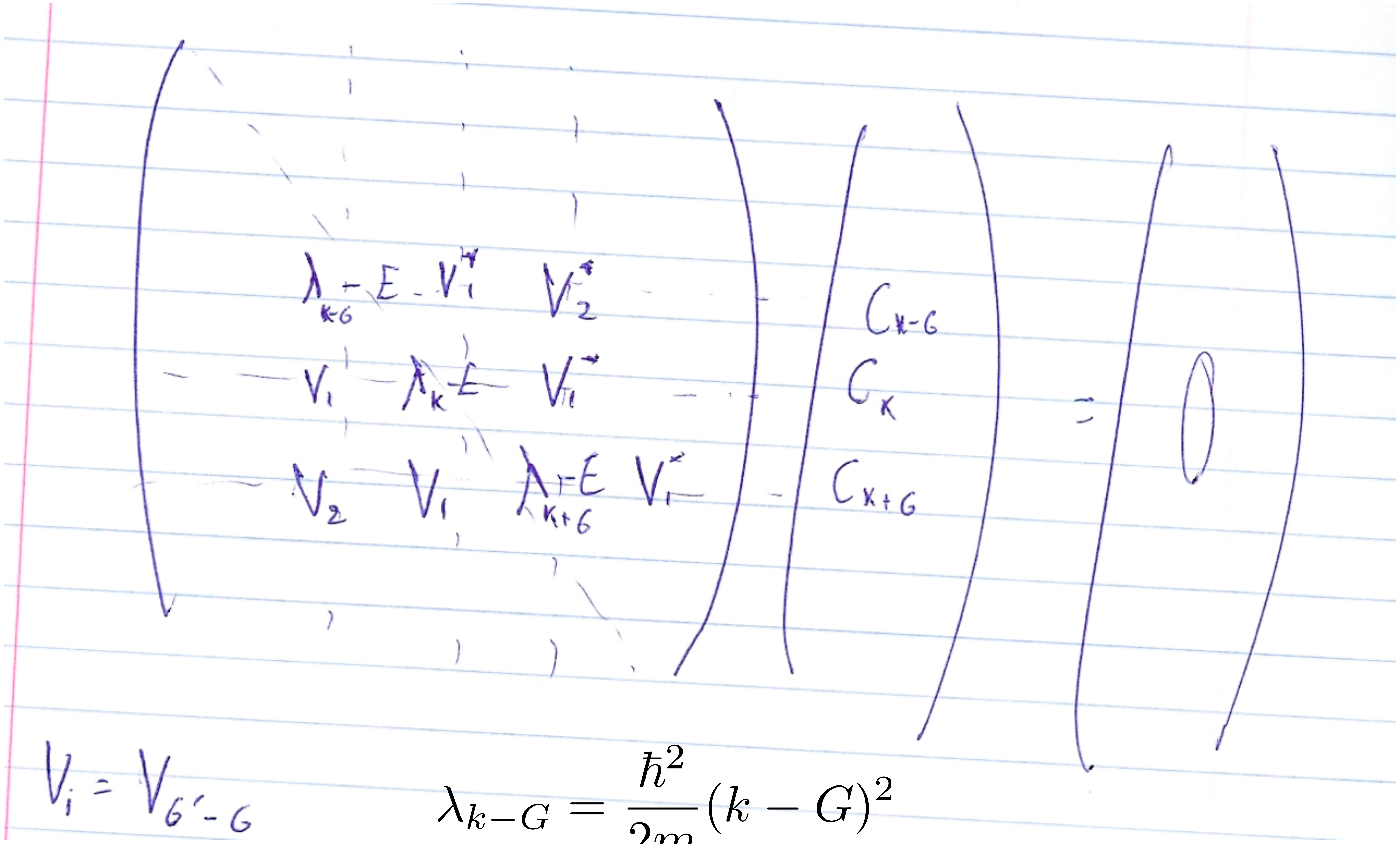
$$H|\psi\rangle = E|\psi\rangle$$

where $$H = \begin{pmatrix} \left(\vec{k}+\vec{G}_1\right)^2 & V\left(\vec{G}_1-\vec{G}_2\right) & \cdots & V\left(\vec{G}_1-\vec{G}_n\right) \\ V\left(\vec{G}_2-\vec{G}_1\right) & \left(\vec{k}+\vec{G}_2\right)^2 & \cdots & V\left(\vec{G}_2-\vec{G}_n\right) \\ \vdots & \vdots & \ddots & \vdots \\ V\left(\vec{G}_n-\vec{G}_1\right) & V\left(\vec{G}_n-\vec{G}_2\right) & \cdots & \left(\vec{k}+\vec{G}_n\right)^2 \end{pmatrix}$$ and $$|\psi\rangle = \begin{pmatrix} c\left(\vec{k}+\vec{G}_1\right) \\ c\left(\vec{k}+\vec{G}_2\right) \\ \vdots \\ c\left(\vec{k}+\vec{G}_n\right) \end{pmatrix}$$

units: Rydberg atomic units: $\hbar=2m=e^2/2=1$

$$\phi_k(r) = \sum_G C_{k-G} e^{i(k-G)r}$$

$$\left(\frac{\hbar^2}{2m}(k-G)^2 - E\right)C_{k-G} + \sum_{G'} V_{G'-G} C_{k-G'} = 0$$



$$\begin{pmatrix} \ddots & & & & & \\ \cdots & \lambda_{k-G}-E & V_1^* & V_2^* & \cdots & \\ \cdots & V_1 & \lambda_k-E & V_1^* & \cdots & \\ \cdots & V_2 & V_1 & \lambda_{k+G}-E & V_1^* & \cdots \\ & & & & & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ C_{k-G} \\ C_k \\ C_{k+G} \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \end{pmatrix}$$

$V_i = V_{G'-G}$

$$\lambda_{k-G} = \frac{\hbar^2}{2m}(k-G)^2$$

• Lecture 9 : Bloch's Theorem (Cont.)

• Summary Bloch's Th :

. Form 1 $$\psi_{nk}(x) = e^{ikx}\, u_{nk}(x) \;\Big/\; u_{nk}(x+R) = u_{nk}(x)$$

. Form 2 : $$\psi_{nk}(x+\underset{\sim}{R}) = e^{ikR} \cdot \psi_{nk}(x)$$

DLV

. We associate k to our translational symmetry, it is our quantum number ($k \longleftrightarrow l, m$)

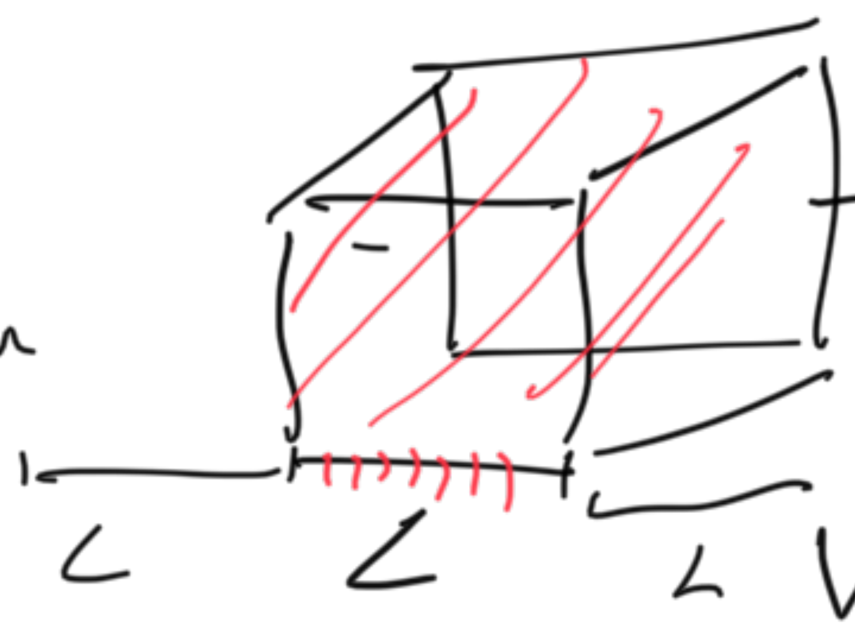
solid atom

→ What about "n" (principal quantum number ? → band index)

• Periodic Boundary conditions

→ In Sommerfield free electron

k's quantized ⟶



→ e^- confined to volume $V = L^3$

$\epsilon_k = \frac{\hbar^2 k^2}{2m}$; $\boxed{\Delta k_i = \frac{2\pi}{L}}$

• Let's do the same for an infinite crystalline solid:

we will apply periodic boundary conditions as follows

• Let there be N primitive unit cells : $N = \underbrace{N_1 \times N_2 \times N_3}_{\vec{x}\quad \vec{y}\quad \vec{z}}$

Total # of cells in crystal

$N_1 \times a_1 = L$; $N_2 \times a_2 = L$; $N_3 \times a_3 = L$ $\quad V_T = L^3$

→ $\Psi_k(\vec{r} + N_i \vec{a}_i) = \Psi_k(\vec{r})$ BVK PBC

→ Apply Bloch's Th. to Ψ_k

$$\rightarrow \psi_{nk}(\vec{r}+\underbrace{N_i \vec{a}_i}) = \underbrace{e^{i\vec{k} N_i \vec{a}_i}}\psi_{nk}(r)$$

$$e^{i\vec{k} N_i \vec{a}_i} = 1 \Rightarrow \boxed{\vec{k} = \sum_i x_i \vec{b}_i}$$

→ Note $\vec{k}$ is a wave vector and can always be expanded by the RL Vectors, x_i not necessarily an integer.

$$e^{i2\pi x_i N_i} = 1 \Rightarrow \boxed{x_i = \frac{m_i}{N_i},\ m_i \text{ integer}}$$

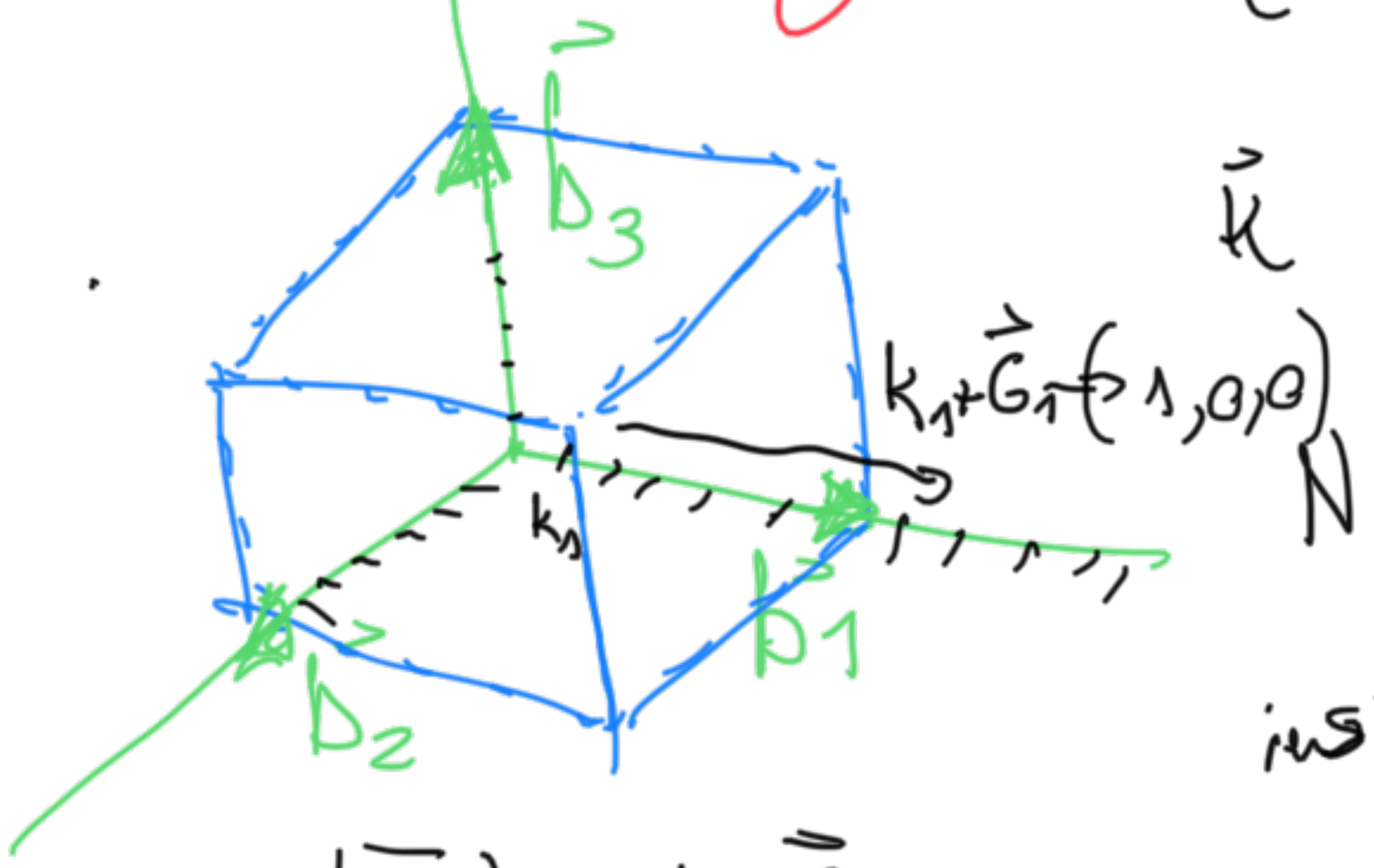
Therefore : $\boxed{\vec{k} = \sum_i \frac{m_i}{N_i}\vec{b}_i,\ m_i \text{ integer}}$

$k \to 0 \to \vec{b}_i$

$\vec{K}$ is a real vector (it can be complex, as we will see, only when Translational sym. is broken, like surfaces or impurity states...)

· Understanding $\vec{k}$

(let's choose a cubic cell for simplicity)



$\vec{k}$ is within the cell if $0 \leq m_i \leq N_i$

$N = N_1 \times N_2 \times N_3 = \#$ of different k's allowed inside this cell

$$\boxed{\bar{k}} \leftrightarrow k+\vec{G}$$

$N = \#$ unit cells in real space

$N = \#$ allowed $\vec{k}$ values in a reciprocal unit cell

$N = \#$ allowed $\vec{k}$ values in the 1st Brillouin zone

· Volume per k point $$\Delta\vec{k} = \frac{V^{1st\,BZ}}{N} = \frac{1}{N}\,\vec{b}_1\cdot(\vec{b}_2\times\vec{b}_3) = \frac{1}{N}\,\frac{8\pi^3}{V_p}$$

V_p = volume of The primitive unit cell

$N \cdot V_p = V$ = Total volume of The crystal

$\Delta \vec{k} = \frac{8\pi^3}{V}$; $\omega(k) = \frac{1}{\Delta k} = \frac{V}{8\pi^3}$ = density of $\vec{k}$ points

This is The same expression we found in The Sommerfield model

$$\sum_k f(k) = \int d^3k \, \omega(k) f(k) = \frac{V}{8\pi^3} \int d^3k \, \underline{f(k)}$$

- Let's now use what we know To derive The eq. for The eigenstates $\psi_{nk}(r)$ of e^- in a periodic potential

·Crystal with $N = N_1 \times N_2 \times N_3$ unit cell + BVK periodic boundary conditions.

→ We know that any function with the periodicity of the Bravais lattice can be expanded as a linear combination of plane waves that satisfy the boundary condition aka a Fourier Transform or expansion with a set of $\{\vec{G}\}$ vectors such as $\vec{G}_{\{n\}} = \sum_i n_i \vec{b}_i$, $\{n\} = (n_1, n_2, n_3)$

The periodic potential then : $\boxed{U(r) = \sum_{\vec{G}}^{G_{max}} U_G \, e^{i\vec{G}\vec{r}}}$

with $U_G = \dfrac{1}{V_p} \displaystyle\int_{V_p} dr \, e^{-iGr} \, U(r)$ → Fourier coefficients

Note that the periodic potential is defined up to a constant, we fix our constant (gauge) such as $\langle U(r) \rangle_{V_p} = 0$

$$\Rightarrow U_0 = \frac{1}{V_p} \int d\vec{r}\, U(\vec{r}) = 0$$

- As $U(\vec{r})$ is real we know that the Fourier coefficients need to satisfy $\boxed{U_{-G} = U_G^*}$

- We can also impose inversion symmetry (not needed, just for simplicity)

$$\Rightarrow U(\vec{r}) = U(-\vec{r}) \Rightarrow U_G = U_{-G} = U_G^* \Rightarrow \underline{\text{Real}}$$

→ What about the form of $\psi(r)$?

We know that $\psi(r)$ needs to satisfy the BVK PBC.

$$\boxed{\psi(r) = \sum c_{\vec{q}}\, e^{i\vec{q}r}} \quad \text{with} \quad \boxed{\vec{q} = \sum_i \frac{m_i}{N_i}\vec{b}_i}$$

We can expand any function obeying PBC in a set of plane waves with w.v $\vec{q}$.

$$\rightarrow H = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + U(r) \quad \leftarrow \text{apply this to our WF}$$

$$\boxed{H\psi(r) = \boxed{\epsilon}\,\psi(r)}$$

- $$-\frac{\hbar^2}{2m}\nabla^2\left[\sum_q C_q e\right] = \sum_q \frac{\hbar^2 q^2}{2m} \boxed{C_q} e$$

- $$V(r)\,\psi(r) = \sum_G V_G e^{iGr} \sum_q C_q e^{iqr} = \sum_{Gq} V_G C_q e^{i(G+q)r}$$

→ change of variable $\boxed{q' = G+q}$ $\quad q = q' - G$

$$V(r)\,\psi(r) = \sum_{G,q'} V_G C_{q'-G} e^{iq'r} = \sum_{G',q} V_{G'} C_{q-G'} e^{iqr}.$$

rename

$q' \rightarrow q$

$G \rightarrow G'$

Total sch. eq:

$$\sum_{q} e^{iqr} \underbrace{\left\{ \left(\frac{\hbar^2 q^2}{2m} - \varepsilon \right) C_q + \sum_{G'} U_{G'} C_{q-G'} \right\}}_{\alpha_q} = 0$$

↑ This is a linear combination of w's with coefficient α_q

→ as PW are orthogonal, a linear combination of PW's = 0 only if all coefficients = 0 $\Longrightarrow \alpha_q = 0 \;\; \forall q$

$$\boxed{\left(\frac{\hbar^2 q^2}{2m} - \varepsilon \right) C_q + \sum_{G'} U_{G'} C_{q-G'} = 0}$$

eq's for α_q = # $\vec{G}$ vectors in my expansion.

let's make $\boxed{\vec{q} = \vec{k} - \vec{G}}$ → choice such that $\vec{G}$ is a given RLV that ensures that $\vec{k}$ is in the 1st BZ. We can always do this! i.e for any q vector we can find a G that makes $\vec{k} = \vec{q} + \vec{G}$ being in the 1st BZ. Note {- or +} does not make a difference $\left(+G = -(-\vec{G}) \right)$ .... }

.So we can rewrite the eq. for the coefficients

$$\left(\frac{\hbar^2}{2m}\left(k-\boxed{G}\right)^2 - \varepsilon\right) C_{k-G} + \underline{\sum_{G'}^{G_{max}} V_{G'}\, C_{k-\underline{G}-G'}} = 0$$

As G, G' are RLV $G-G' = \text{RLV} \Rightarrow G' \rightarrow G-G'$

$$\left(\frac{\hbar^2}{2m}(K-G)^2 - \varepsilon\right) C_{k-G} + \sum_{G'} \boxed{V_{G-G'}}\, C_{k-G'} = 0$$

$G \quad |G-G'| \quad k-G$

→ For a fixed $\vec{k}$ we have G different equations

This is a hermitian eigenvalue problem in the basis e^{iGr} with G being all RLV. $(H-\varepsilon)\psi = 0$

- For each k in the 1st BZ we have {G} different solutions;

How many G's?? → as many as we want, the larger G_{max} the more accurate our expansion.

The Band index n corresponds to each of these solutions, we will have as many bands as PWs in our basis expansion.

. Note that we wrote $\psi_q = \sum_q C_q e^{iqr}$; Here we have ended with an eq. that only allows coefficients $C_k, C_{k-G}, C_{k-G'}, C_{k-G''} \dots$

$$\boxed{\psi(r) = \sum_G C_{k-G} e^{i(k-G)r} = e^{ikr}\left(\sum_G C_{k-G} e^{-iGr}\right)}$$

This is a Bloch Function with $U(r) = \sum_G C_{k-G} e^{-iGr}$

Hence we have proven that $\psi(r)$, the eigenstates of e^- in a periodic potential need to be Bloch functions.

So Beautifull and Simple !

Important clarifications about k

1.- $\vec{k}$ is the crystal momentum, $\vec{k}$ is not proportional to the electronic momentum

Bloch WF are no longer eigenfunctions of the momentum operator

$$\frac{\hbar}{i}\vec{\nabla}\psi_{nk} = \frac{\hbar\vec{\nabla}}{i}\left(e^{ikr}u(r)\right) = \hbar k\psi_{nk} + e^{ikr}\frac{\hbar}{i}\vec{\nabla}u_{nk}(r)$$

$\hbar\vec{k}$ is the crystal momentum, it's the generalization of $\vec{p}$ to a periodic potential

2.- $\vec{k} \rightarrow$ in the 1st BZ, any k can be expressed in the 1st BZ $k' = k + G$

3.- Bloch's Th: $\psi_{nk}(r+R) = e^{ikR}\,\psi_{nk}(r)$ can also be seen as:

$$\psi_{nk}(r) = e^{ikr}\,u_{nk}(r) \quad \text{with} \quad u_{nk}(r+R) = u_{nk}(r)$$

$$\text{because} \quad \psi_{nk}(r) = \underbrace{\left(u_{nk}(r)\,e^{-i\vec{G}r}\right)}_{\text{periodic because } e^{i\vec{G}\vec{R}} = 1} e^{i(k+G)r}$$

This implies that $\vec{k}$ is defined up to the addition of an arbitrary RL vector $\vec{G}$

. A way to avoid this arbitrarity is to use the reduced zone scheme : choose k in the 1st BZ and then each $\vec{k}$ is unique, so there are only N different k's

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Band structure :

k fixed, k in 1st Brillouin zone :

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi_{nk}(r) = \varepsilon_{n,k}\,\psi_{nk}(r)$$

$\psi \qquad {}^{ikr} \qquad (r)$

$\psi_{nk} = e \quad u_{nk}(r)$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{nk}(r) = e^{ikr}\left(-k^2+2i\vec{k}\vec{\nabla}+\vec{\nabla}^2\right)u_{nk}(r)\left(\frac{-\hbar^2}{2m}\right)$$

$$V(r)\psi_{nk} = e^{ikr}\,V(r)\,u_{nk}(r)$$

$* \; V(r) = \sum_G e^{iGr} V_G$

and this commutes with e^{ikr}

$\Longrightarrow$

$$-\frac{\hbar^2}{2m}\left[\nabla^2+2i\vec{k}\vec{\nabla}-\vec{k}^2\right]u_{kn}(r) + V(r)\,u_{kn}(r) = \varepsilon_{k,n}\,u_{nk}(r)$$

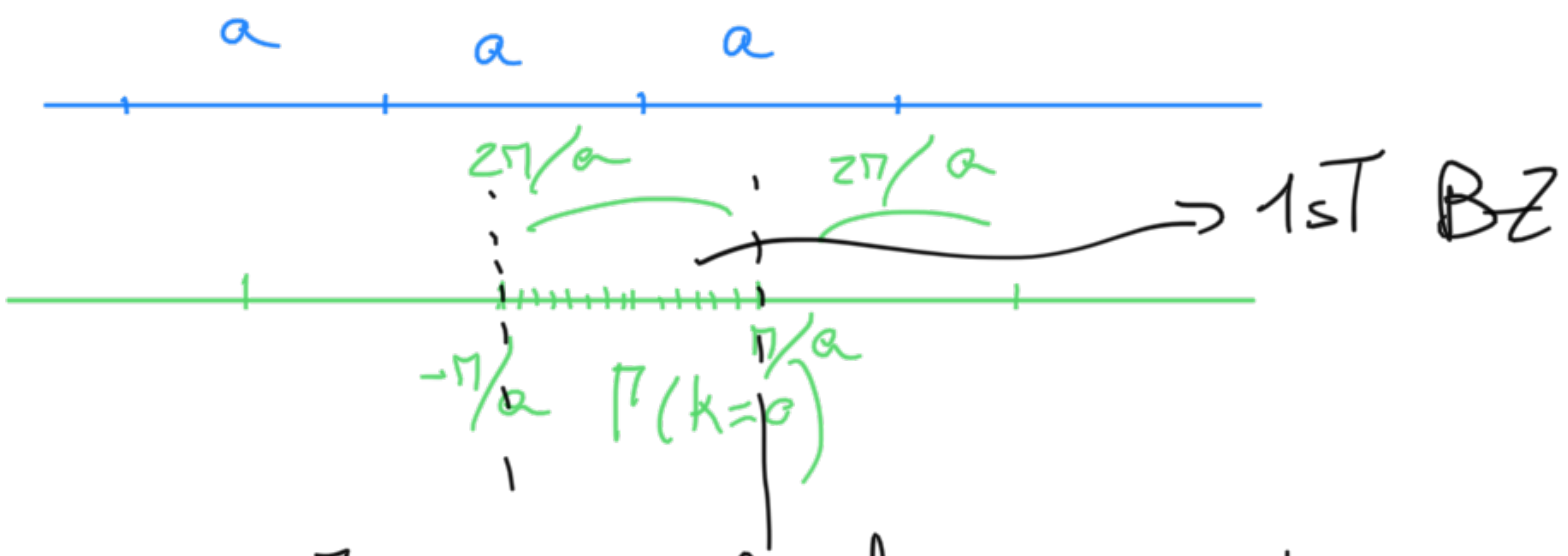
$\rightarrow H_k \quad u_{nk}(r) = \varepsilon_{kn}\,u_{nk}(r) \rightarrow H_k$ is an effective Hamiltonian for $u_{nk}(r)$

k is a parameter in the Hamiltonian. Given k, we get

a set of solutions with a discrete set of eigenvalues (# of G's)
That we label by n ⟶ Band index

