6.730 Physics for Solid State Applications

Lecture 17: Nearly Free Electron Bands

Outline

- Free Electron in Reduced Zone Representation
- Nearly Free Electron Bands
- Labeling Eigenvectors

March 12, 2004

LCAO and Nearly Free Electron Bandstructure

$$\psi_i(r) = \sum_{\alpha} \sum_{\mathbf{R}_n} c_{i,\alpha[\mathbf{R}_n]} \phi_\alpha(r - \mathbf{R}_n) \qquad \psi(r) = \sum_{\mathbf{R}} c_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}$$

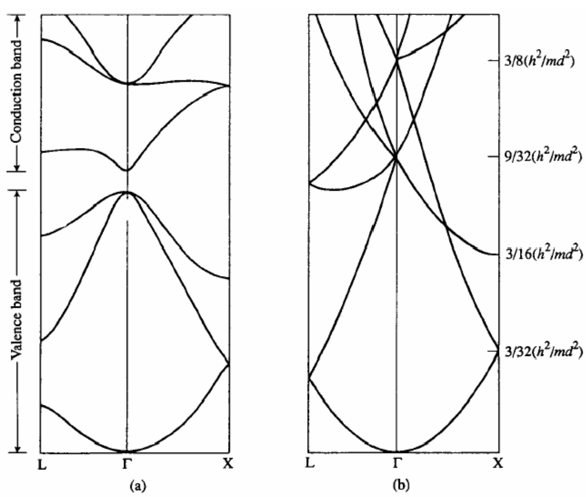
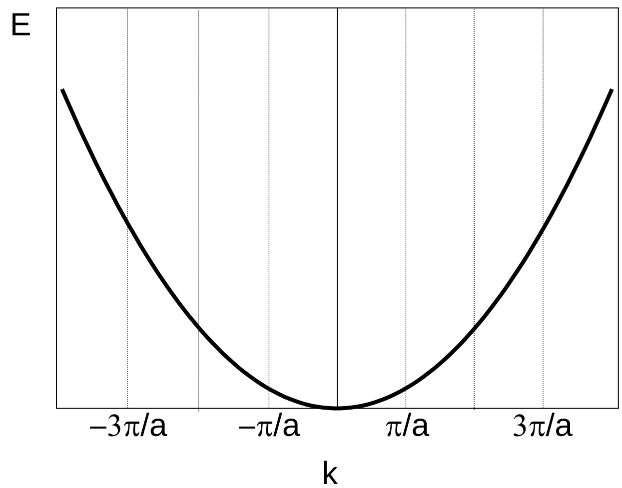


Fig. 7.6 Comparison between the LCAO bands for Ge, computed with an sp^3 basis, and the free electron bands. From Harrison (1980).

Free Electron Dispersion Relation

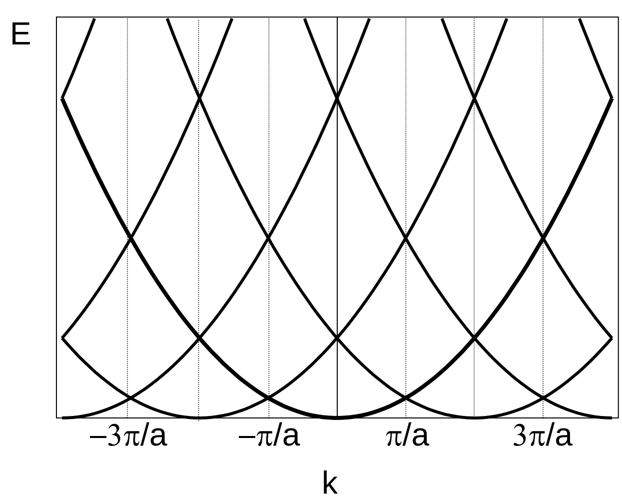
$$E = \frac{\hbar^2 k^2}{2m}$$



Nearly Free Electron Dispersion Relation

For weak lattice potentials, E vs k is still approximately correct... $E = \frac{\hbar^2 k^2}{2m}$