Since H_k is a smooth function of k $\Rightarrow \mathcal{E}_{n,k} \equiv \mathcal{E}_n(k)$
is a smooth function of k ⇒ Band

• Ex 1D Band structure



$k = \frac{m}{N} b = \frac{m}{N} \frac{2\pi}{a}$ Reduced zone $-\frac{N}{2} < m < \frac{N}{2}$

$H \, u = \mathcal{E}(k) u$

$H_k U_{nk} = \mathcal{E}_n(k) U_{nk}$

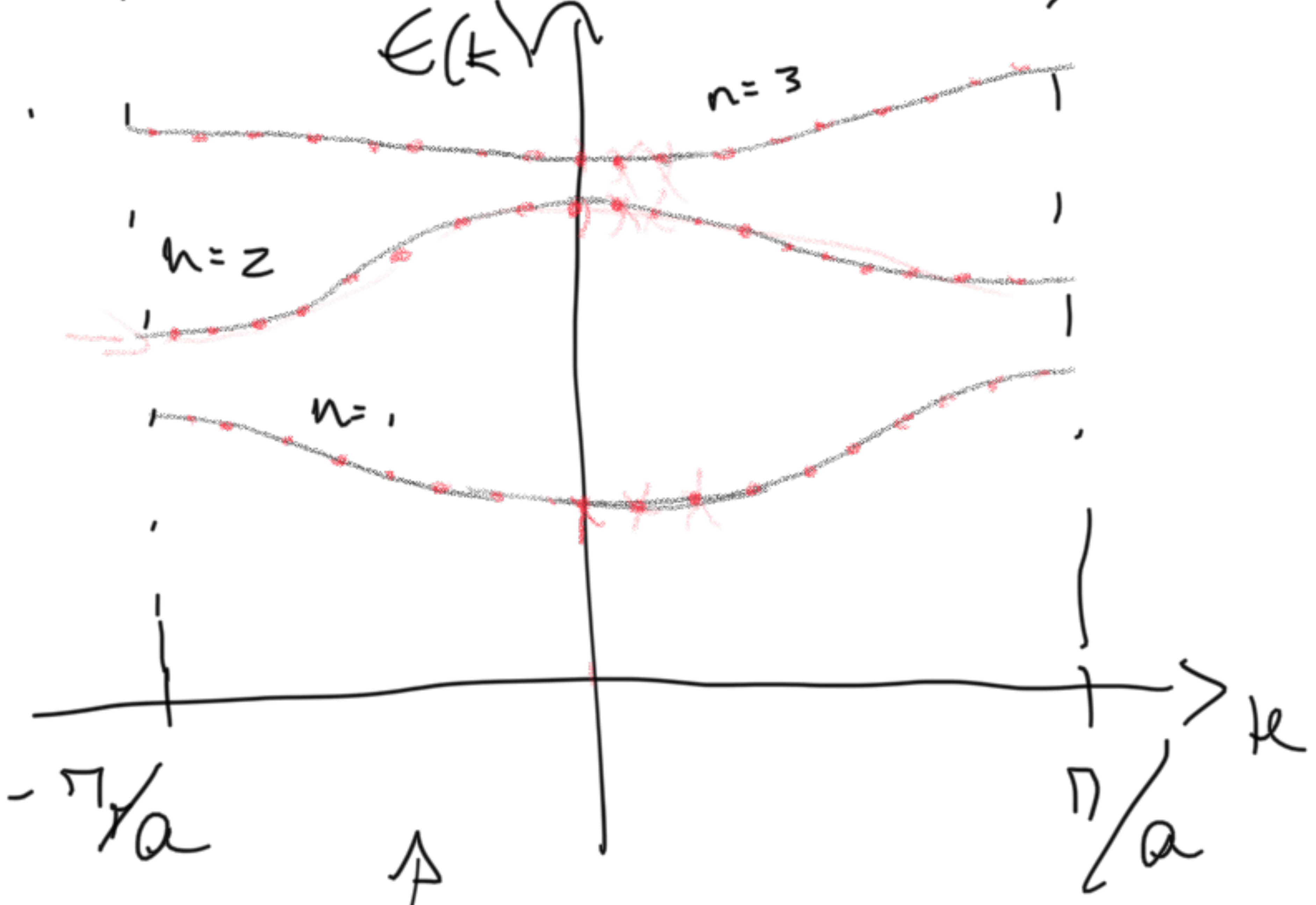
$\rightarrow k = 0 \ (\Gamma) \qquad H_0 U_{n0} = \mathcal{E}_{n0} U_{n0}$

$\rightarrow k = k_1 = \frac{1}{N}\frac{2\pi}{a} \qquad H_1 U_{n1} = \mathcal{E}_{n1} U_{n1}$

.... For each k we solve a different eigenvalue problem.

→ How bands appear?

→ Plot $\mathcal{E}_{n,k}$



Band dispersion ($\mathcal{E}_n(\vec{k})$)

→ Regions where $\mathcal{E}_n(k)$ does not exist for all k's ⇒ energy gaps

In 3D $\varepsilon_n(\vec{k})$ for fixed $|\vec{k}|$ $\Longrightarrow$ 3D surface (can be very complicated. Hence we plot $\varepsilon_n(\vec{k})$ along high symmetry lines in the 1st BZ

. Note that $V_n(k) = \frac{1}{\hbar} \nabla_k \varepsilon_n(k) \equiv$ velocity of a Bloch state ψ_{nk}

$\rightarrow$ stationary levels with well defined $\vec{v}$.

Nearly Free electrons NFE

$$\psi_k = \sum_G C_{k-G}\, e^{i(k-G)r}$$ ⟵ A Bloch WF

These states satisfy the equation of e^- in a periodic potential

$$\left[\frac{\hbar^2}{2m}(k-G)^2-\varepsilon\right]C_{k-G}+\sum_{G'}V_{G'-G}\,C_{k-G'}=0 \quad (1)$$

This is the eq. that we solve to compute the eigenvalues for each k point.

→ For fixed k there are G equations like (1)

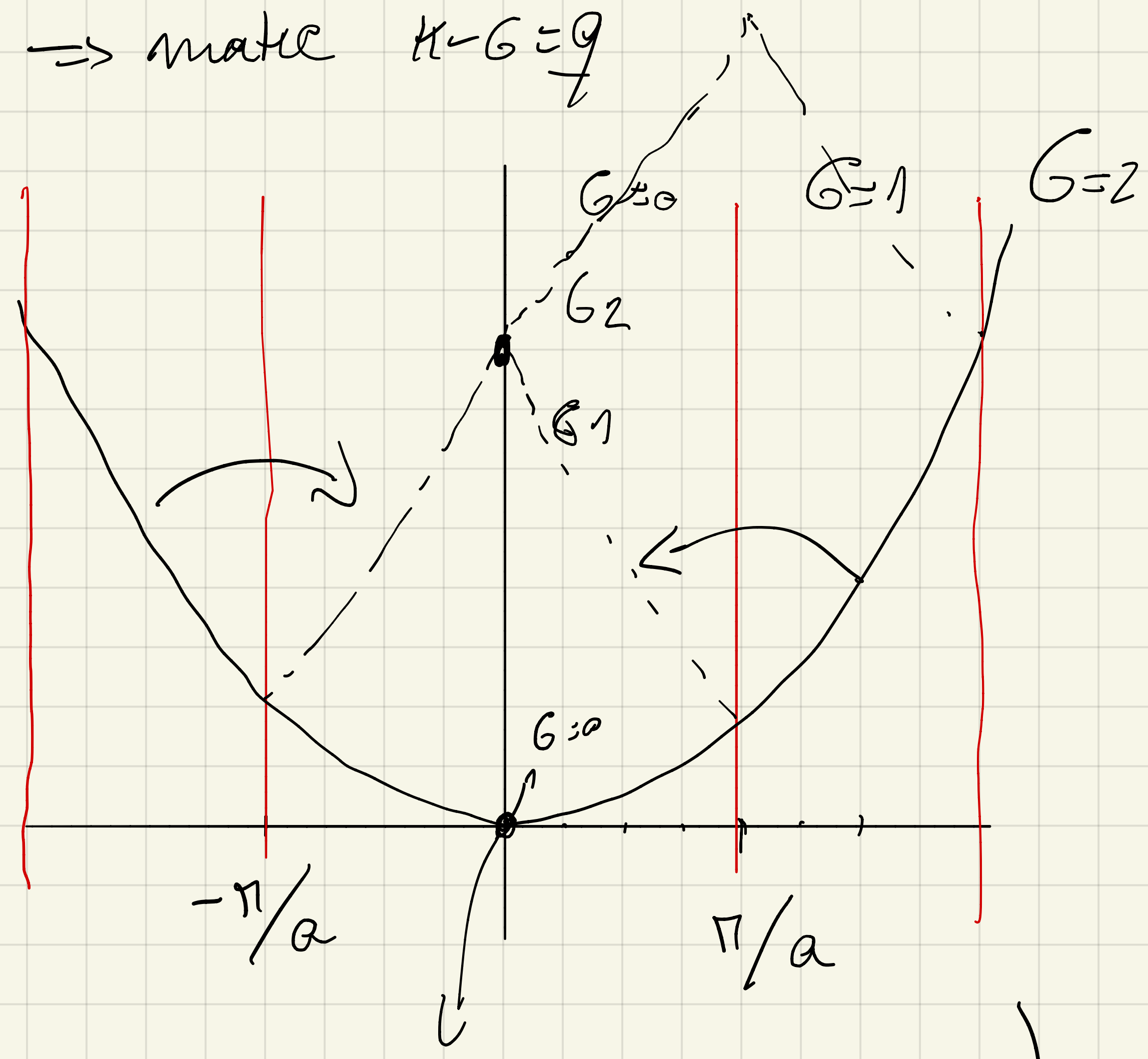
n = # of eigenstates = # G's or plane waves in the expansion.

. Free e^- : $U(r)=\sum_G U_G\, e^{iGr} \Rightarrow U_0=V(r)=0$

Then (1) $\Rightarrow \left(\frac{\hbar^2}{2m}(k-G)^2-\varepsilon\right)C_{k-G}=0$

$\mathcal{E}(k-G) = \frac{\hbar^2}{2m}(k-G)^2$ => make $k-G=q$

$\mathcal{E}(q) = \frac{\hbar^2}{2m} q^2$

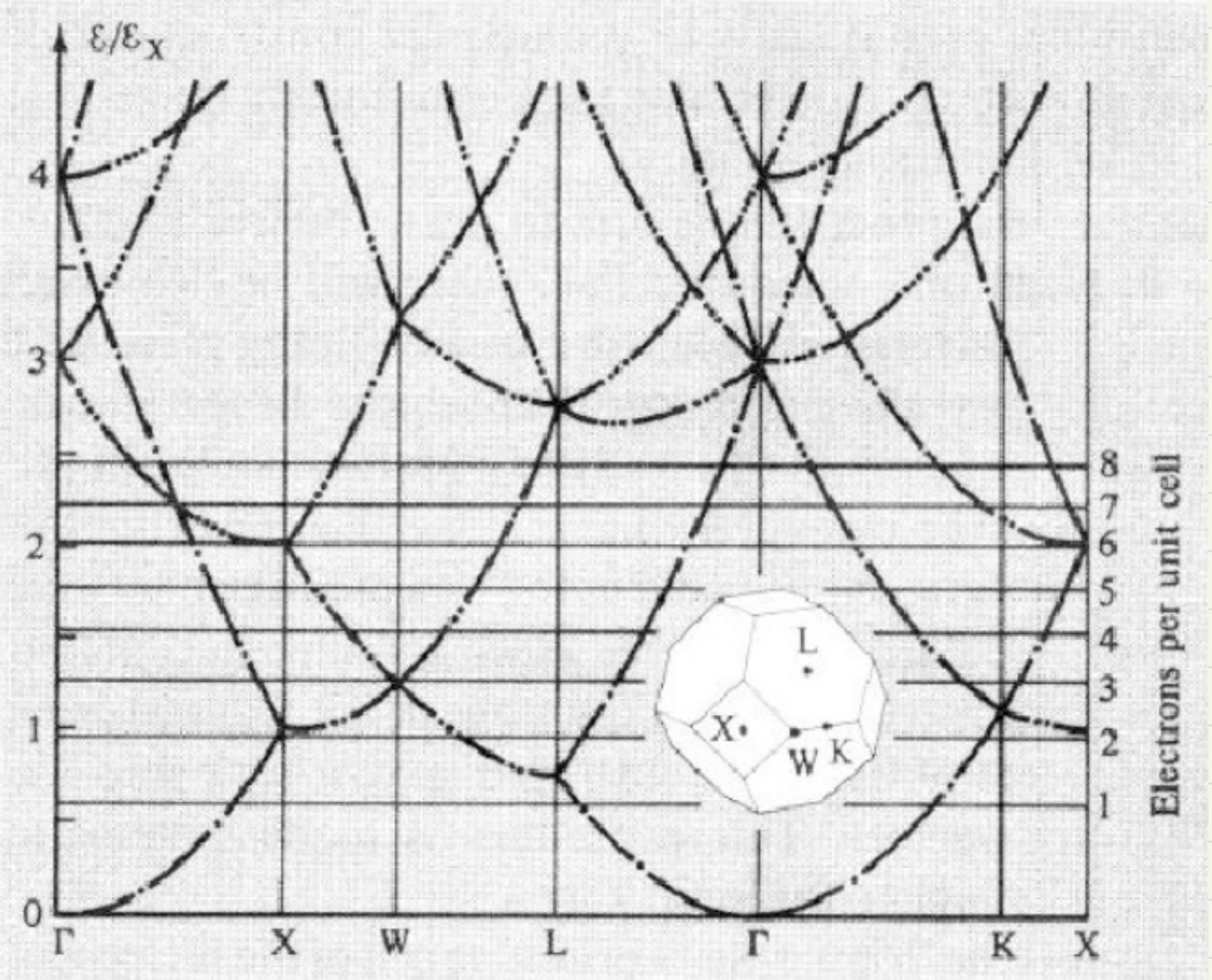


$G=0 \quad \frac{\hbar^2 k^2}{2m} \quad k \in (0, \pi/a)$

$G=1\,(\pi/a) \rightarrow \mathcal{E} = \frac{\hbar^2 (k-\pi/a)^2}{2m}$

$k \in (0, \pi/a)$

→ This is the free electron solution



Crystal structures from x-ray diffraction

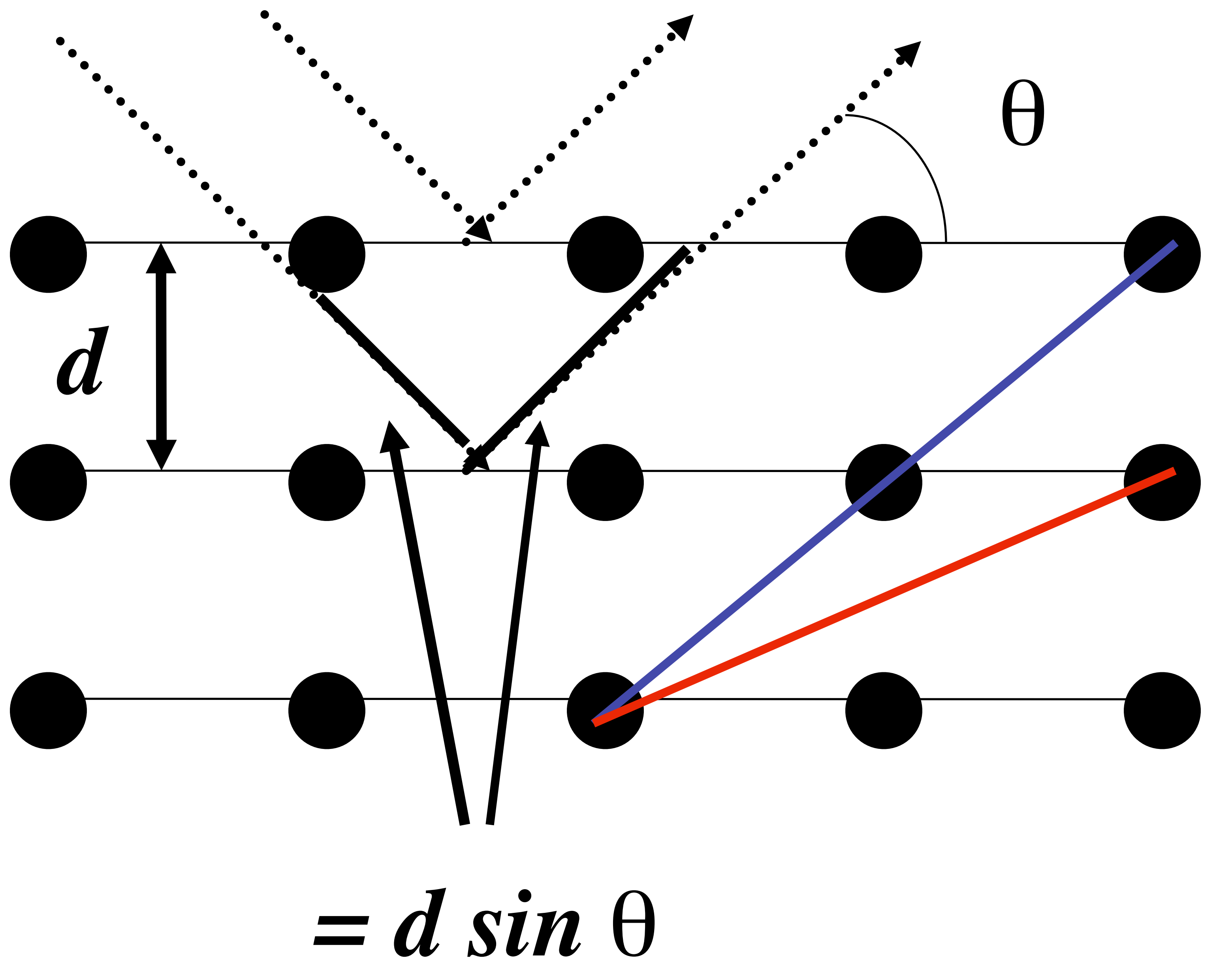
Determination of crystal structure

- In 1913 W. H. and W. L. Bragg found crystalline gave characteristic patterns of reflected x-rays.

- Assuming specular reflection off lattice planes.
- The condition for constructive interference becomes

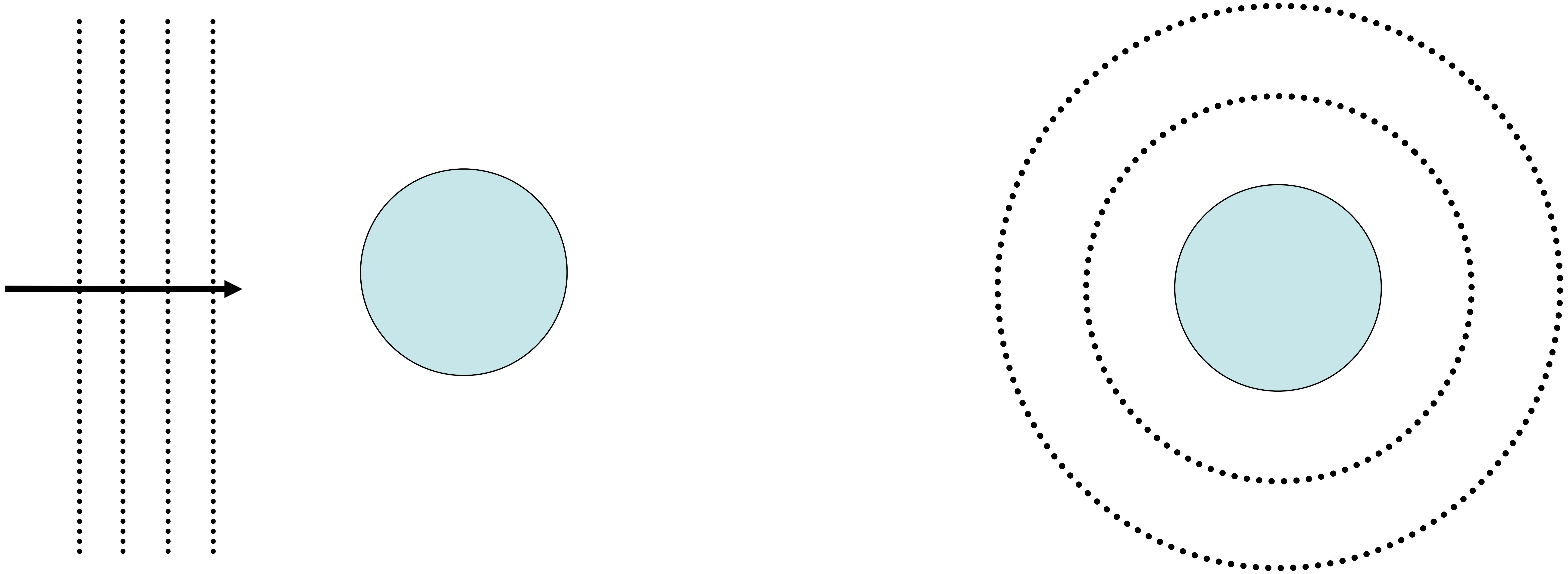
  $2d \sin \theta = n\lambda$

- This is known as the Bragg condition



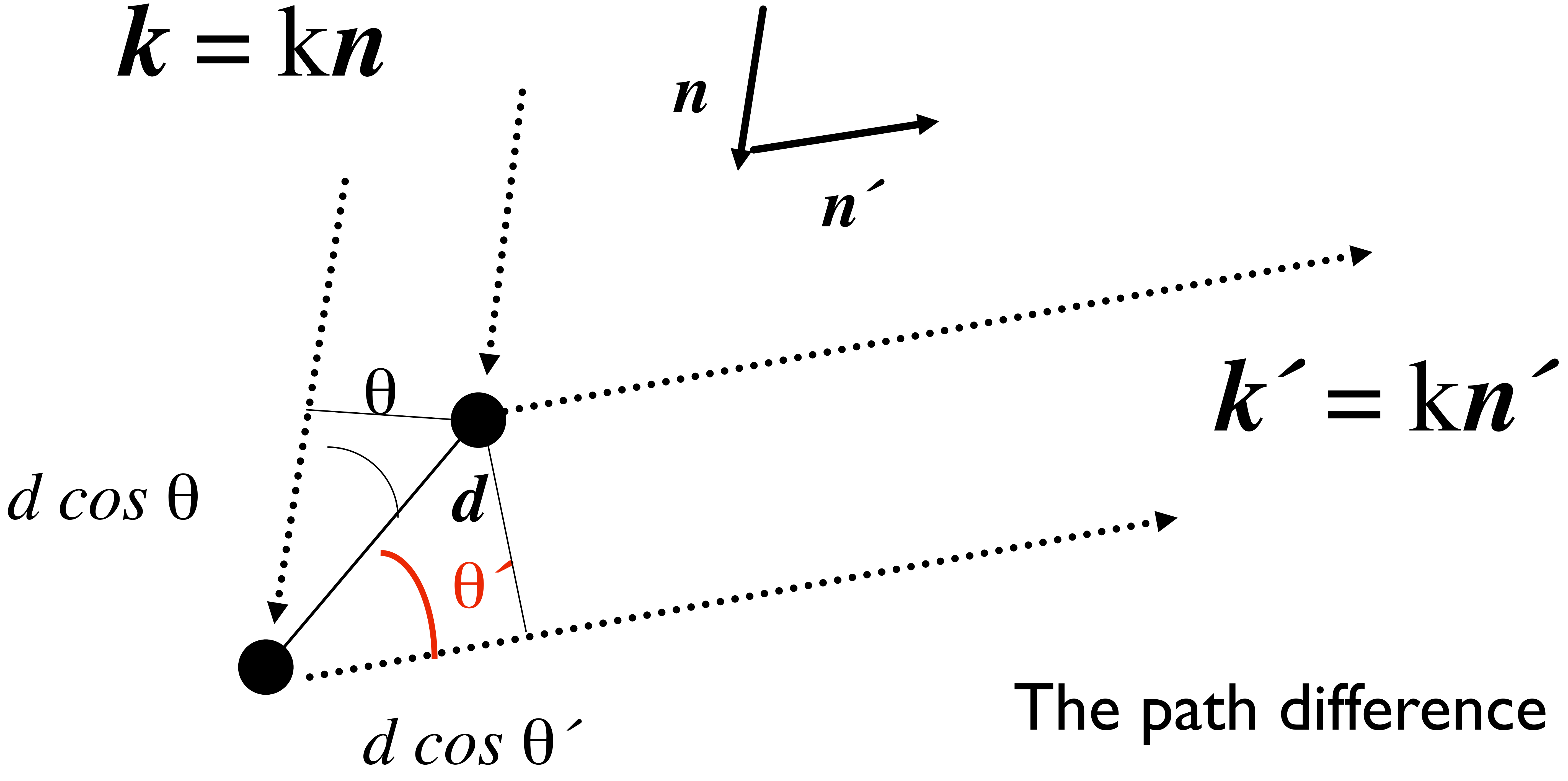
The Von Laue formulation

- Doesn’t assume specular reflection
- No sectioning by planes
- Rather, at each point on the Bravais lattice the incident ray is allowed to be scattered in all directions



Von Laue Formulation

First, consider only two scatterers.



$k = 2\pi/\lambda$

$k´ = 2\pi/\lambda$

The path difference is then

$d \cos \theta + d \cos \theta´ = \mathbf{d} \bullet (\mathbf{n} - \mathbf{n}´)$,

Constructive interference is,

$\mathbf{d} \bullet (\mathbf{n} - \mathbf{n}´) = m\lambda$

Von Laue Formulation

- With an array of scatterers; one at each point of the Bravais lattice
- The last slide must hold for each ***d*** that are Bravais lattice vectors, so

$$\boldsymbol{R} \bullet (\boldsymbol{k} - \boldsymbol{k}') = 2\pi \mathrm{m}$$

or

$$e^{i\boldsymbol{R} \bullet (\boldsymbol{k} - \boldsymbol{k}')} = 1!!!!$$

Compare to the definition for the reciprocal lattice!

The Laue condition - *constructive interference will occur provided that the change in wave vector,* ***K*** *=* ***k´*** *-* ***k****, is a vector in the reciprocal lattice.*

Elastic scattering: Both incident and scattered wave vectors have the same magnitude.

Lets express it as a function of the incident vector

$$|\vec{k}| = |\vec{k'}| = k$$

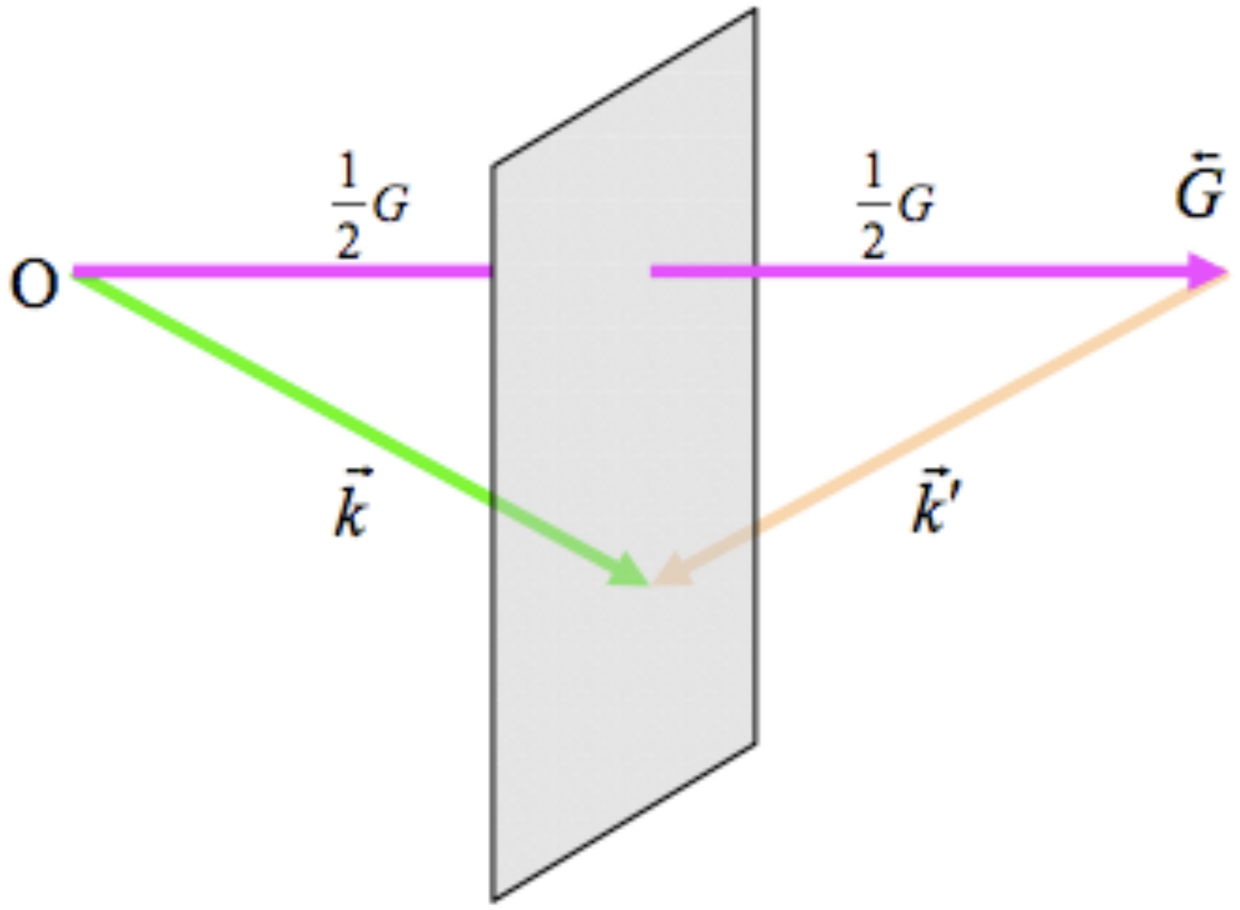
$$\vec{k'} = \vec{G} + \vec{k};$$

$$|\vec{k'}| = |\vec{G} + \vec{k}| \longrightarrow k = |\vec{G} + \vec{k}|$$

$$k^2 = G^2 + k^2 + 2\vec{G}\vec{k} \longrightarrow G^2 + 2\vec{G}\vec{k} = 0 \longrightarrow \vec{G} + 2\vec{k} = 0$$

$$\vec{k}\frac{\vec{G}}{G} = \frac{1}{2}G$$

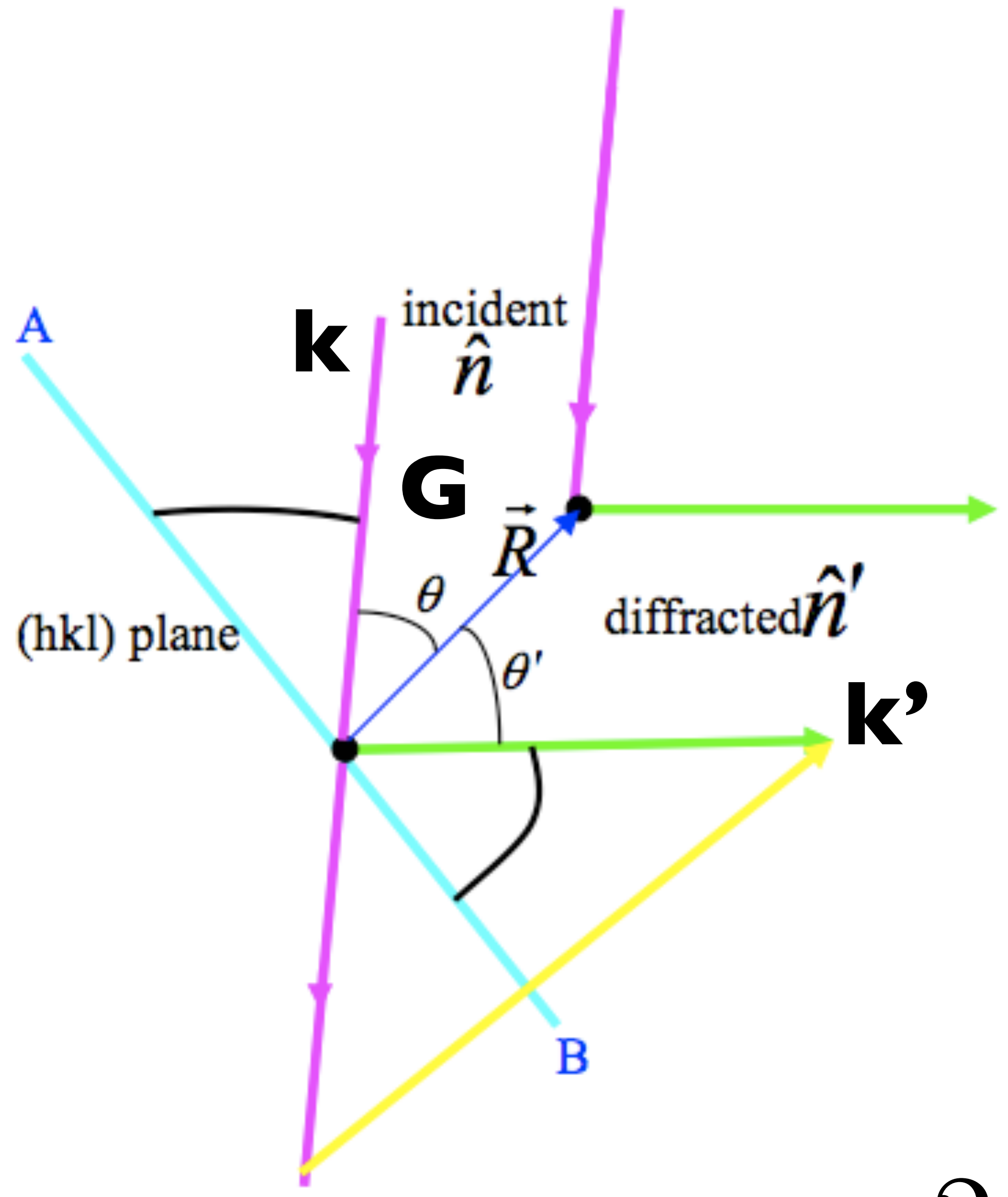
$$\vec{k}\vec{n} = 1/2G \qquad with \qquad \vec{n} = \frac{\vec{G}}{G}$$



Which means that the component of the incident wave vector **K** along the reciprocal lattice vector **G** must be 1/2 G.

Equivalence of Braggs and Von Laue Formulations:

The key is to notice that the scattering is elastic, therefore the specular reflection condition in Bragg translates to the condition that the incident wave vector **k** along the reciprocal lattice vector **G** (**G**=difference between incident and reflected wave vectors) must be 1/2G.



G₀ is the shortest RL vector in the **G** direction.

$$|\vec{G}_0| = \frac{2\pi}{d}; G = \frac{2\pi}{d}n$$

$$2ksin\theta = \frac{2\pi}{d}n; k = \frac{2\pi}{\lambda} \longrightarrow 2dsin\theta = n\lambda$$

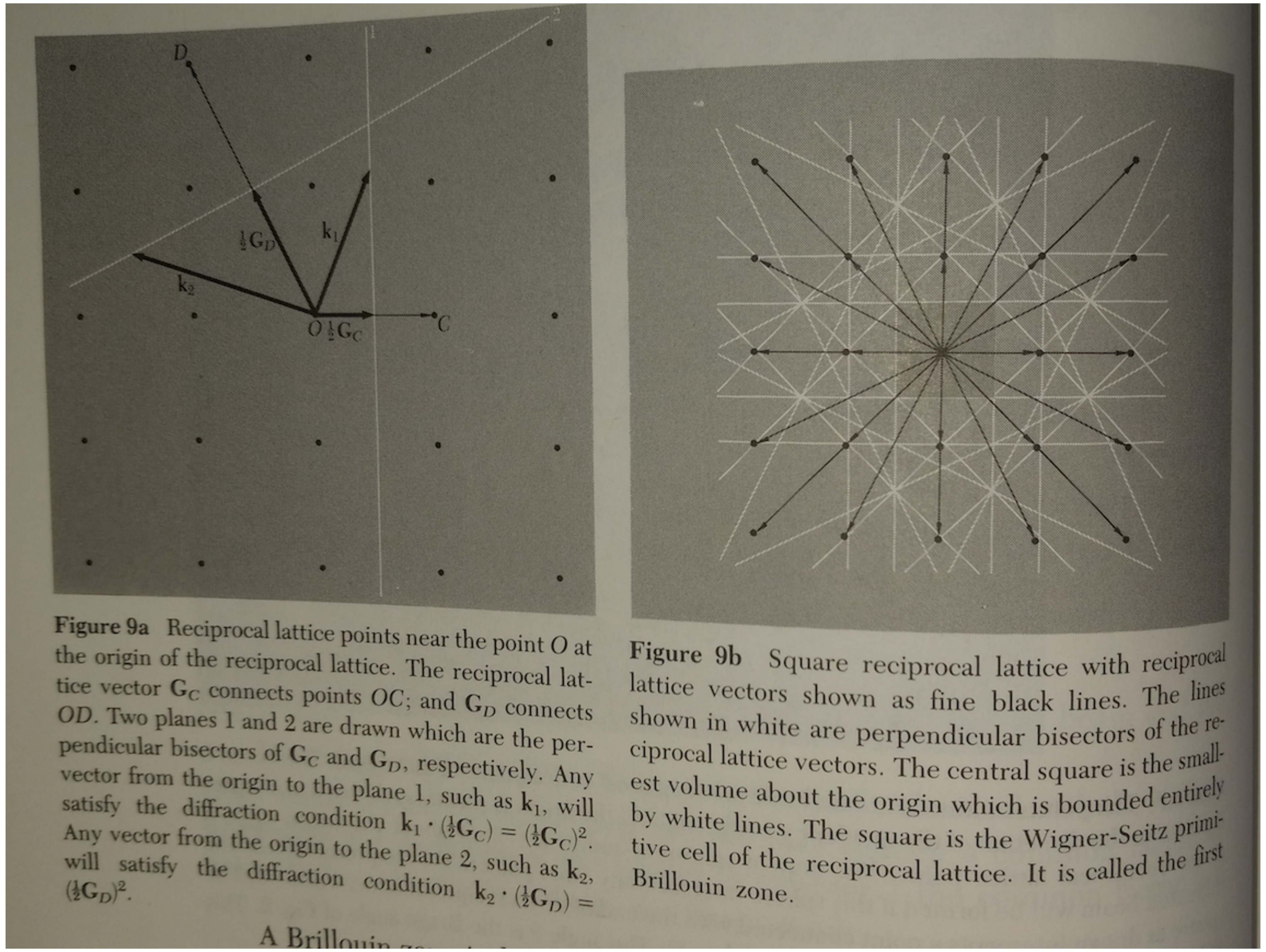


Figure 9a Reciprocal lattice points near the point O at the origin of the reciprocal lattice. The reciprocal lattice vector $\mathbf{G}_C$ connects points OC; and $\mathbf{G}_D$ connects OD. Two planes 1 and 2 are drawn which are the perpendicular bisectors of $\mathbf{G}_C$ and $\mathbf{G}_D$, respectively. Any vector from the origin to the plane 1, such as $\mathbf{k}_1$, will satisfy the diffraction condition $\mathbf{k}_1 \cdot (\frac{1}{2}\mathbf{G}_C) = (\frac{1}{2}\mathbf{G}_C)^2$. Any vector from the origin to the plane 2, such as $\mathbf{k}_2$, will satisfy the diffraction condition $\mathbf{k}_2 \cdot (\frac{1}{2}\mathbf{G}_D) = (\frac{1}{2}\mathbf{G}_D)^2$.

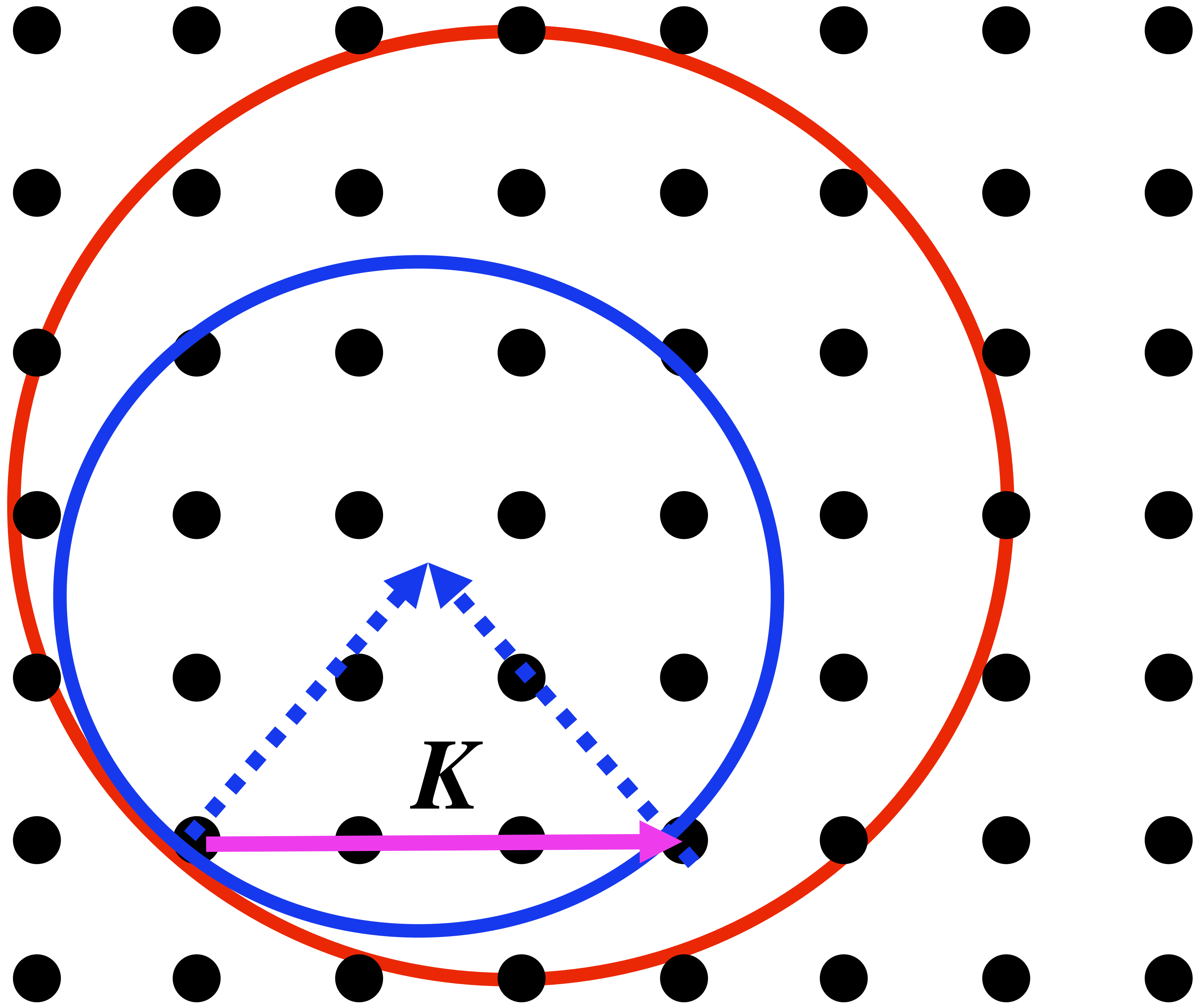
Figure 9b Square reciprocal lattice with reciprocal lattice vectors shown as fine black lines. The lines shown in white are perpendicular bisectors of the reciprocal lattice vectors. The central square is the smallest volume about the origin which is bounded entirely by white lines. The square is the Wigner-Seitz primitive cell of the reciprocal lattice. It is called the first Brillouin zone.

A Brillouin

Planes normal to vectors G at their midpoint are zone boundary planes.
An x-ray beam in the crystal will be diffracted if it satisfy: **k***(1/2 **G**)=((1/2 G)^2
The diffracted beam beam will be in the direction **k**-**G**. The Brillouin construction has all the wave vectors **k** that can be diffracted by the crystal.

Ewald Construction

Condition for constructive interference, $\boldsymbol{K} = \boldsymbol{k}' - \boldsymbol{k}$, is a vector of the reciprocal lattice.



Note this is the RECIPROCAL lattice

Back to the NFE model

1-dimensional NFE model

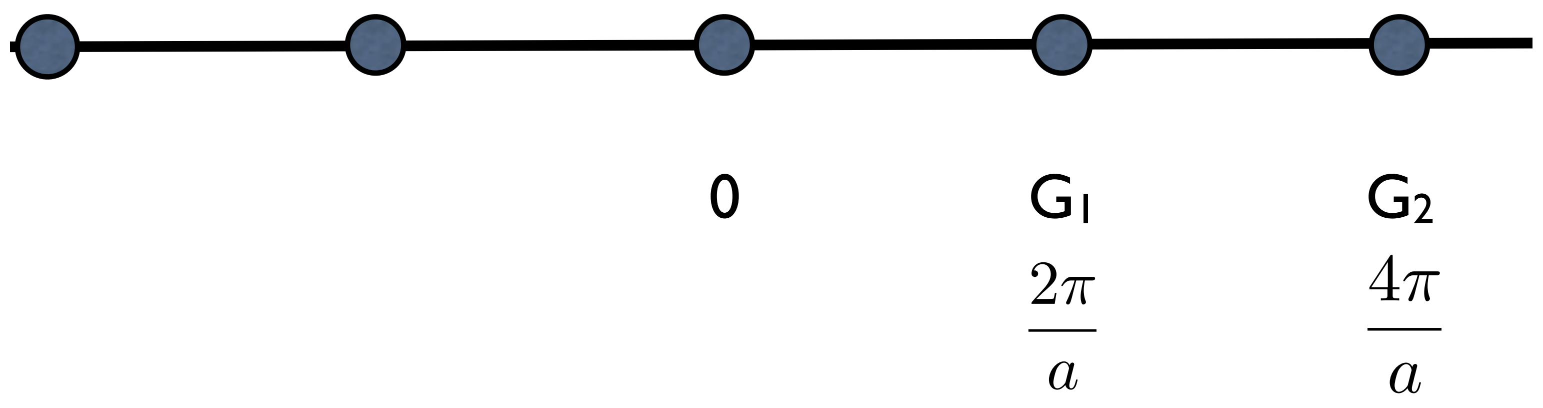
(a) k away from BZ boundaries

$$\epsilon(k) = \epsilon^0(k) + O(V^2)$$

(b) k on Bragg planes

$$|k| = |k - G_n|$$

$$k = G_n/2 = nb/2 = n\pi/a$$

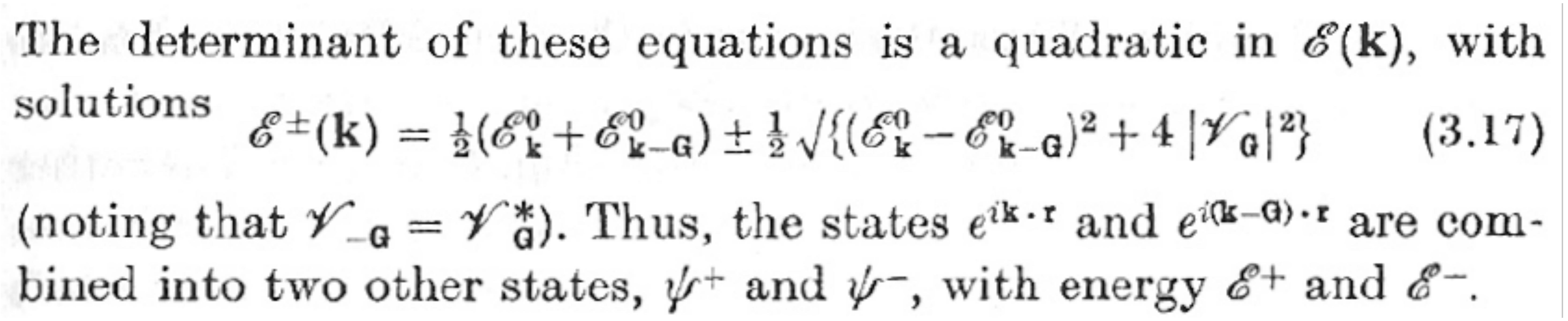


$$\epsilon(k = \frac{G_n}{2}) = \epsilon^0(k = \frac{G_n}{2}) \pm |V_n|$$

(c) k near BZ boundaries

$$\epsilon^{\pm}(k) = \frac{1}{2}(\epsilon^0(k) + \epsilon^0(k - G) \pm \sqrt{(\epsilon^0(k) + \epsilon^0(k - G))^2 + 4|V_G|^2})$$

Truncate Schrödinger equation to 2 x 2
alternate view: do “degenerate perturbation theory” for
the case where two plane waves have nearly the same kinetic energy.



The determinant of these equations is a quadratic in $\mathscr{E}(\mathbf{k})$, with solutions

$$\mathscr{E}^{\pm}(\mathbf{k}) = \tfrac{1}{2}(\mathscr{E}^0_{\mathbf{k}}+\mathscr{E}^0_{\mathbf{k}-\mathbf{G}}) \pm \tfrac{1}{2}\sqrt{\{(\mathscr{E}^0_{\mathbf{k}}-\mathscr{E}^0_{\mathbf{k}-\mathbf{G}})^2+4|\mathscr{V}_{\mathbf{G}}|^2\}} \qquad (3.17)$$

(noting that $\mathscr{V}_{-\mathbf{G}} = \mathscr{V}^*_{\mathbf{G}}$). Thus, the states $e^{i\mathbf{k}\cdot\mathbf{r}}$ and $e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}}$ are combined into two other states, ψ^+ and ψ^-, with energy $\mathscr{E}^+$ and $\mathscr{E}^-$.

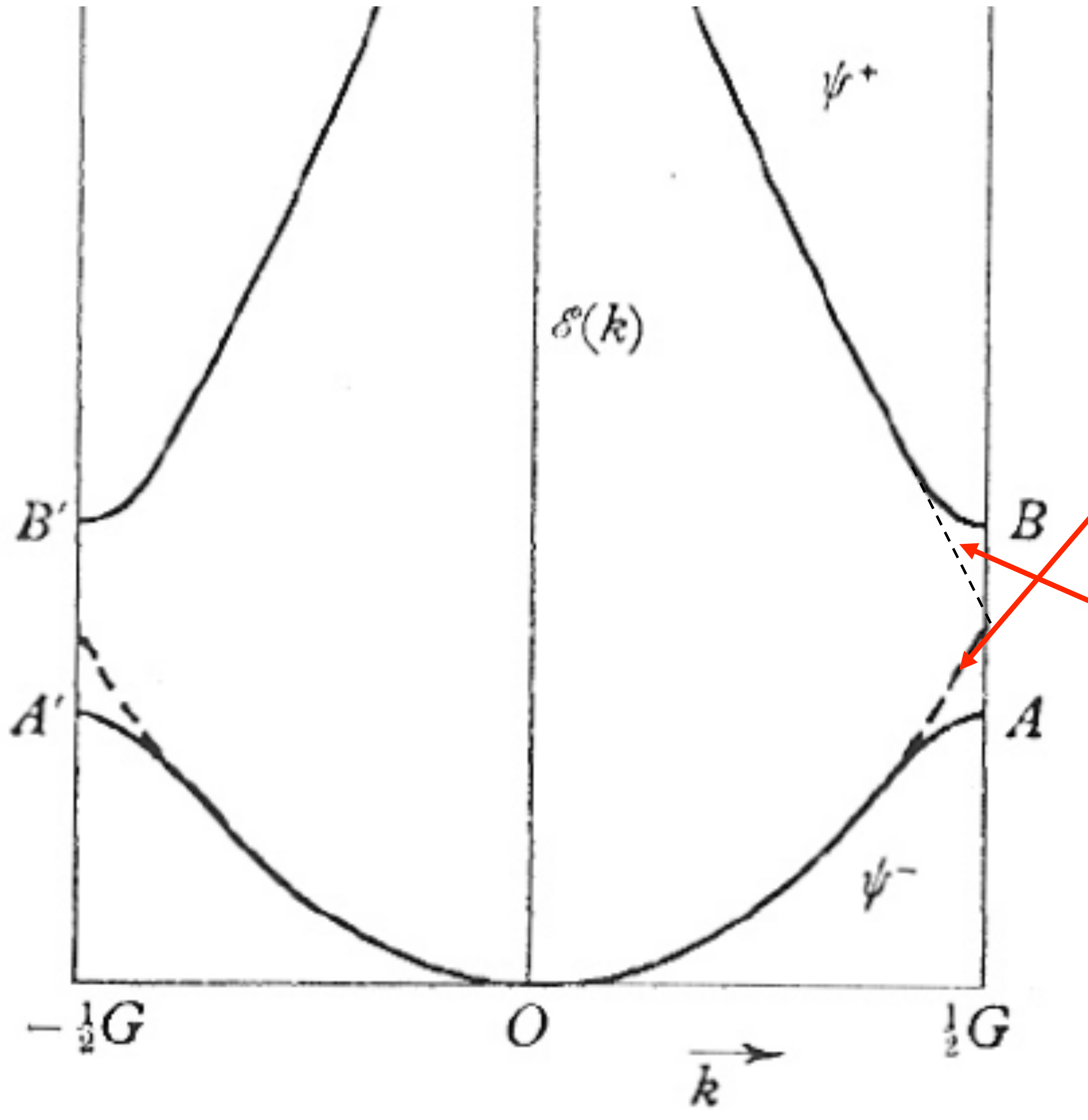


Fig. 38. Electron energy in one dimension: reduced zone scheme.

energy lowered

energy raised

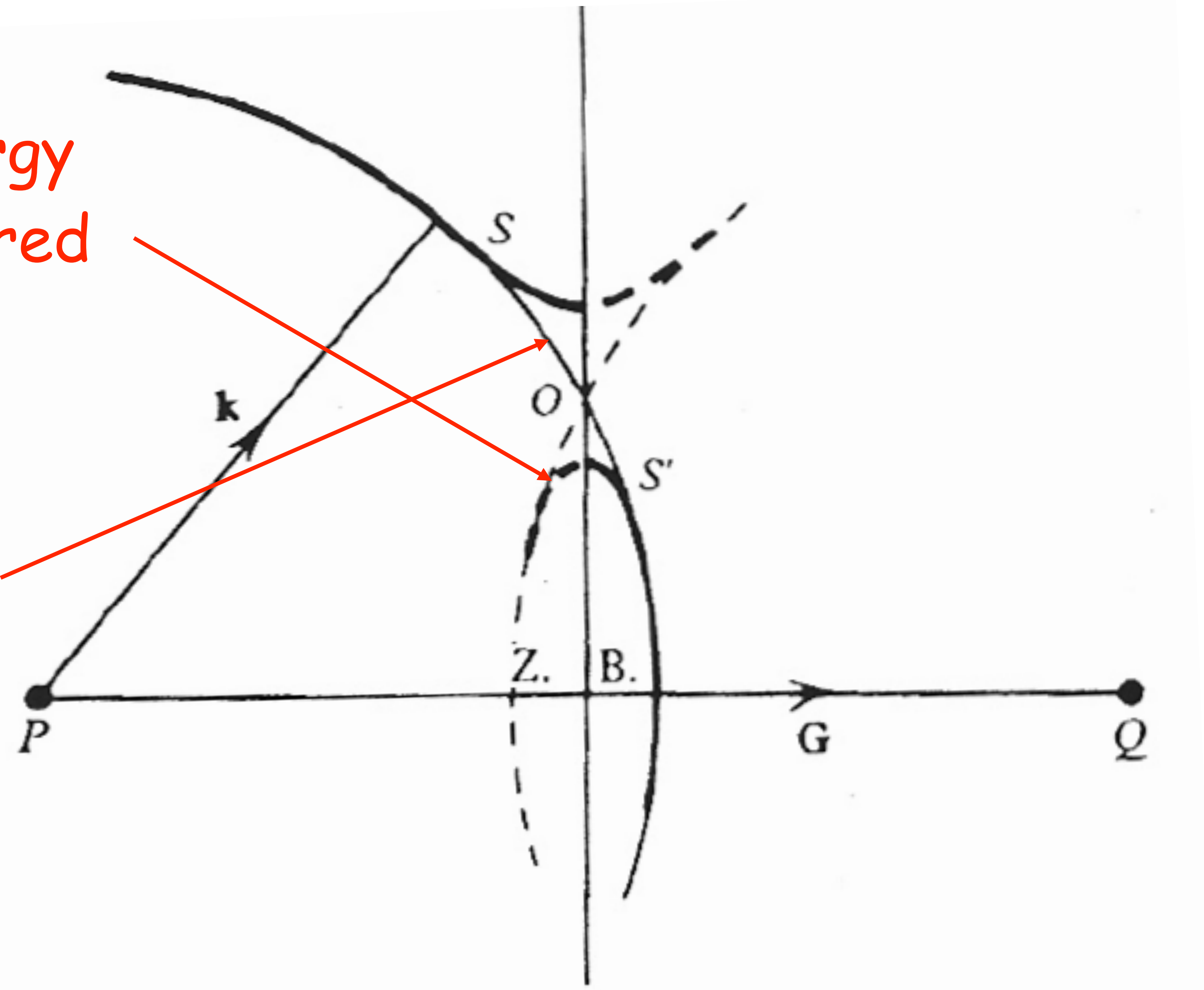


Fig. 42. Discontinuity of energy contour at zone boundary.

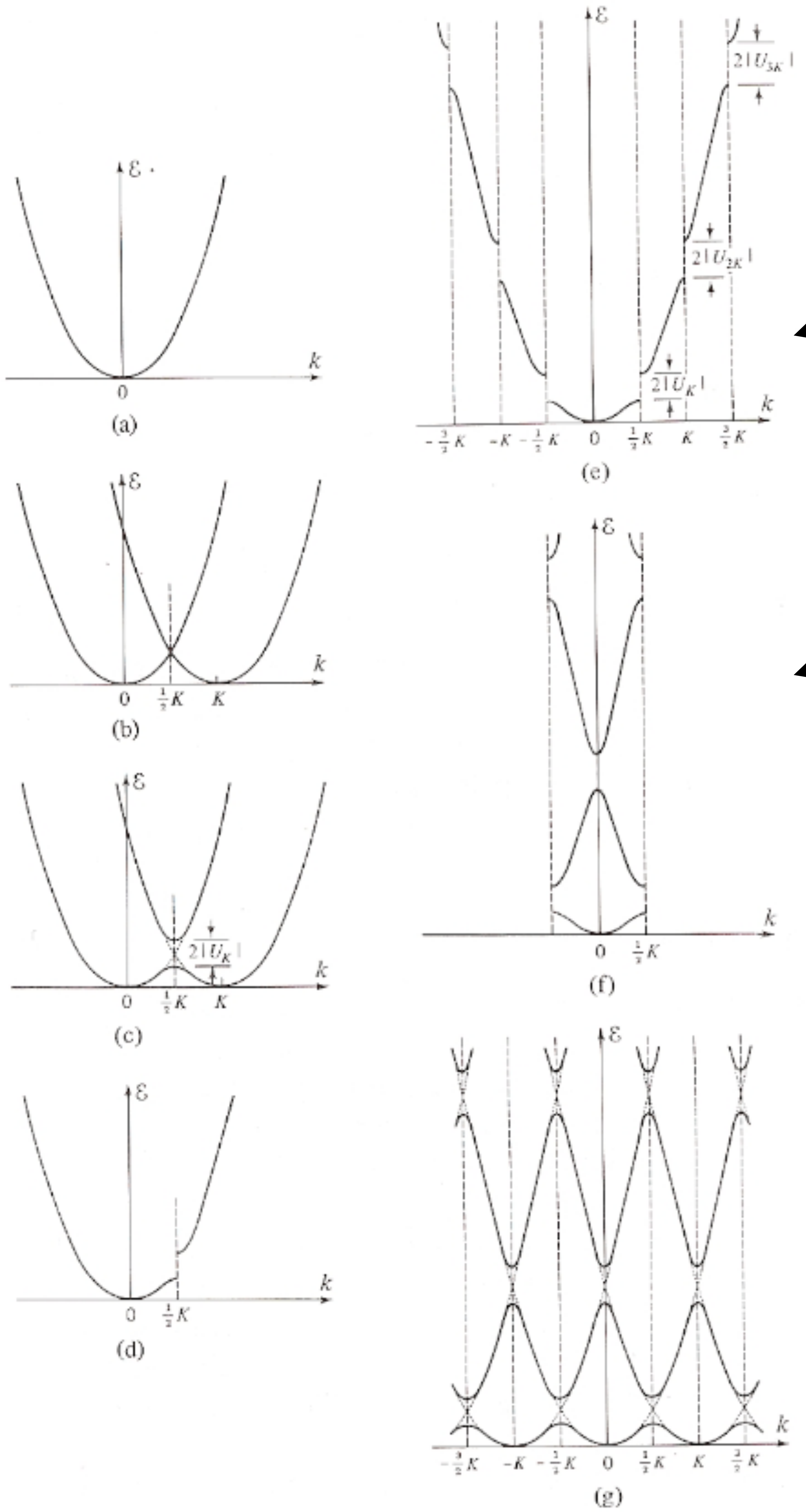


Figure 9.4

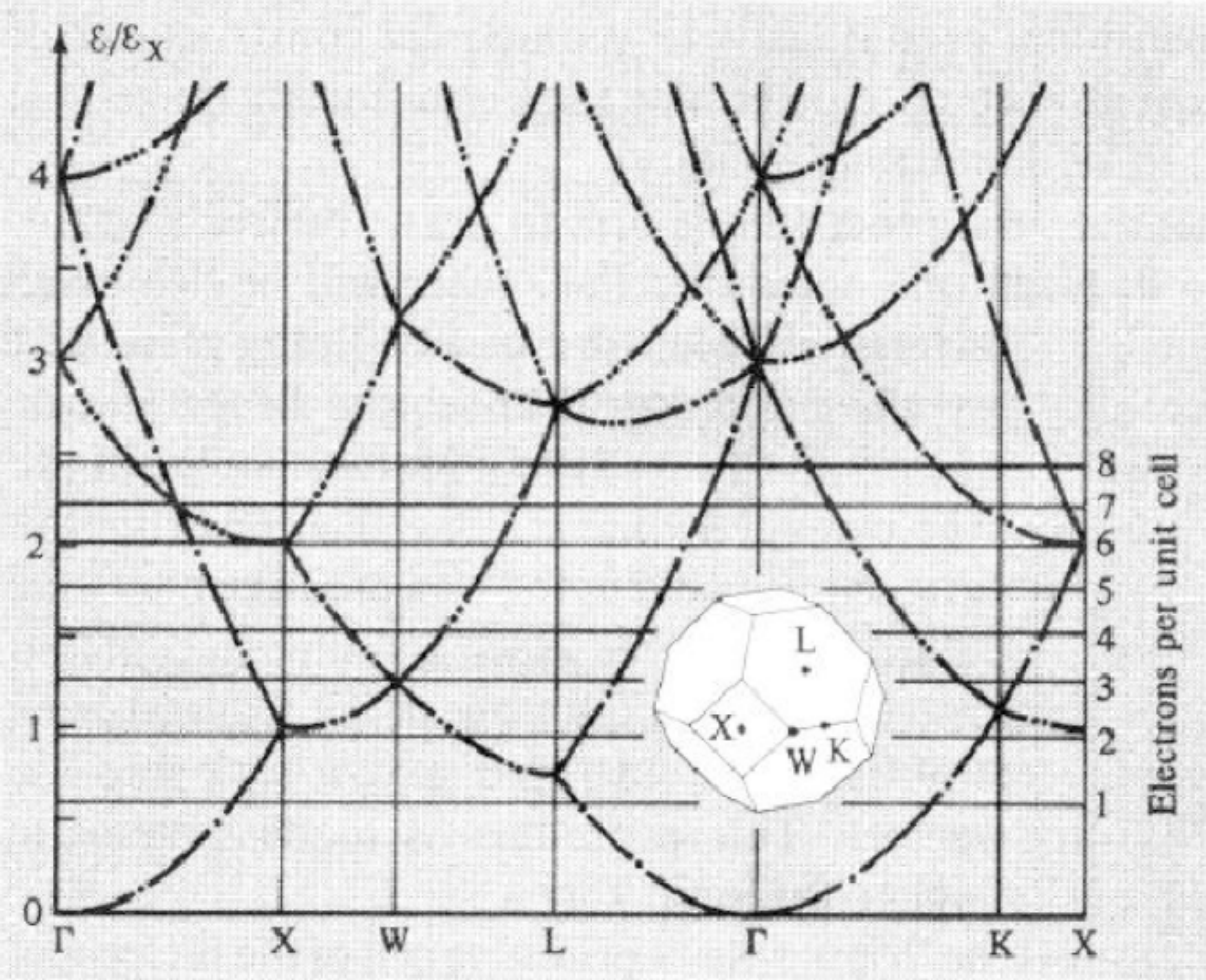
(a) The free electron ℰ vs. k parabola in one dimension. (b) Step 1 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane," due to a weak periodic potential. If the Bragg "plane" is that determined by K, a second free electron parabola is drawn, centered on K. (c) Step 2 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane." The degeneracy of the two parabolas at $K/2$ is split. (d) Those portions of part (c) corresponding to the original free electron parabola given in (a). (e) Effect of all additional Bragg "planes" on the free electron parabola. This particular way of displaying the electronic levels in a periodic potential is known as the *extended-zone scheme*. (f) The levels of (e), displayed in a *reduced-zone scheme*. (g) Free electron levels of (e) or (f) in a *repeated-zone scheme*.

Extended Zone scheme

Reduced Zone scheme

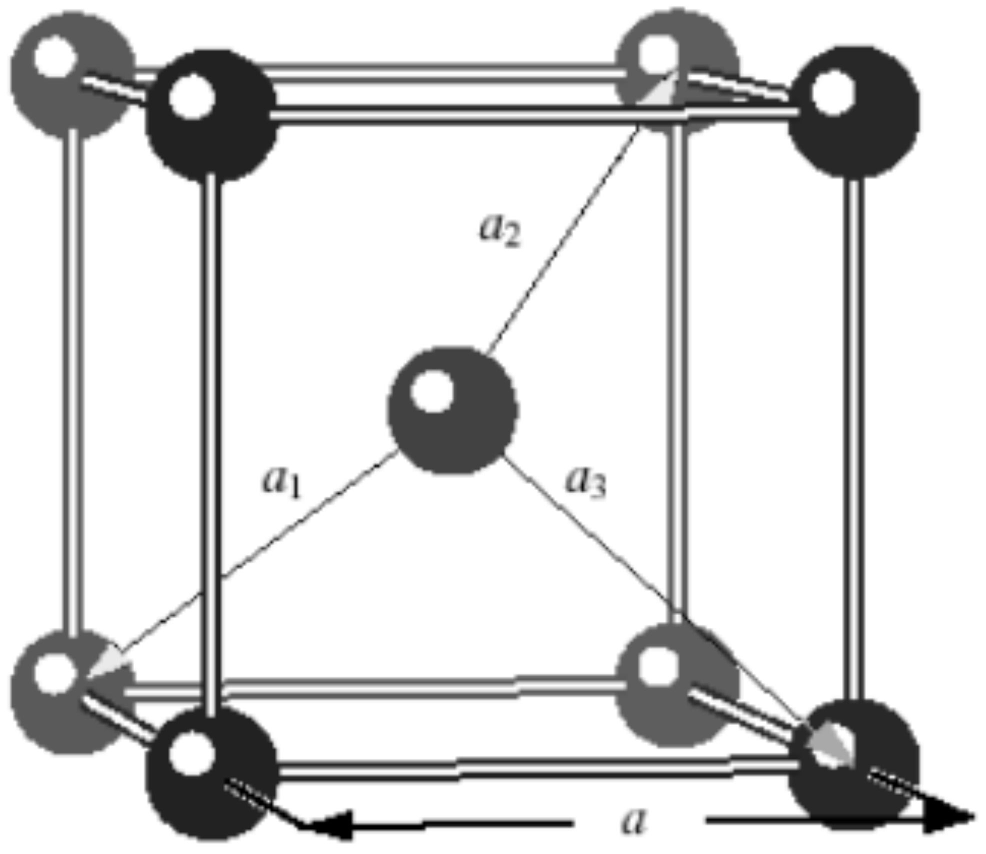
Repeated Zone scheme

3D free electrons, folded into 1st BZ, FCC



Na: bcc lattice, reciprocal lattice fcc

Conventional unit cell
(a cube with 2 atoms per cell)



In units of $2\pi/a$

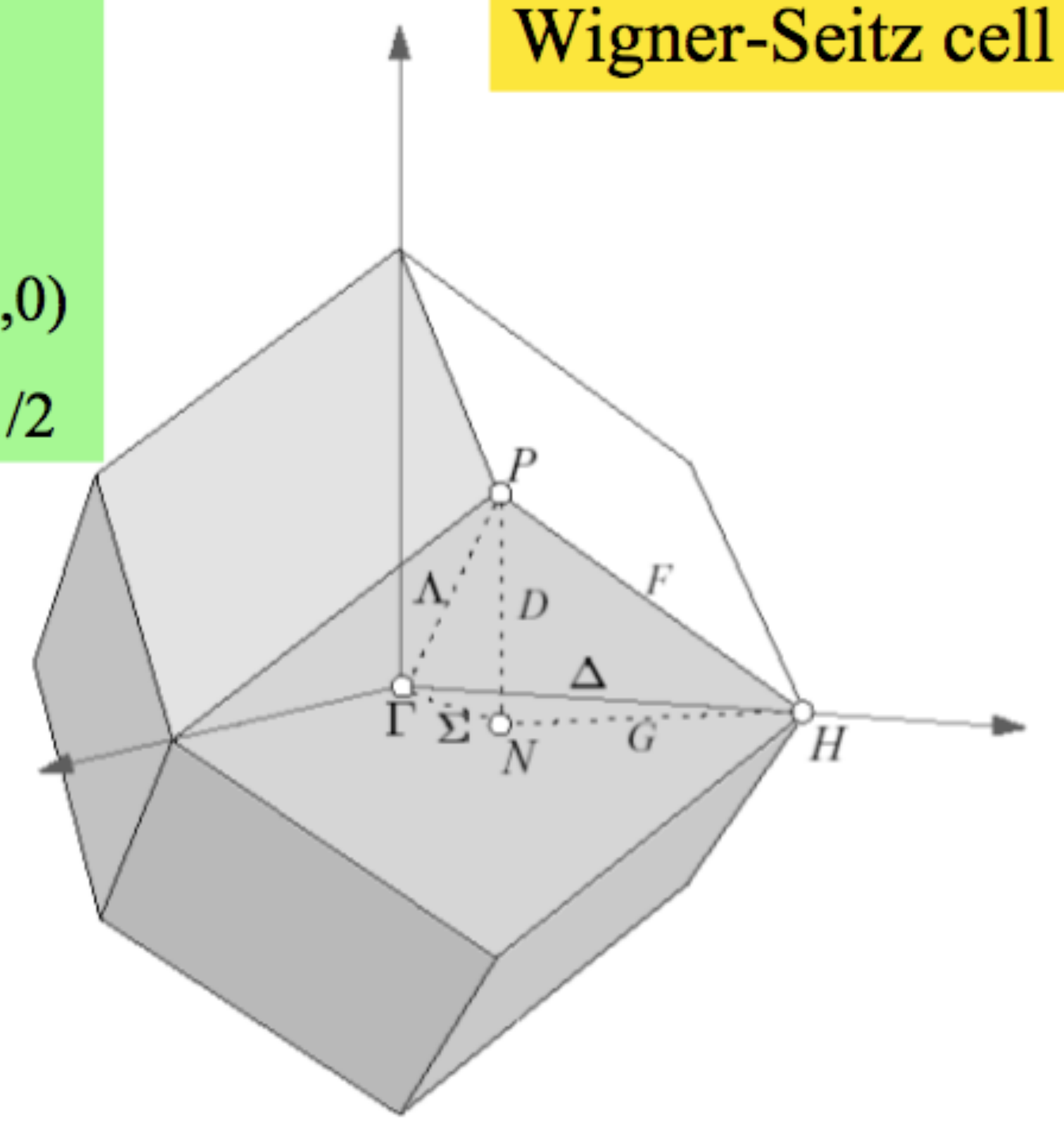
$\Gamma = (0,0,0)$,

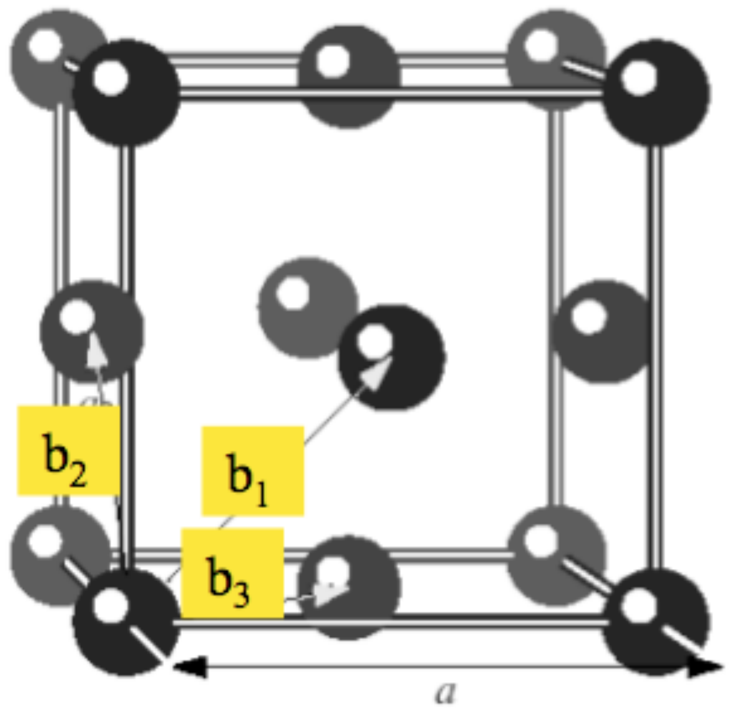
$H = (0,1,0)$,

$N = (1/2,1/2,0)$,

$P = (1,1,1)\ 1/2$

Wigner-Seitz cell of fcc





VOLUME 55, NUMBER 18 PHYSICAL REVIEW LETTERS 28 OCTOBER 1985

Experimental Band Structure of Na

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(Received 16 July 1985)

Normal-emission angle-resolved photoemission data from Na(110) are presented. Two discrepancies between these data and the predictions of free-electron theory are observed. First, the occupied-band width is 2.5 eV, while theory predicts 3.2 eV. Second, the bands near the Fermi level appear to have been severely distorted, as could be produced by a charge-density wave oriented normal to the surface.

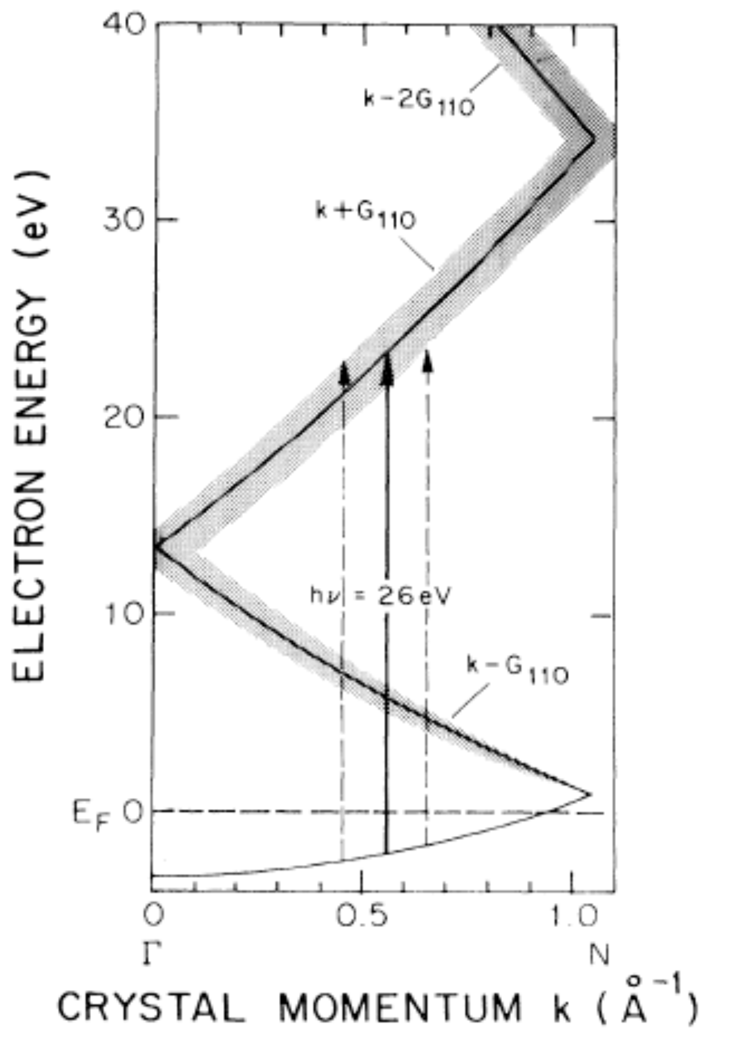


FIG. 1. Plot of the relevant free-electron bands along the Σ axis in Na. The solid arrow shows the center of the direct transition at 26-eV photon energy. The shaded region illustrates the energy uncertainty in the final band due to the finite mean free path of the photoelectron, and the dashed arrows show the effect that this has on the width of the observed peak.

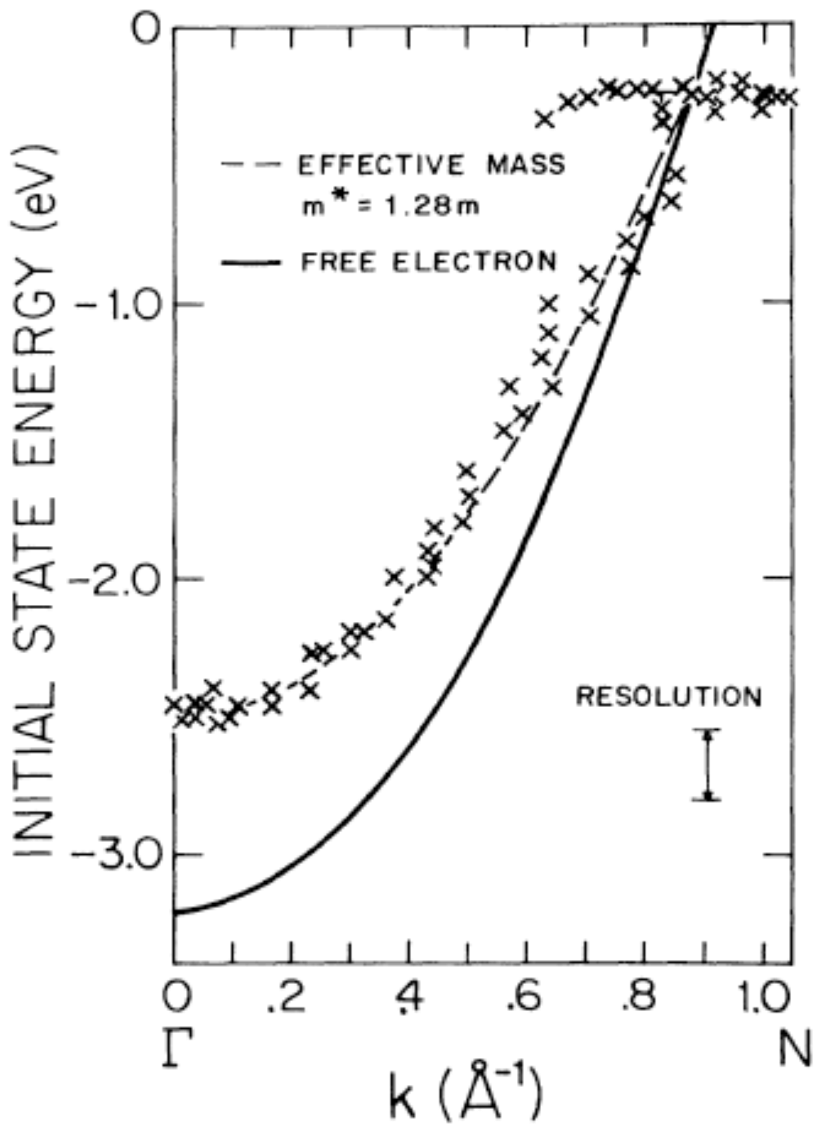
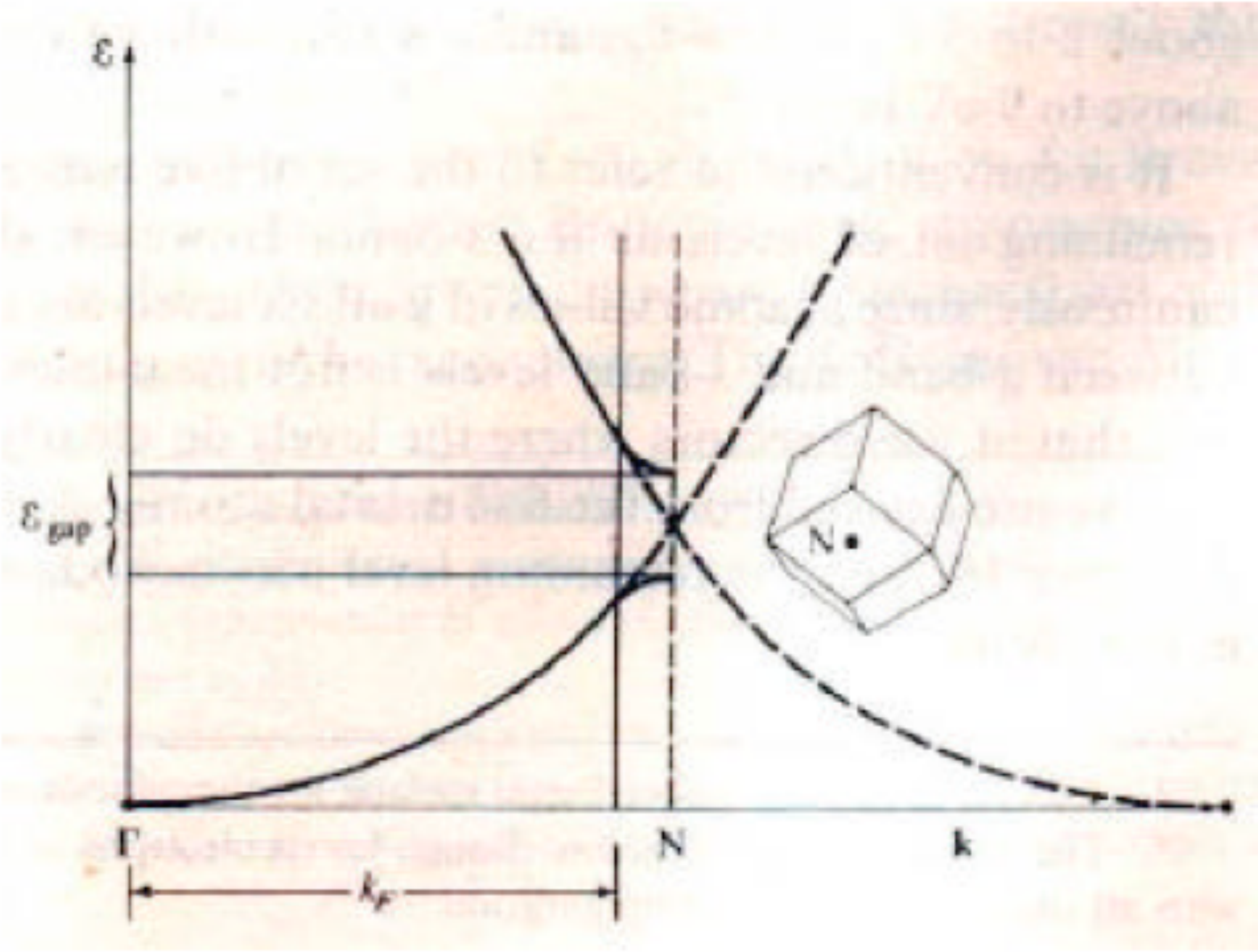


FIG. 4. Measured dispersion of the Na band along the normal Σ axis. The final bands are assumed to be nearly free electron (see text).

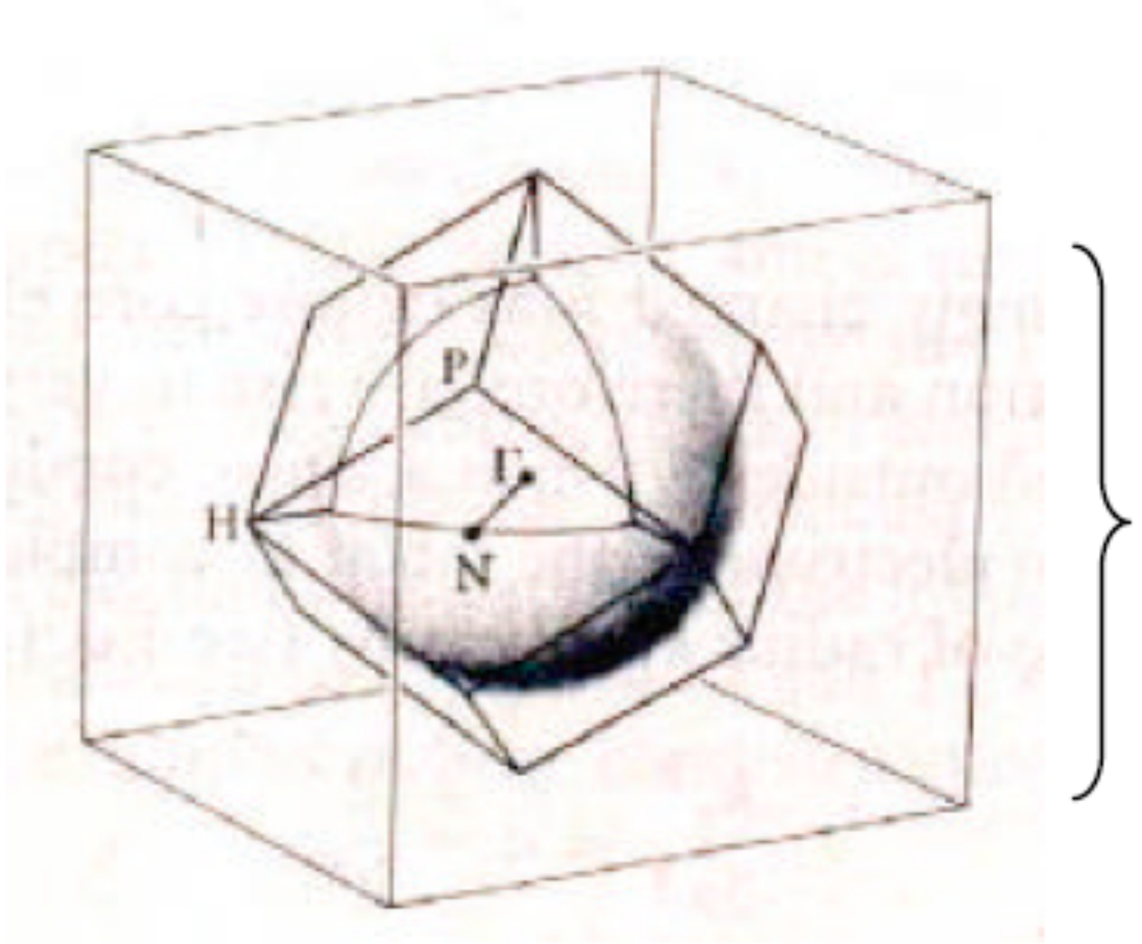
Alkali metals (Li, Na, K, Rb, Cs)



$$k_F = (3\pi^2 n)^{1/3},$$
$$n = 2/a^3$$

$$\mathrm{k}_F = (3/4\pi)^{1/3}(2\pi/a)$$
$$\Gamma N = (2\pi/a)[(1/2)^2 + (1/2)^2]^1/2$$
$$\mathrm{k}_F = 0.877\Gamma N$$

First BZ (of a bcc lattice) and the Fermi sphere

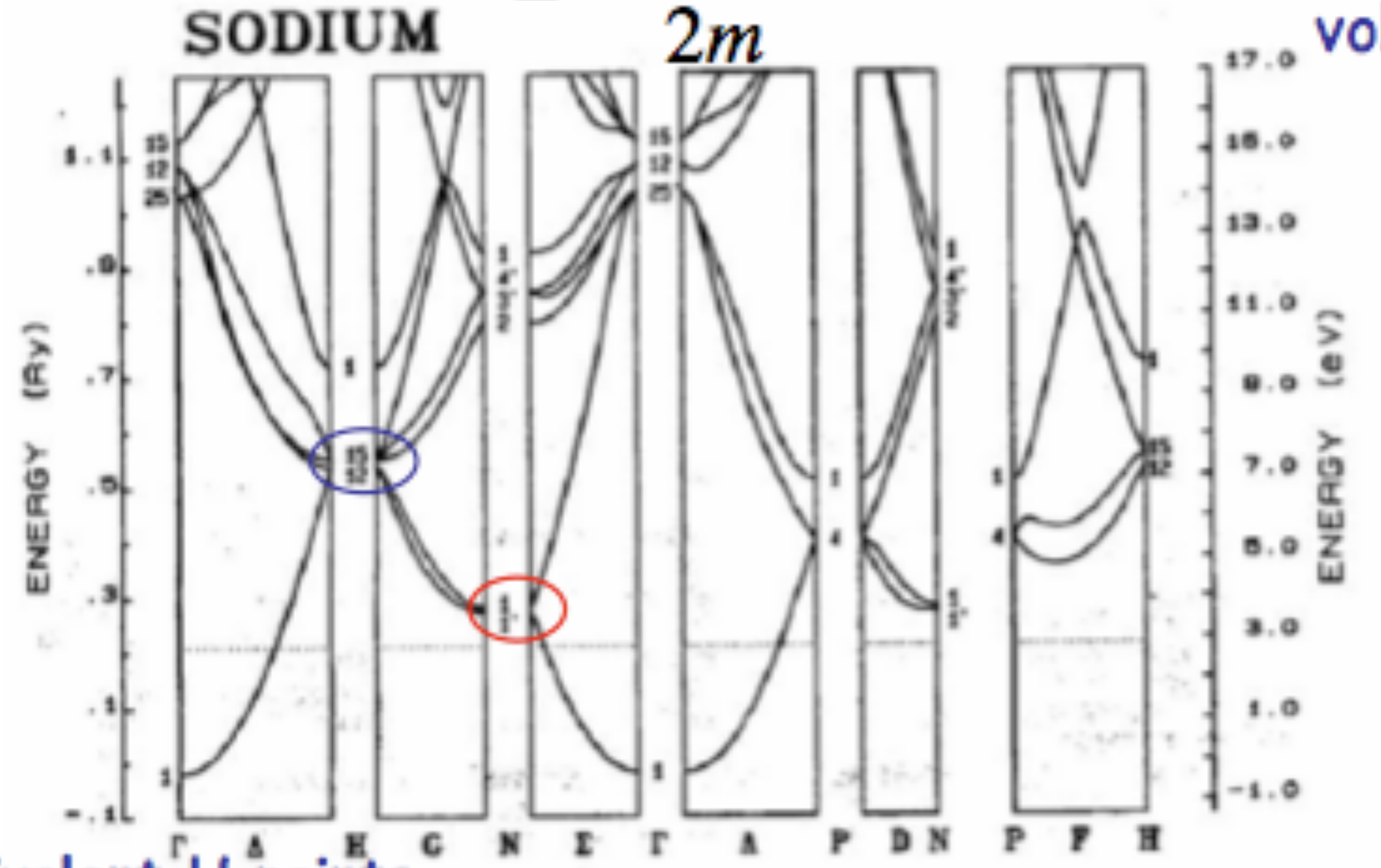


4π/a

A Nearly Free-Electron Metal

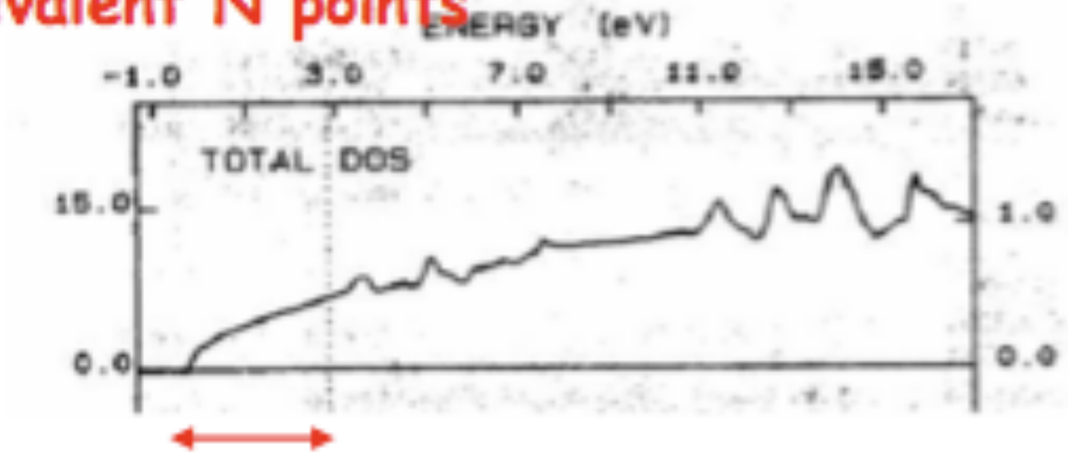
D. A. Papaconstantopoulos, *Handbook*

$$E \approx \frac{\hbar^2 k^2}{2m}$$



6 equivalent H points

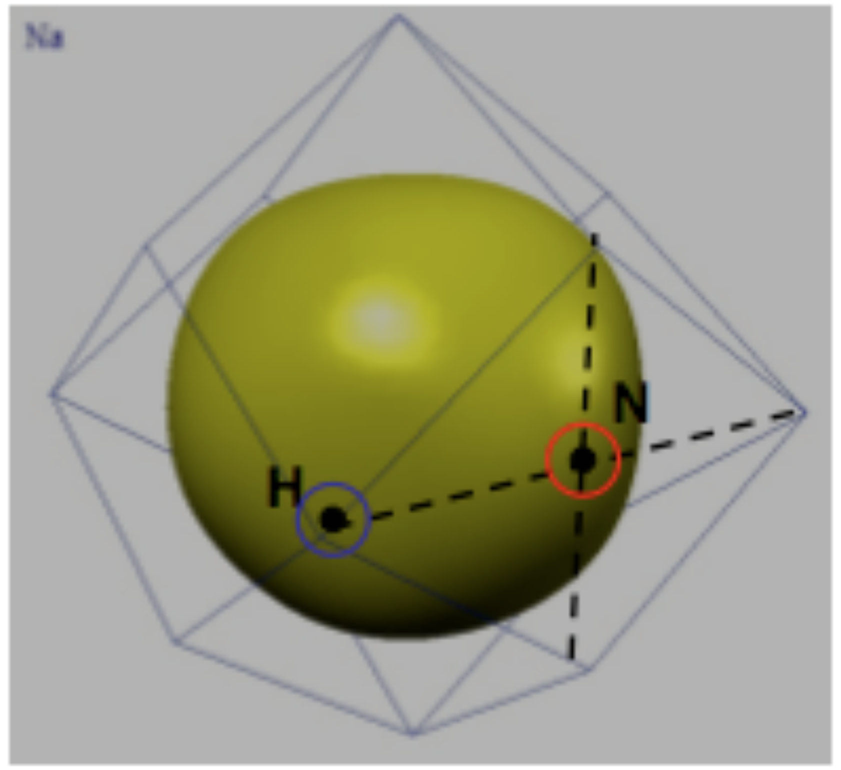
2 equivalent N points



E_F = 4.2 eV (free electrons)

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$$

The Brillouin zone has N k-states. Each can be occupied twice. Na has 1 atom/cell, 1 electron/atom, occupied states take only $\frac{1}{2}$ the volume of the Brillouin zone.



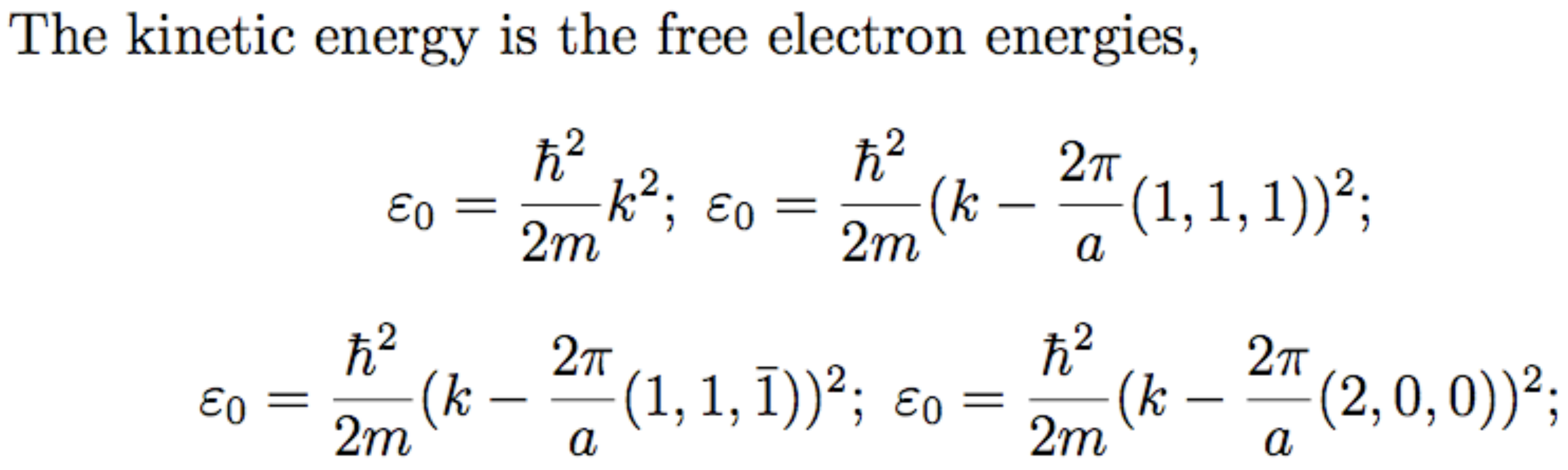
Tat-Sang Choy's Fermi surface data base

$$\mathcal{D}(E) \approx \frac{1}{N}\sum_k^N \delta\left(E - E(k)\right)$$

$$\mathcal{D}_{\text{f.e.}}(E) = \frac{3}{2E_F}\left(\frac{E}{E_F}\right)^{1/2}$$

A&M Chapter 9 problem 3

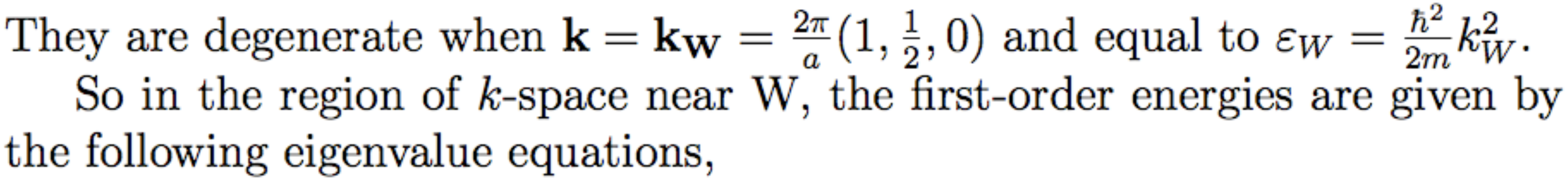
Consider the point W (k_w=(2pi/a)(1,1/2,0) in the brillouin zone of the fcc structure. Here three Bragg planes (200),(111),(11-1) meet, and accordingly the free electron energies are degenerate when k=k_w



The kinetic energy is the free electron energies,

$$\varepsilon_0 = \frac{\hbar^2}{2m}k^2;\ \varepsilon_0 = \frac{\hbar^2}{2m}(k - \frac{2\pi}{a}(1,1,1))^2;$$

$$\varepsilon_0 = \frac{\hbar^2}{2m}(k - \frac{2\pi}{a}(1,1,\bar{1}))^2;\ \varepsilon_0 = \frac{\hbar^2}{2m}(k - \frac{2\pi}{a}(2,0,0))^2;$$



They are degenerate when $\mathbf{k} = \mathbf{k_W} = \frac{2\pi}{a}(1, \frac{1}{2}, 0)$ and equal to $\varepsilon_W = \frac{\hbar^2}{2m}k_W^2$.

So in the region of k-space near W, the first-order energies are given by the following eigenvalue equations,

$$(\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{K_i}})c_{\mathbf{k}-\mathbf{K_i}} = \sum_{j=1}^{m} U_{\mathbf{K_j}-\mathbf{K_i}} c_{\mathbf{k}-\mathbf{K_j}} \ , \ \ i = 1, 2, ..., m$$

For this case, $m = 3$, and $\mathbf{K_1} = \frac{2\pi}{a}(1,1,1)$,$\mathbf{K_2} = \frac{2\pi}{a}(1,1,\bar{1})$ $\mathbf{K_3} = \frac{2\pi}{a}(2,0,0)$. So the possible potential energy $U_{K_j-K_i}$ is,

$$U_{K_1-K_2} = U_{K_2-K_1} = U_{002} = U_{200} \equiv U_2;$$

$$U_{K_1-K_3} = U_{K_3-K_1} = U_{\bar{1}11} = U_{111} \equiv U_1;$$

$$U_{K_2-K_3} = U_{K_3-K_2} = U_{\bar{1}1\bar{1}} = U_{1\bar{1}1} = U_{\bar{1}11} \equiv U_1;$$

Here we have use the symmetry of fcc structure.

$$\begin{pmatrix} \varepsilon_1^0 - \varepsilon & U_1 & U_1 & U_2 \\ U_1 & \varepsilon_2^0 - \varepsilon & U_2 & U_1 \\ U_1 & U_2 & \varepsilon_3^0 - \varepsilon & U_1 \\ U_2 & U_1 & U_1 & \varepsilon_4^0 - \varepsilon \end{pmatrix} \begin{pmatrix} c_{\mathbf{k_w}} \\ c_{\mathbf{k_w}-\mathbf{K_1}} \\ c_{\mathbf{k_w}-\mathbf{K_2}} \\ c_{\mathbf{k_w}-\mathbf{K_3}} \end{pmatrix} = 0$$

So the eigenvalues are determined by the following equation,

$$\begin{vmatrix} \varepsilon_1^0 - \varepsilon & U_1 & U_1 & U_2 \\ U_1 & \varepsilon_2^0 - \varepsilon & U_2 & U_1 \\ U_1 & U_2 & \varepsilon_3^0 - \varepsilon & U_1 \\ U_2 & U_1 & U_1 & \varepsilon_4^0 - \varepsilon \end{vmatrix} = 0$$

In the above equation, using the fact that the kinetic energies are degenerate at $\mathbf{k_W}$. We can simplify equation,

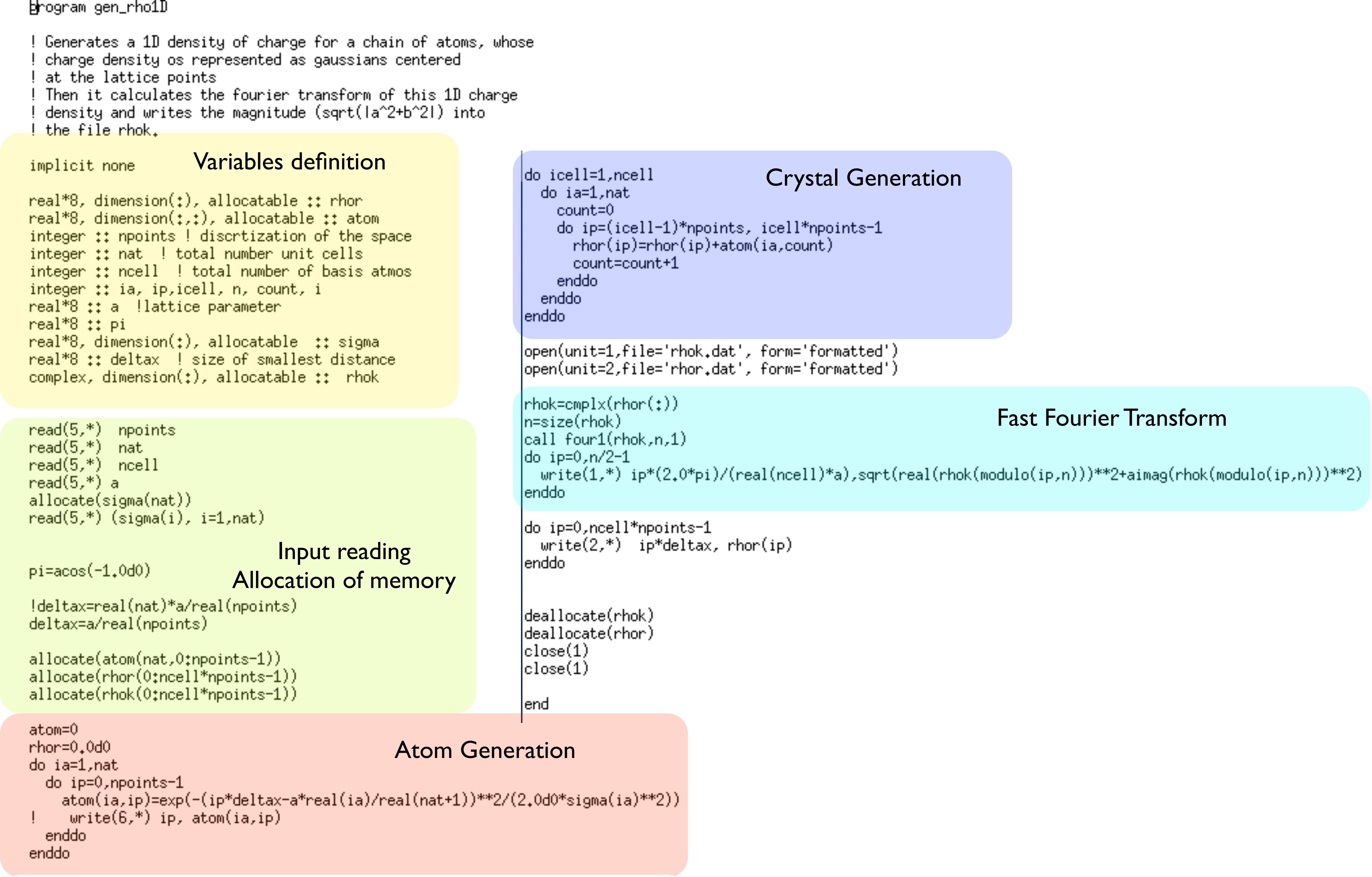
$$\begin{vmatrix} \varepsilon_W^0 - \varepsilon & U_1 & U_1 & U_2 \\ U_1 & \varepsilon_W^0 - \varepsilon & U_2 & U_1 \\ U_1 & U_2 & \varepsilon_W^0 - \varepsilon & U_1 \\ U_2 & U_1 & U_1 & \varepsilon_W^0 - \varepsilon \end{vmatrix}$$

$$= (\varepsilon_W - \varepsilon - U_2)^2[(\varepsilon_W - \varepsilon)^2 + 2U_2(\varepsilon_W - \varepsilon) + U_2^2 - 4U_1^2] = 0$$

So we have solutions,

$$\varepsilon = \varepsilon_W - U_2 \ (twice); \ \ \varepsilon = \varepsilon_W + U_2 \pm 2U_1;$$

Appendix: Xray diffraction+atoms in the basis



```
program gen_rho1D

! Generates a 1D density of charge for a chain of atoms, whose
! charge density os represented as gaussians centered
! at the lattice points
! Then it calculates the fourier transform of this 1D charge
! density and writes the magnitude (sqrt(|a^2+b^2|) into
! the file rhok.
```

Variables definition

```
implicit none

real*8, dimension(:), allocatable :: rhor
real*8, dimension(:,:), allocatable :: atom
integer :: npoints ! discrtization of the space
integer :: nat  ! total number unit cells
integer :: ncell  ! total number of basis atmos
integer :: ia, ip,icell, n, count, i
real*8 :: a  !lattice parameter
real*8 :: pi
real*8, dimension(:), allocatable  :: sigma
real*8 :: deltax  ! size of smallest distance
complex, dimension(:), allocatable ::  rhok
```

Input reading

Allocation of memory

```
read(5,*)  npoints
read(5,*)  nat
read(5,*)  ncell
read(5,*) a
allocate(sigma(nat))
read(5,*) (sigma(i), i=1,nat)


pi=acos(-1.0d0)

!deltax=real(nat)*a/real(npoints)
deltax=a/real(npoints)

allocate(atom(nat,0:npoints-1))
allocate(rhor(0:ncell*npoints-1))
allocate(rhok(0:ncell*npoints-1))
```

Atom Generation

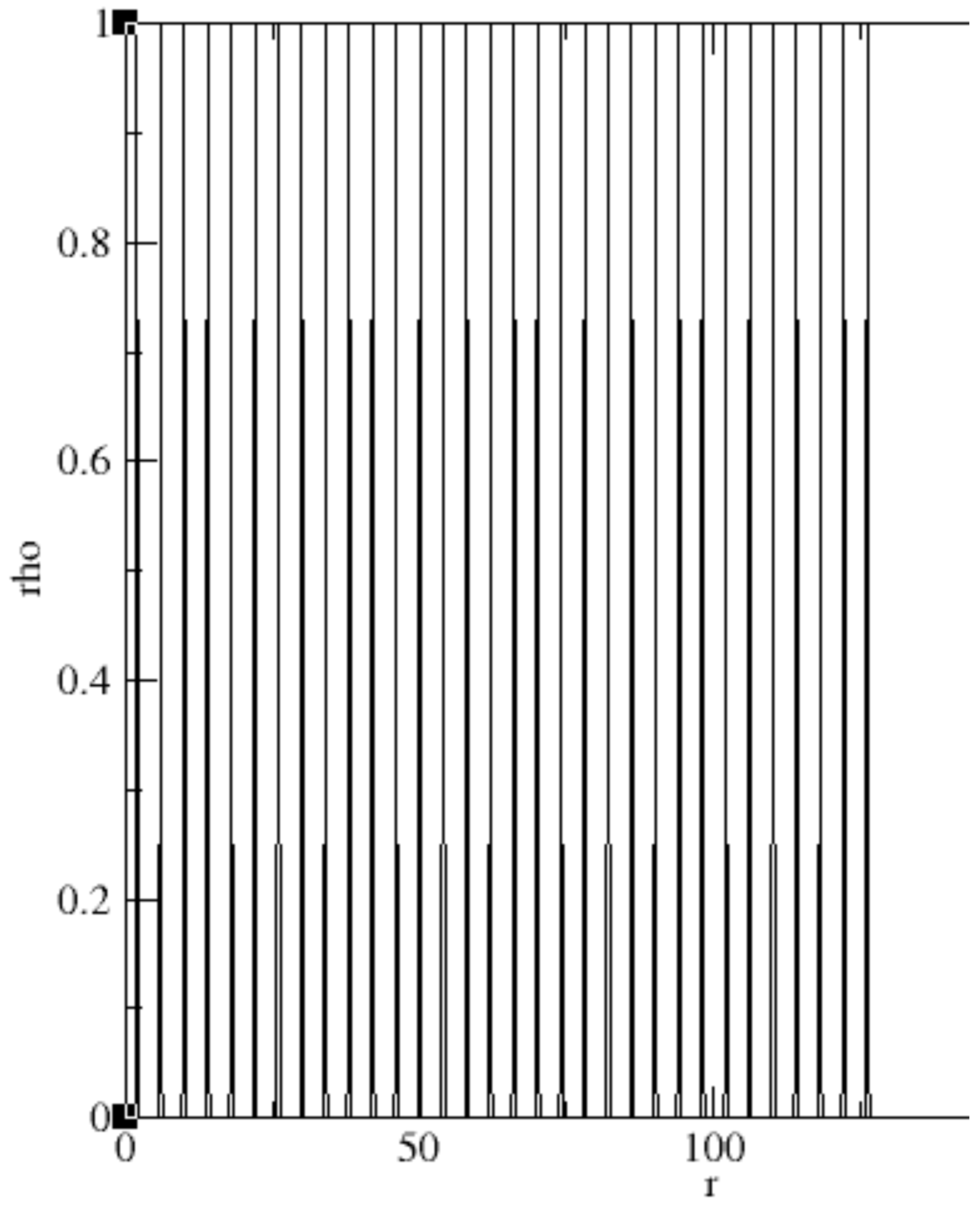
```
atom=0
rhor=0.0d0
do ia=1,nat
  do ip=0,npoints-1
    atom(ia,ip)=exp(-(ip*deltax-a*real(ia)/real(nat+1))**2/(2.0d0*sigma(ia)**2))
!    write(6,*) ip, atom(ia,ip)
  enddo
enddo
```

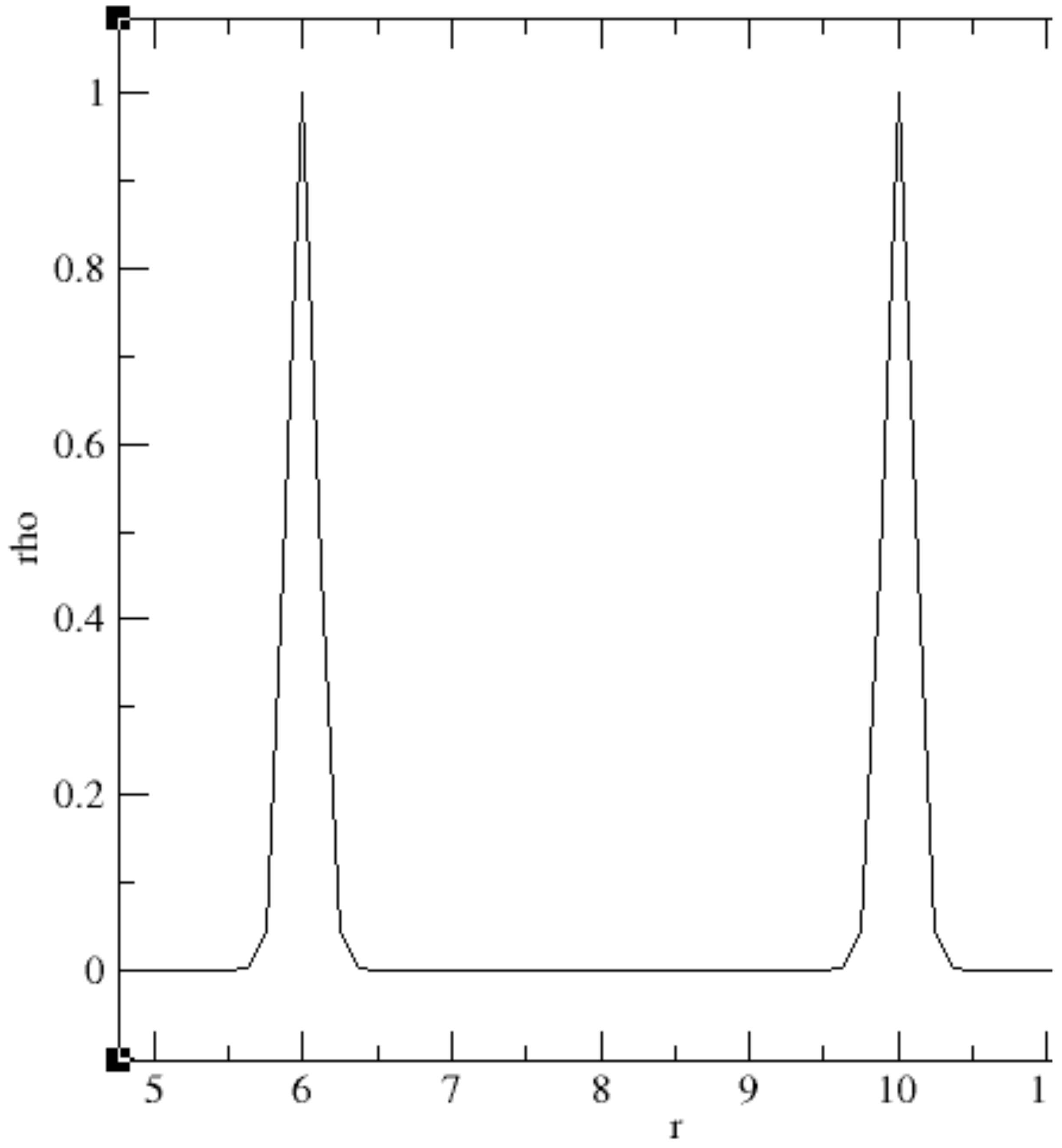
Crystal Generation

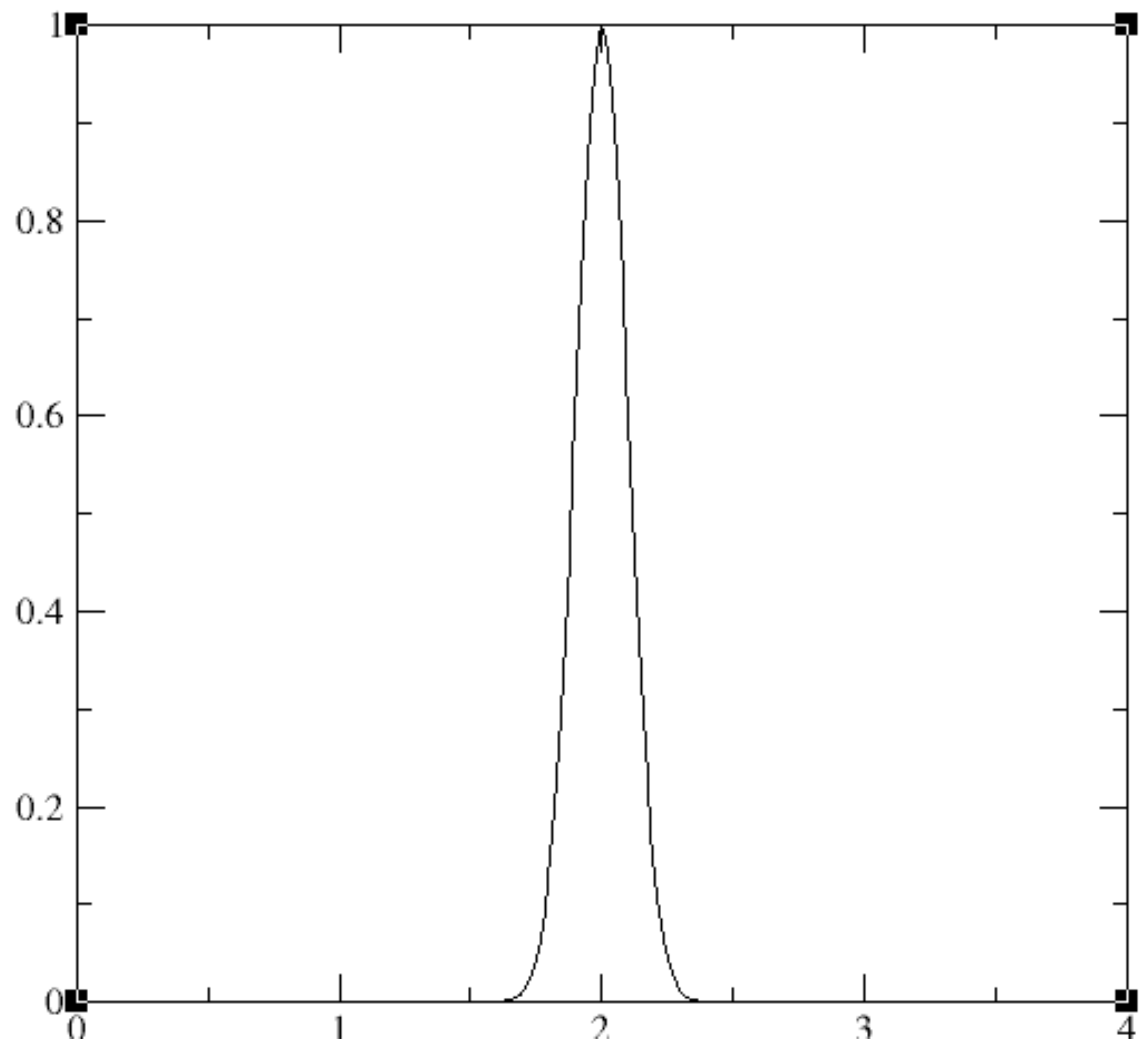
```
do icell=1,ncell
  do ia=1,nat
    count=0
    do ip=(icell-1)*npoints, icell*npoints-1
      rhor(ip)=rhor(ip)+atom(ia,count)
      count=count+1
    enddo
  enddo
enddo

open(unit=1,file='rhok.dat', form='formatted')
open(unit=2,file='rhor.dat', form='formatted')
```

Fast Fourier Transform

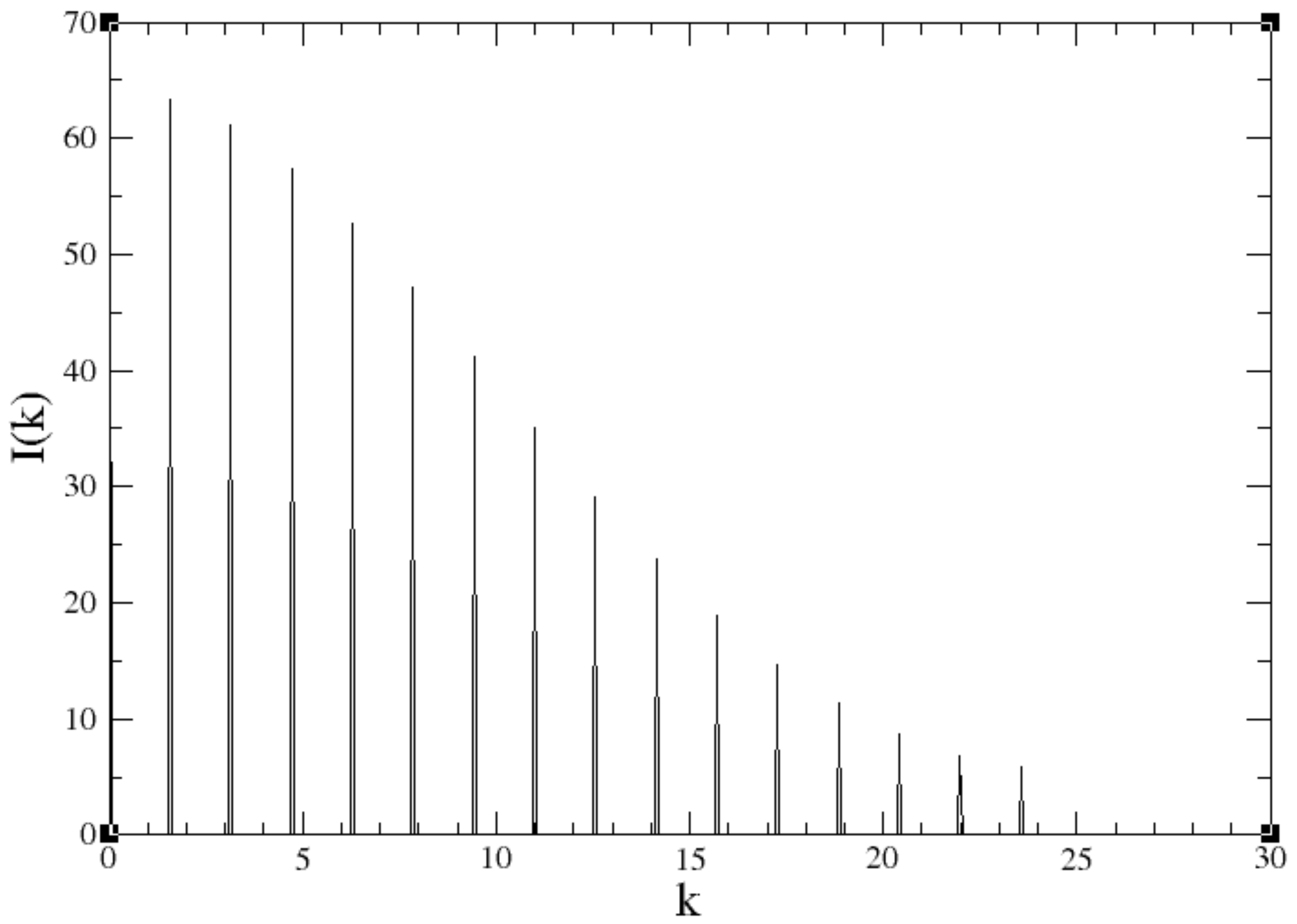
```
rhok=cmplx(rhor(:))
n=size(rhok)
call four1(rhok,n,1)
do ip=0,n/2-1
  write(1,*) ip*(2.0*pi)/(real(ncell)*a),sqrt(real(rhok(modulo(ip,n)))**2+aimag(rhok(modulo(ip,n)))**2)
enddo

do ip=0,ncell*npoints-1
  write(2,*)  ip*deltax, rhor(ip)
enddo


deallocate(rhok)
deallocate(rhor)
close(1)
close(1)

end
```

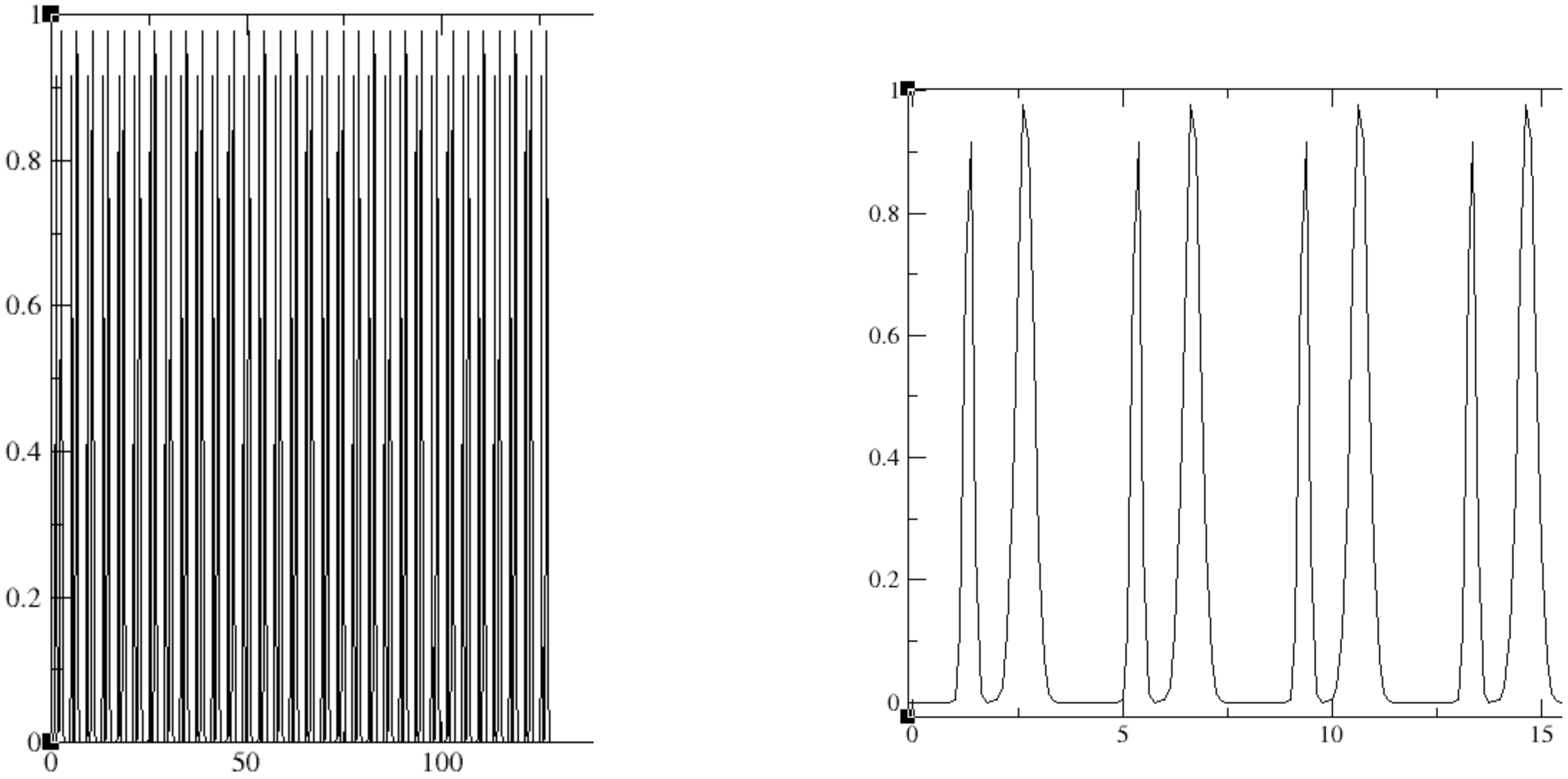




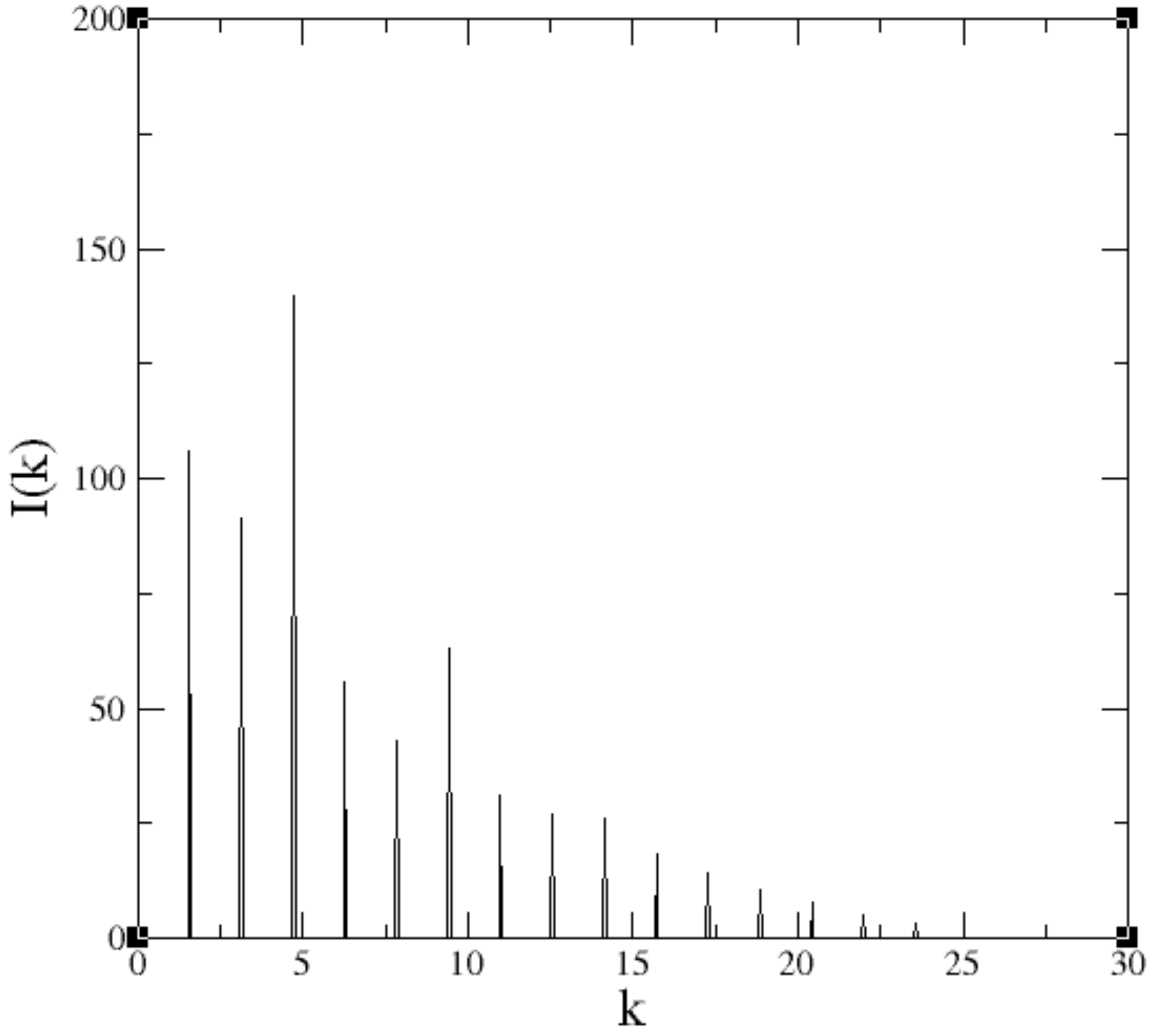


a=4, 1 atom in unit cell





a=4, two atoms in unit cell



Structural Factor and Atomic Form Factor

X-Ray Scattering Amplitude is given by

$\sum_R e(i K \cdot R) \sum_j f_j(K)\, e\, (i K \cdot r_j)$

(j = index running over atoms in the basis)

The 2nd summation is called a structural factor (S_K) and $f_j(K)$ is an atomic form factor

$S_K = \sum_j f_j(K) \exp\, (i K \cdot r_j)$

If atoms are identical then atomic form factors are independent of j, and S_K reduces to a geometrical structural factor.

1. ***Body-Centered Cubic Considered as Simple Cubic with a Basis*** Since the body-centered cubic lattice is a Bravais lattice, we know that Bragg reflections will occur when the change in wave vector **K** is a vector of the reciprocal lattice, which is face-centered cubic. Sometimes, however, it is convenient to regard the bcc lattice as a simple cubic lattice generated by primitive vectors $a\hat{\mathbf{x}}$, $a\hat{\mathbf{y}}$, and $a\hat{\mathbf{z}}$, with a two-point basis consisting of $\mathbf{d}_1 = \mathbf{0}$ and $\mathbf{d}_2 = (a/2)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$. From this point of view the reciprocal lattice is also simple cubic, with a cubic cell of side $2\pi/a$. However, there will now be a structure factor $S_{\mathbf{K}}$ associated with each Bragg reflection. In the present case, (6.13) gives

$$S_{\mathbf{K}} = 1 + \exp\left[i\mathbf{K} \cdot \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})\right]. \qquad \textbf{(6.14)}$$

A general vector in the simple cubic reciprocal lattice has the form

$$\mathbf{K} = \frac{2\pi}{a}(n_1\hat{\mathbf{x}} + n_2\hat{\mathbf{y}} + n_3\hat{\mathbf{z}}). \qquad \textbf{(6.15)}$$

Substituting this into (6.14), we find a structure factor

$$\begin{aligned} S_{\mathbf{K}} &= 1 + e^{i\pi(n_1+n_2+n_3)} = 1 + (-1)^{n_1+n_2+n_3} \\ &= \begin{cases} 2, & n_1 + n_2 + n_3 \quad \text{even,} \\ 0, & n_1 + n_2 + n_3 \quad \text{odd.} \end{cases} \end{aligned} \qquad \textbf{(6.16)}$$

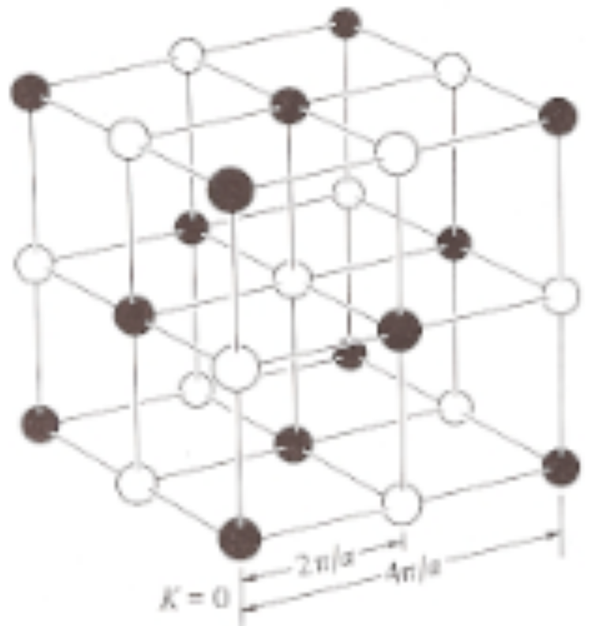


Figure 6.11
Points in the simple cubic reciprocal lattice of side $2\pi/a$, for which the structure factor (6.16) vanishes, are those (white circles) that can be reached from the origin by moving along an odd number of nearest-neighbor bonds. When such sites are eliminated, the remaining sites (black circles) constitute a face-centered cubic lattice with cubic cell of side $4\pi/a$.

2. *Monatomic Diamond Lattice* The monatomic diamond lattice (carbon, silicon, germanium, or grey tin) is not a Bravais lattice and must be described as a lattice with a basis. The underlying Bravais lattice is face-centered cubic, and the basis can be taken to be $\mathbf{d}_1 = \mathbf{0}$, $\mathbf{d}_2 = (a/4)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$, where $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$, are along the cubic axes and a is the side of the conventional cubic cell. The reciprocal lattice is body-centered cubic with conventional cubic cell of side $4\pi/a$. If we take as primitive vectors

$$\mathbf{b}_1 = \frac{2\pi}{a}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \quad \mathbf{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}), \tag{6.17}$$

then the structure factor (6.13) for $\mathbf{K} = \Sigma n_i \mathbf{b}_i$ is

$$\begin{aligned} S_{\mathbf{K}} &= 1 + \exp\left[\tfrac{1}{2} i\pi(n_1 + n_2 + n_3)\right] \\ &= \begin{cases} 2, & n_1 + n_2 + n_3 \text{ twice an even number,} \\ 1 \pm i, & n_1 + n_2 + n_3 \text{ odd,} \\ 0, & n_1 + n_2 + n_3 \text{ twice an odd number.} \end{cases} \end{aligned} \tag{6.18}$$

To interpret these conditions on Σn_i geometrically, note that if we substitute (6.17) into $\mathbf{K} = \Sigma n_i \mathbf{b}_i$, we can write the general reciprocal lattice vector in the form

$$\mathbf{K} = \frac{4\pi}{a}(\nu_1 \hat{\mathbf{x}} + \nu_2 \hat{\mathbf{y}} + \nu_3 \hat{\mathbf{z}}), \tag{6.19}$$

$$\nu_j = \tfrac{1}{2}(n_1 + n_2 + n_3) - n_j, \quad \sum_{j=1}^{3} \nu_j = \tfrac{1}{2}(n_1 + n_2 + n_3). \tag{6.20}$$

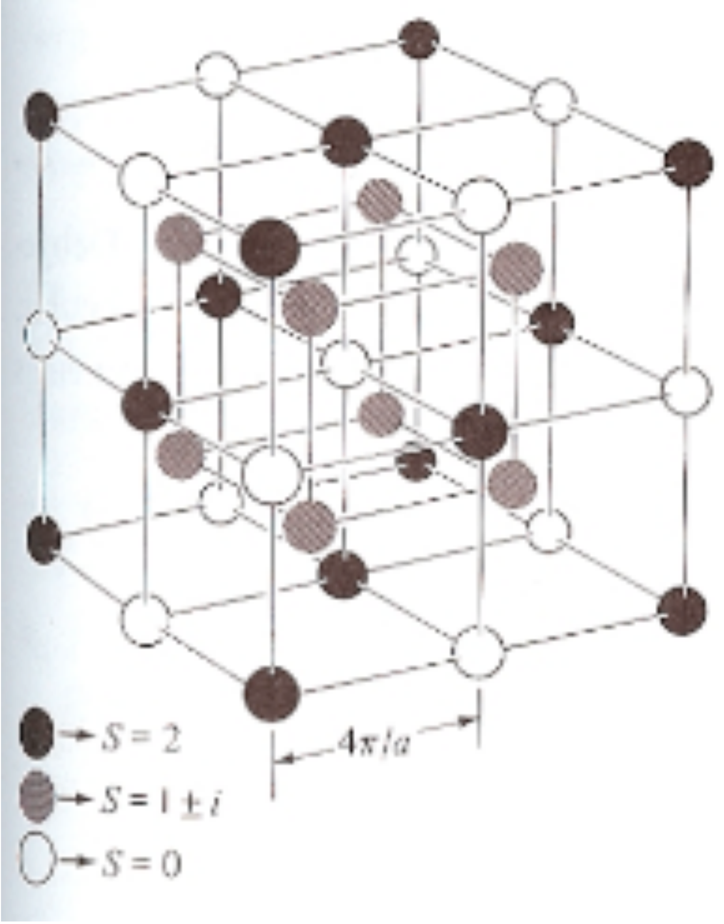
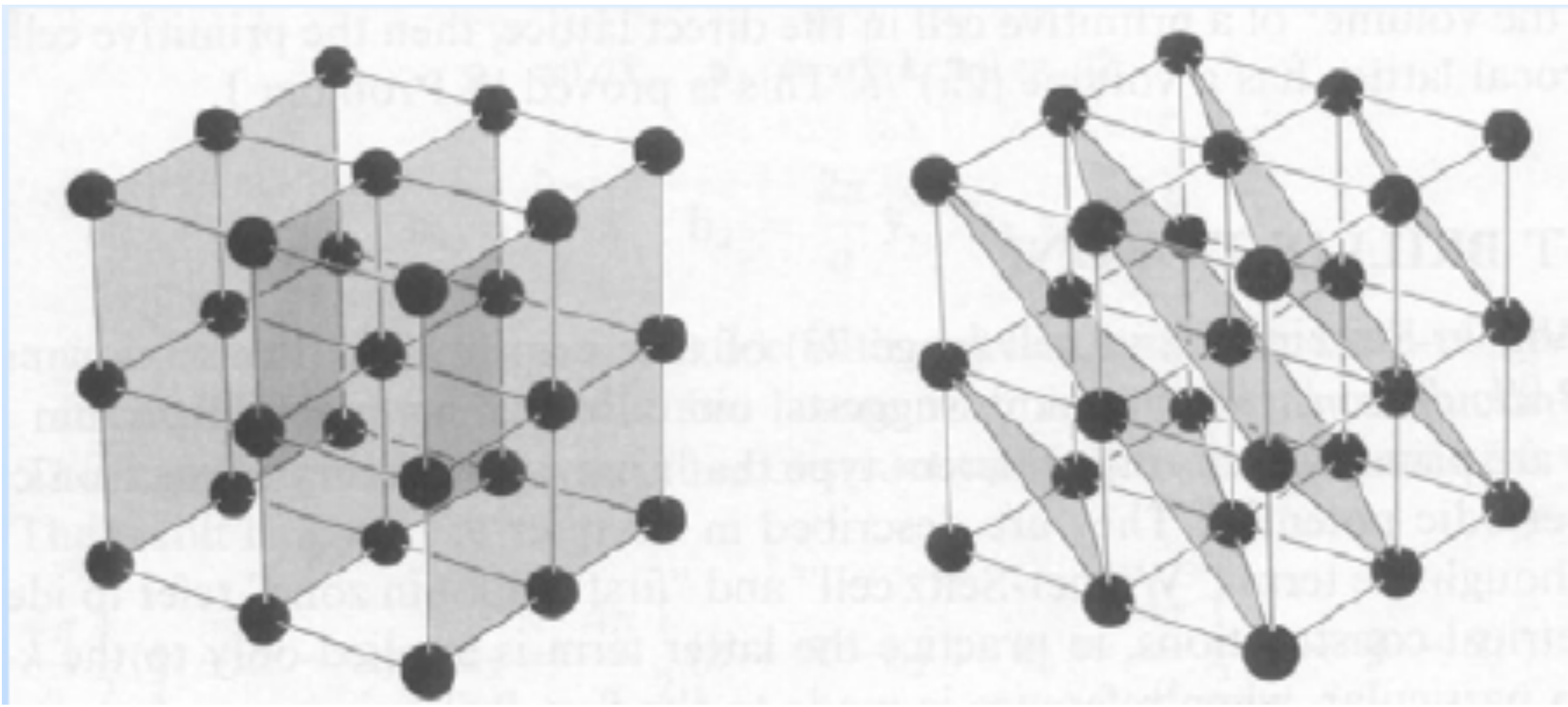


Figure 6.12
The body-centered cubic lattice with cubic cell side $4\pi/a$ that is reciprocal to a face-centered cubic lattice with cubic cell side a. When the fcc lattice is that underlying the diamond structure, then the white circles indicate sites with zero structure factor. (The black circles are sites with structure factor 2, and the gray ones are sites with structure factor $1 \pm i$.)

- V = volume of unit cell
- V* = volume of reciprocal unit cell
- $V V^* = (2\pi)^d$ (d = dimension, 1, 2, 3)
- Reciprocal of fcc is bcc and vice versa
- Reciprocal of hexagonal is hexagonal

[First] **Brillouin zone**≡Wigner Seitz Cell of the momentum (i.e. wave vector) space.

- Any plane containing at least three non-colinear Bravais Lattice points ≡Lattice Plane



- For a given BL and a LP, BL = family of LP

- Any family of lattice planes can be labeled by a reciprocal lattice vector K, which is perpendicular to the lattice planes. The minimum non-zero length of K is given by 2π/d, where d is the spacing between lattice planes.

Any lattice plane is a 2d Bravais Lattice,
characterized by two vectors, which we can call
a1 and **a2**.

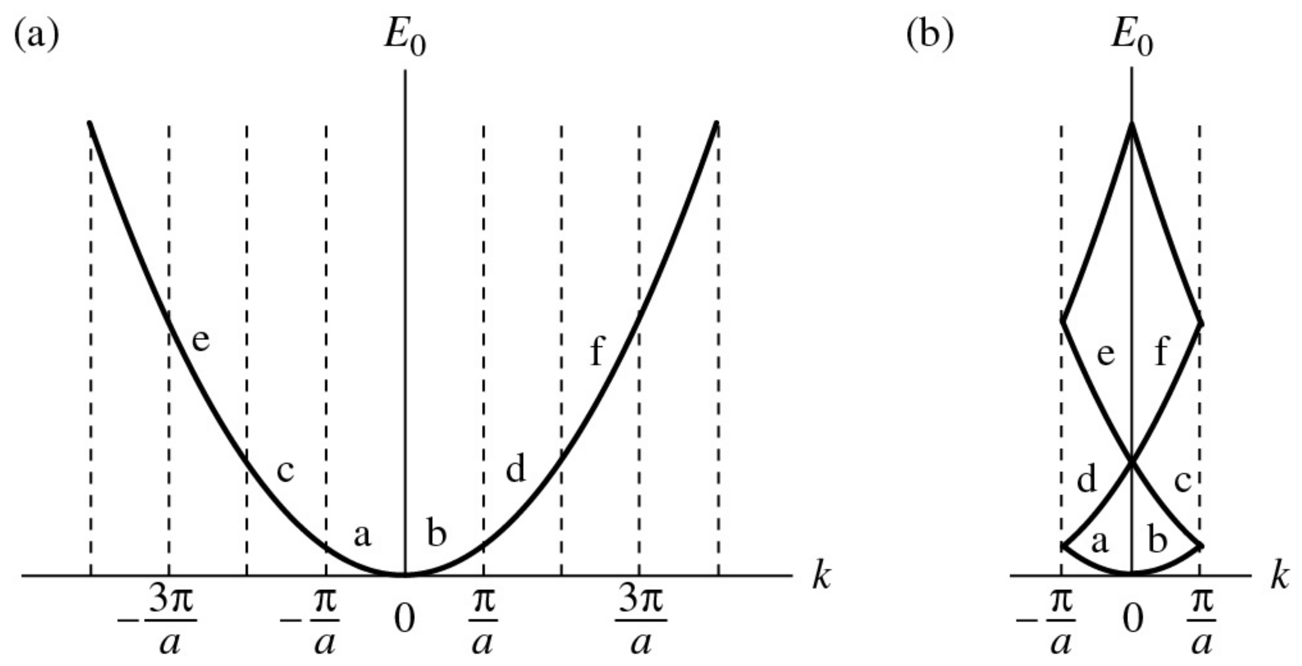
Now, choose any vector connecting
a lattice point of a given lattice plane and
another point of the next lattice plane.Call this **a3**.
a1,a2,a3 are primitive vectors.

Let **b1,b2,b3** be their reciprocal primitive vectors.
By construction, **b3** is perpendicular to our lattice
planes. This is because all 3 rlv are perpendicular to the 3 dlv.

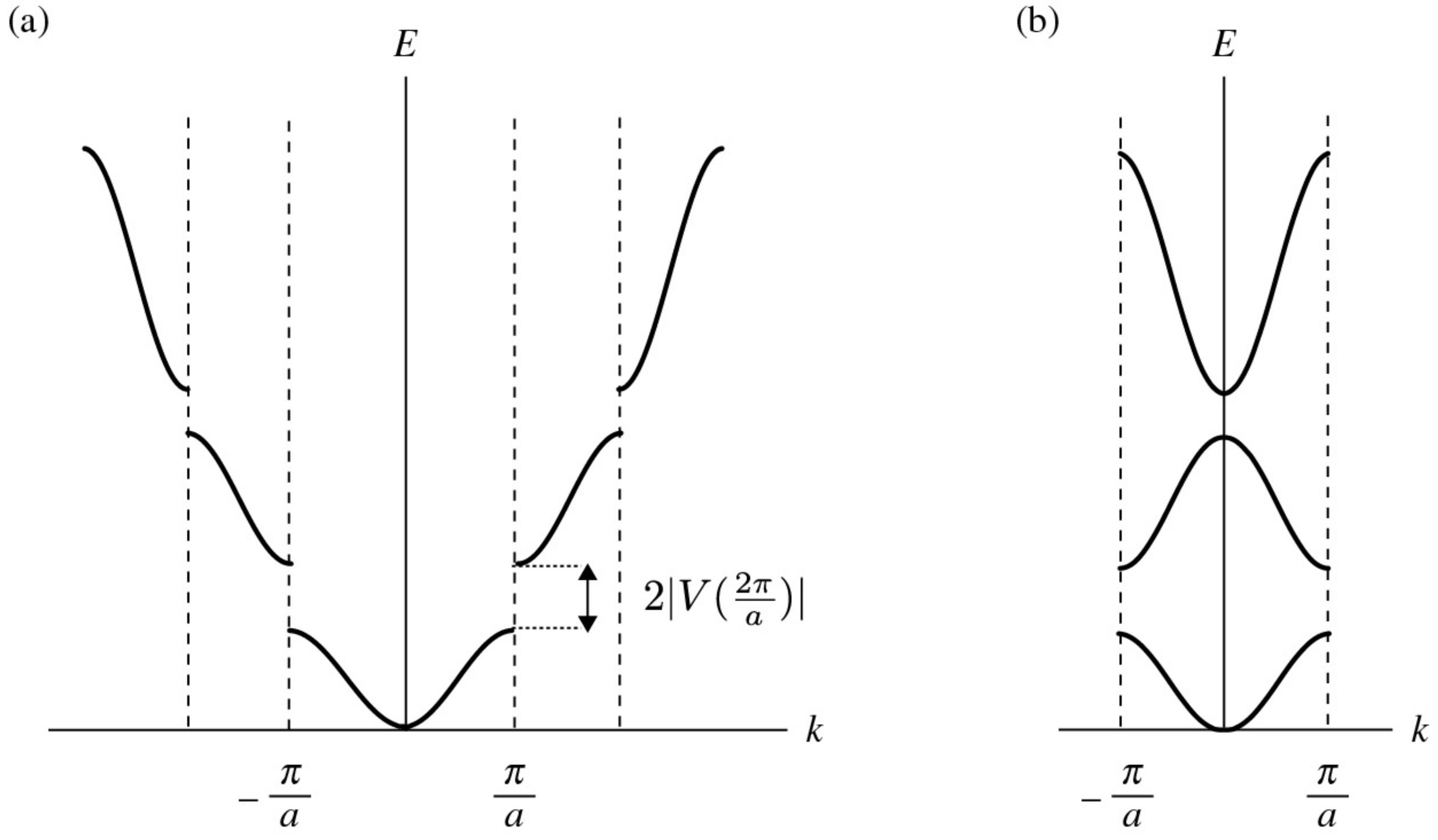
Furthermore, $\mathbf{b3}\cdot\mathbf{a3} = 2\pi$.
Since d is the lattice plane separation, $\mathbf{b3}\cdot\mathbf{a3} = |\mathbf{b3}|d$, and thus
$|\mathbf{b3}| = 2\pi/d$. QED.

CHAPTER 3

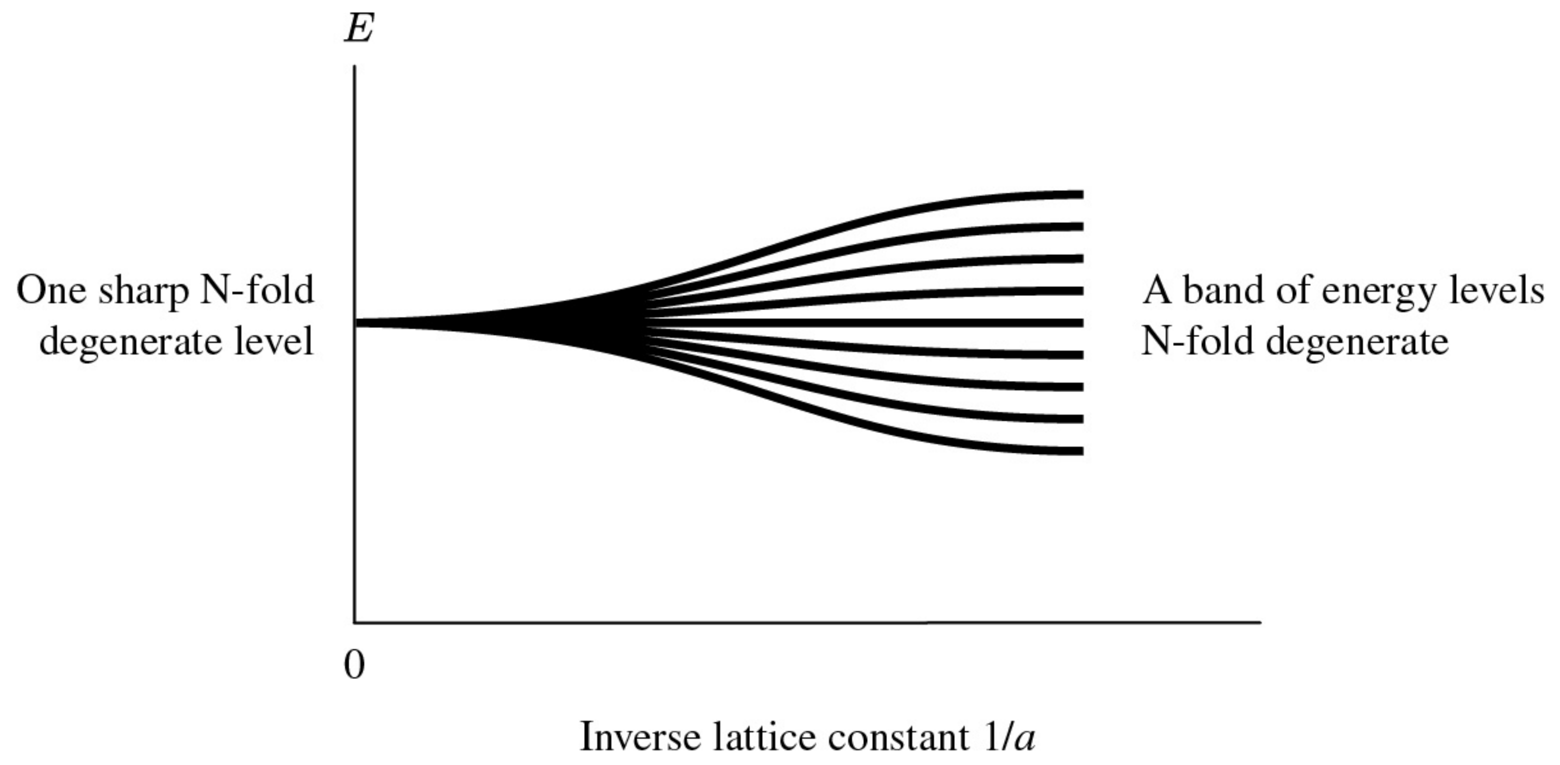
Electronic energy bands



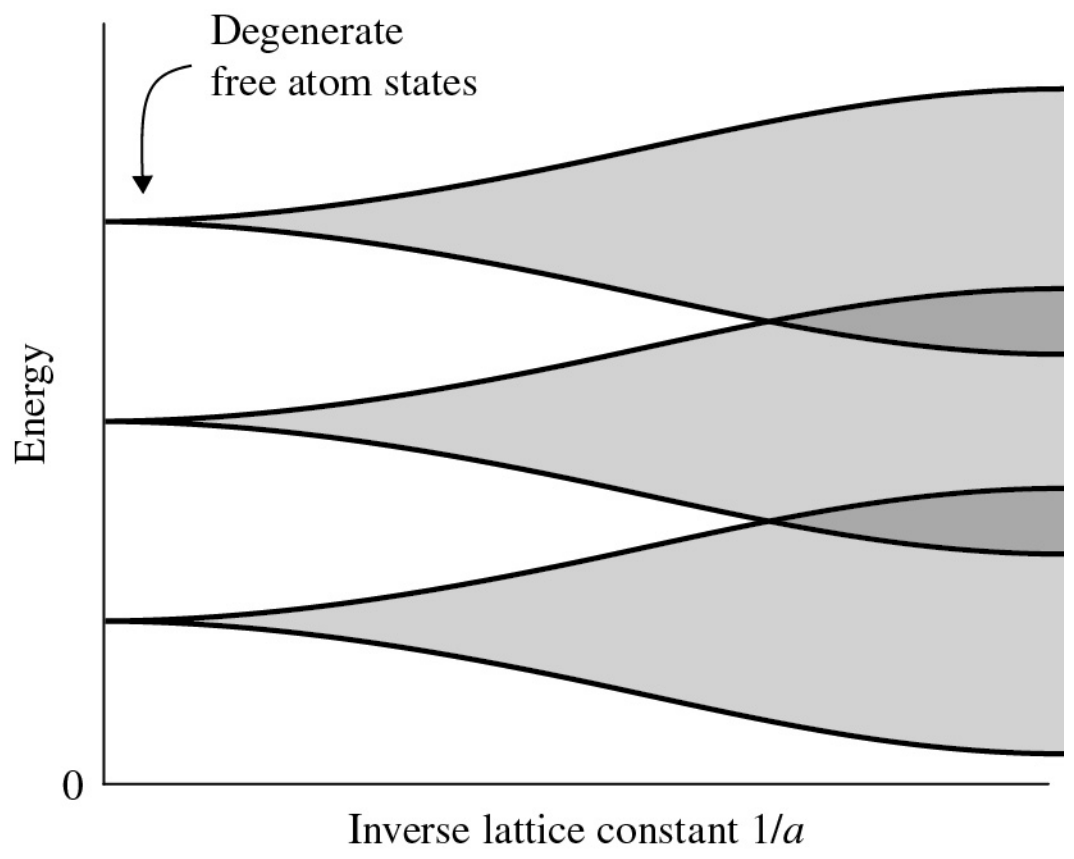
MarvinCohen_Fig.3.1



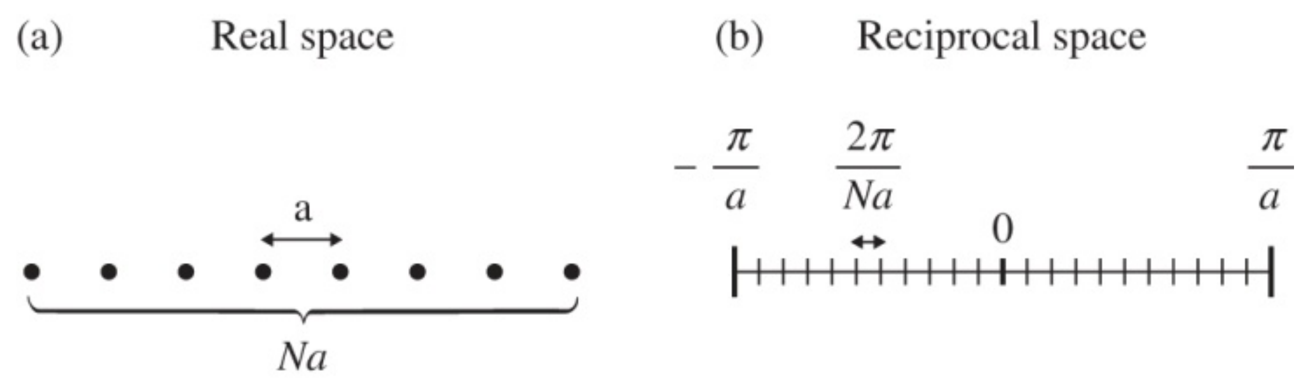
MarvinCohen_Fig.3.5



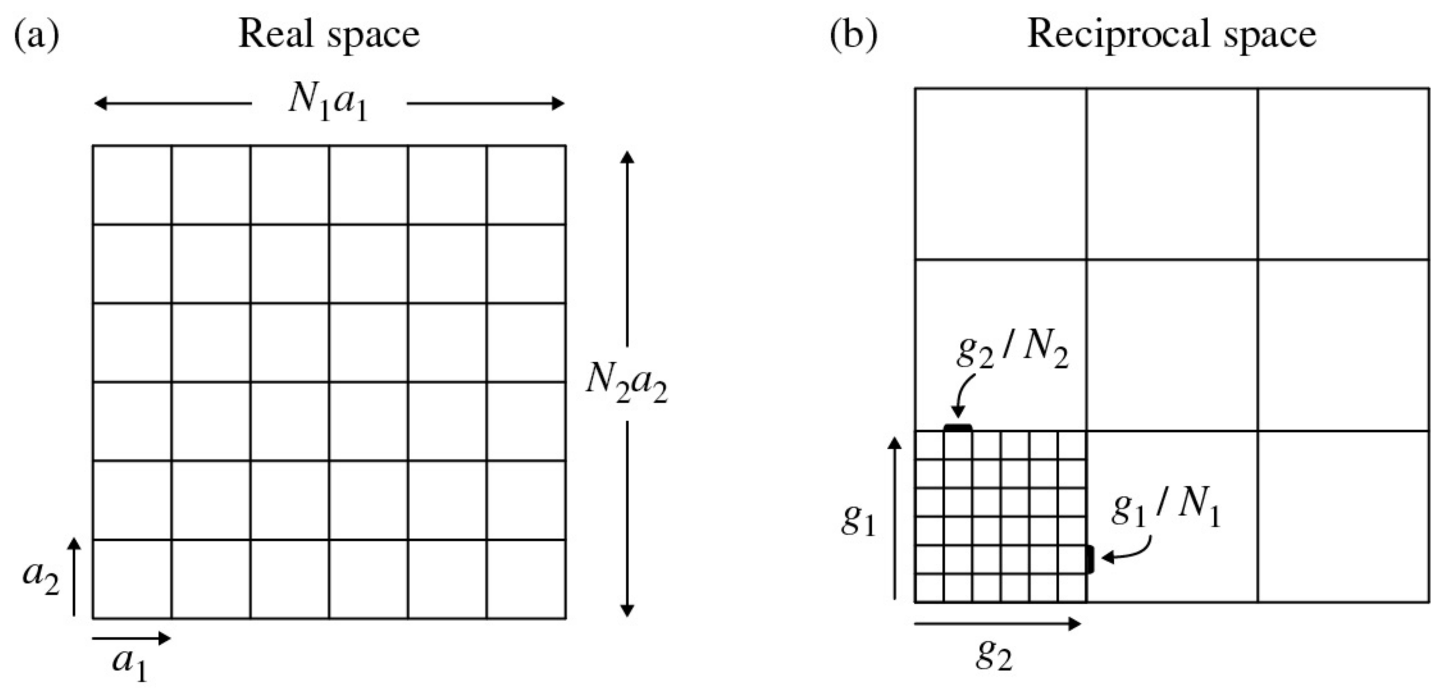
MarvinCohen_Fig.3.6



MarvinCohen_Fig.3.7

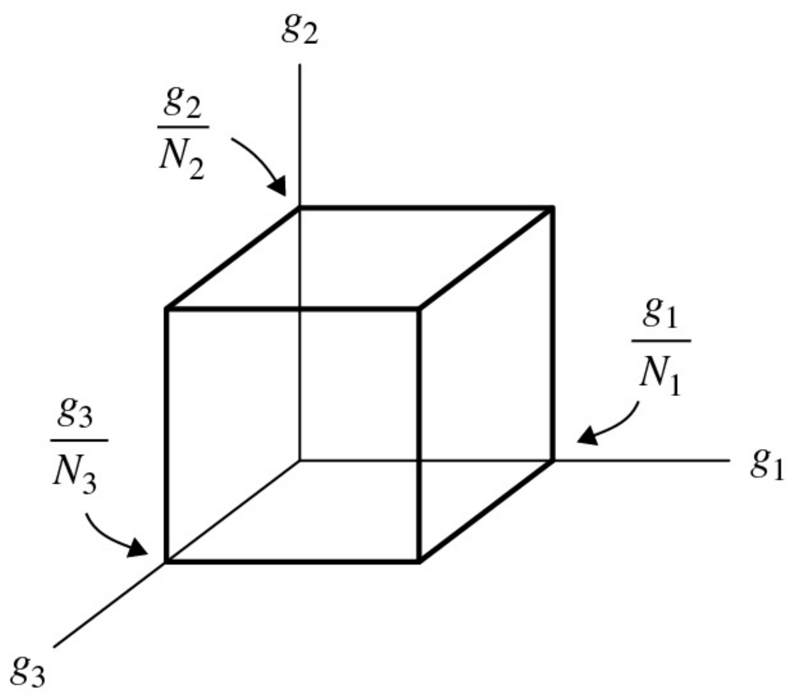


MarvinCohen_Fig.3.10

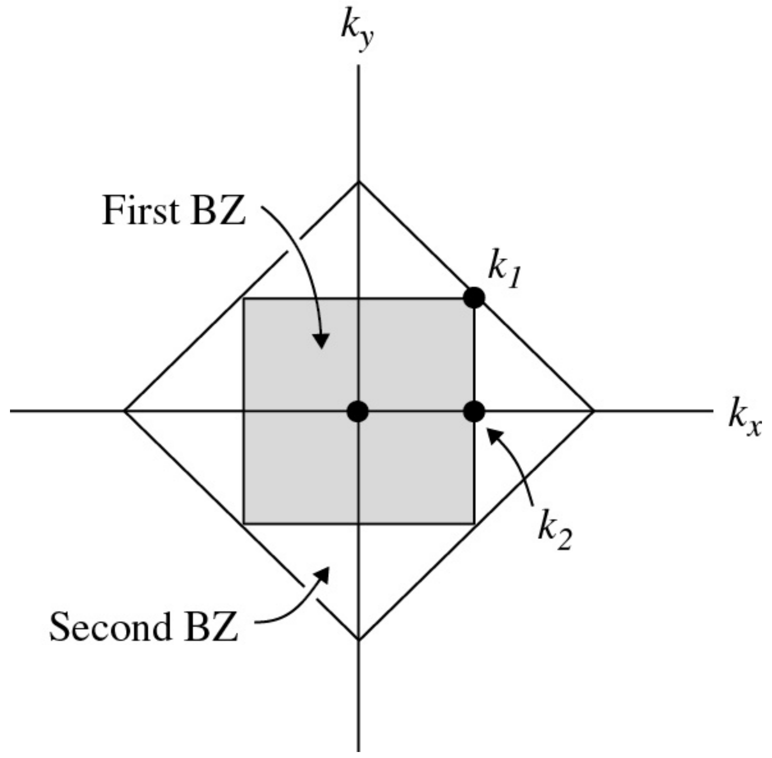

(a) Real space

(b) Reciprocal space

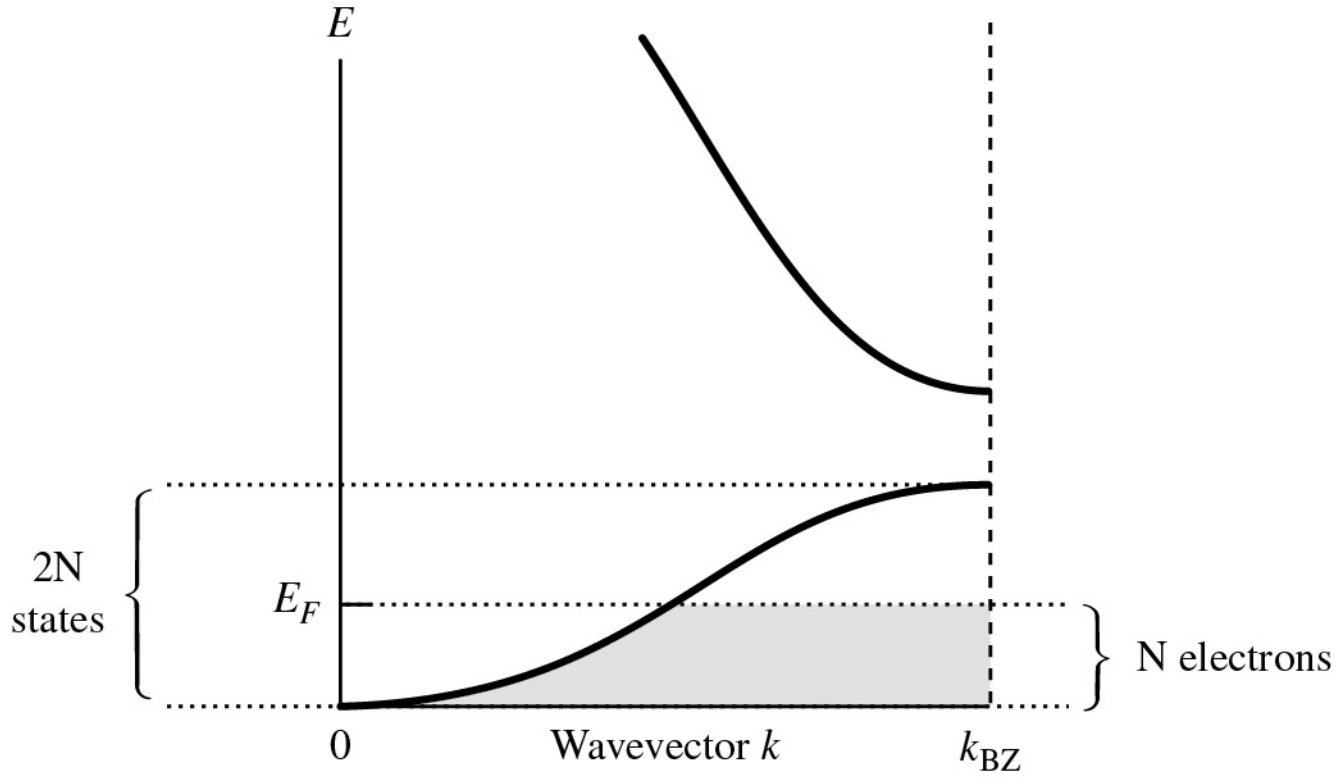
MarvinCohen_Fig.3.11



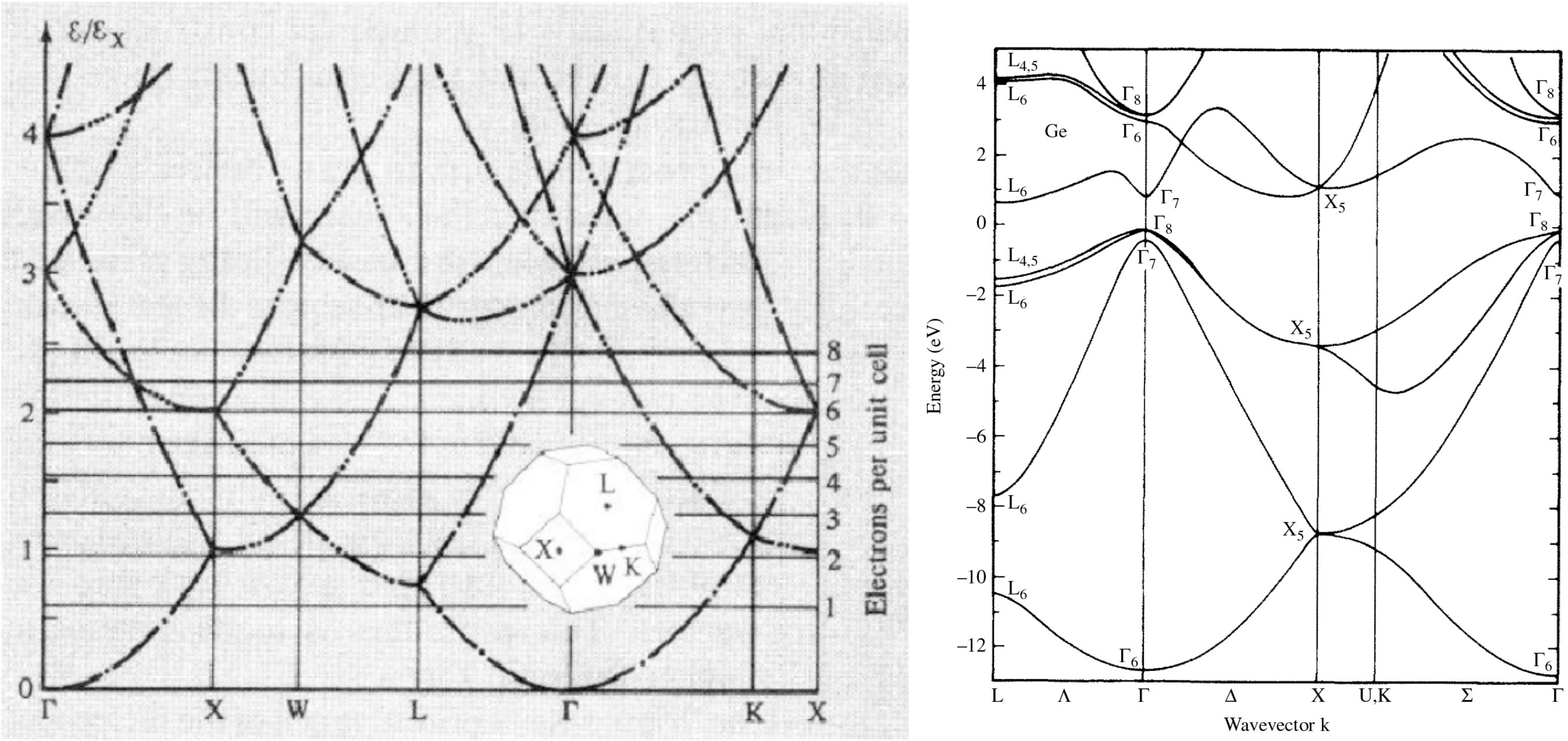
MarvinCohen_Fig.3.12



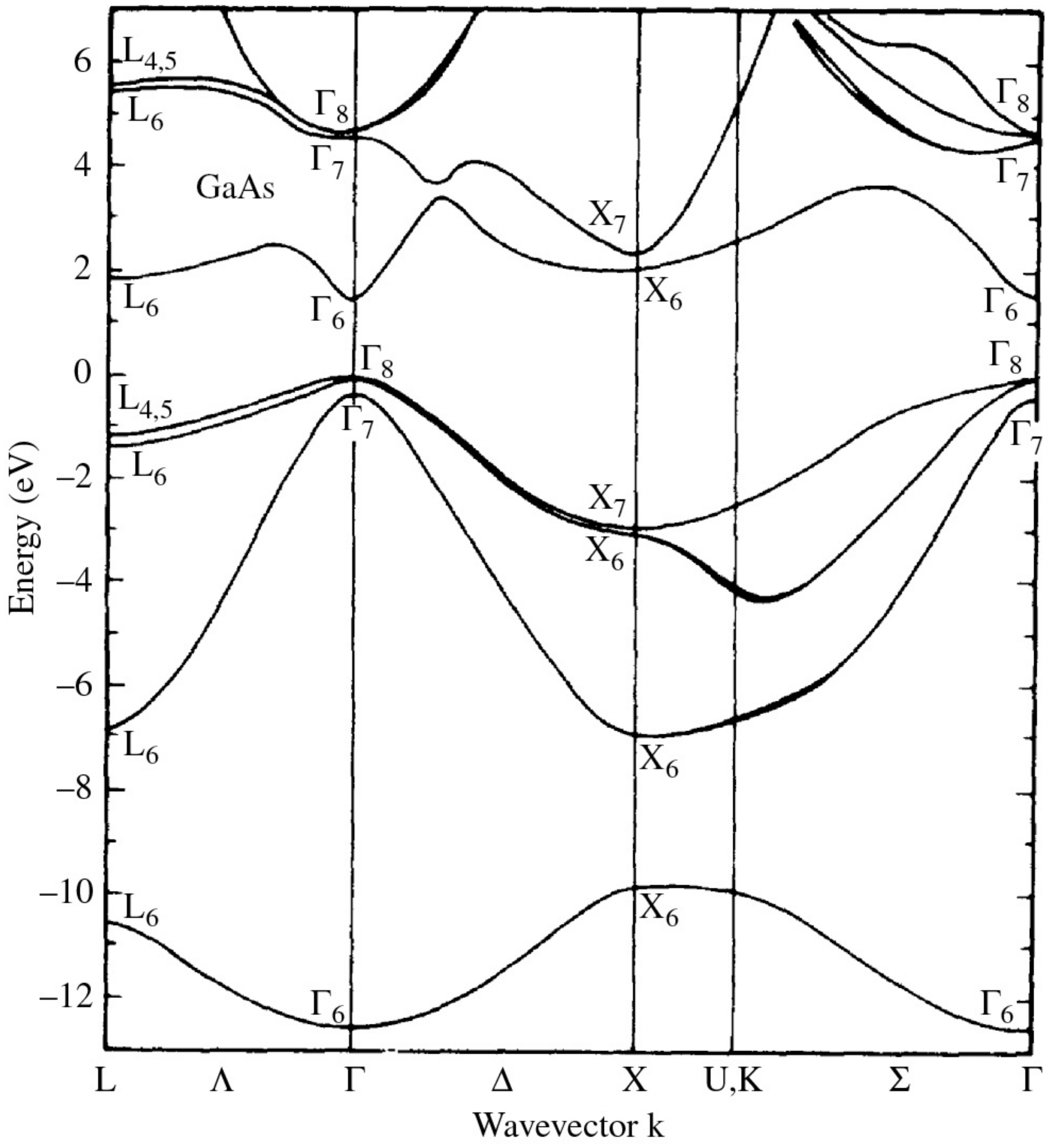
MarvinCohen_Fig.3.13



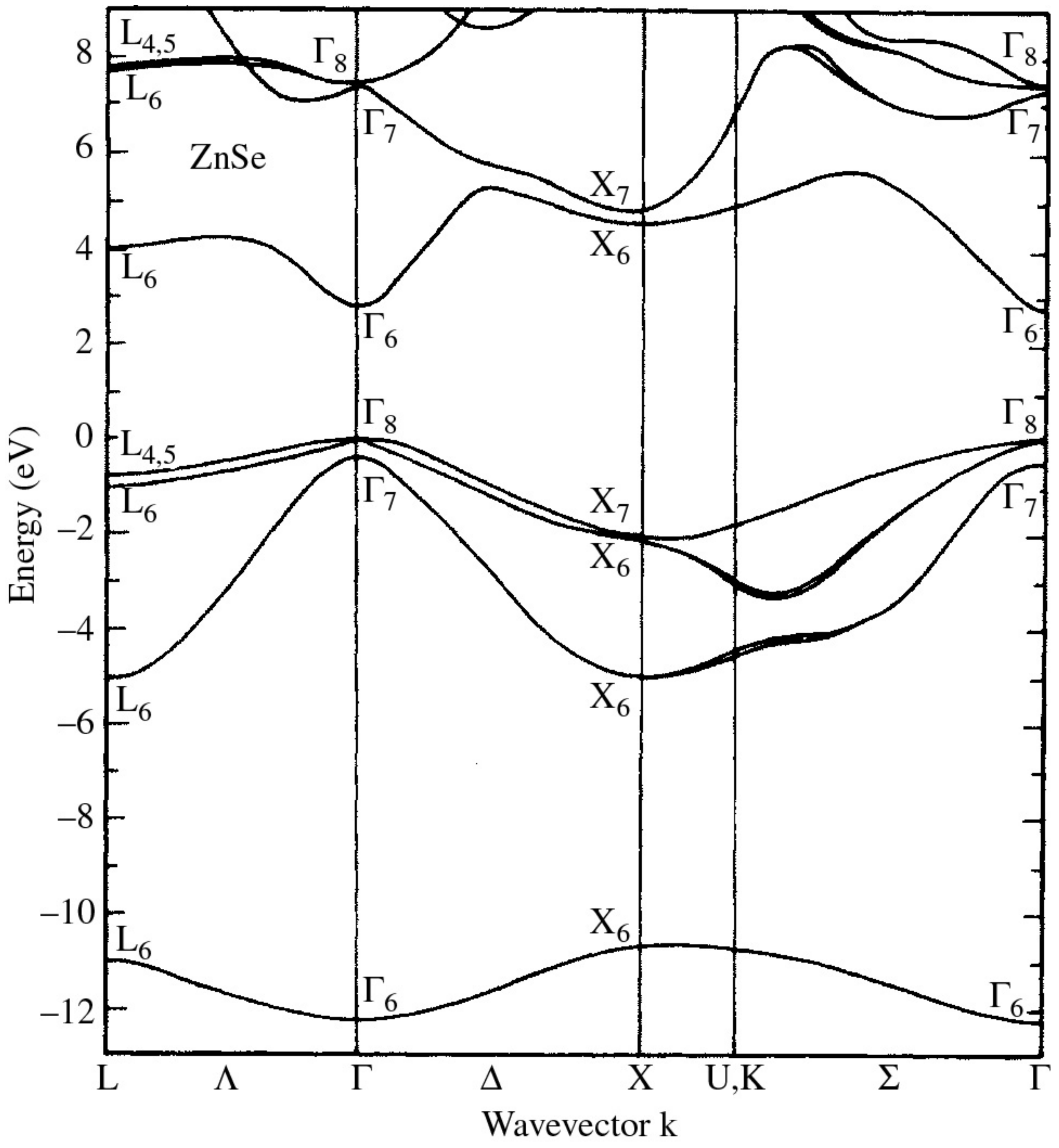
MarvinCohen_Fig.3.14



MarvinCohen_Fig.3.15



MarvinCohen_Fig.3.16



MarvinCohen_Fig.3.17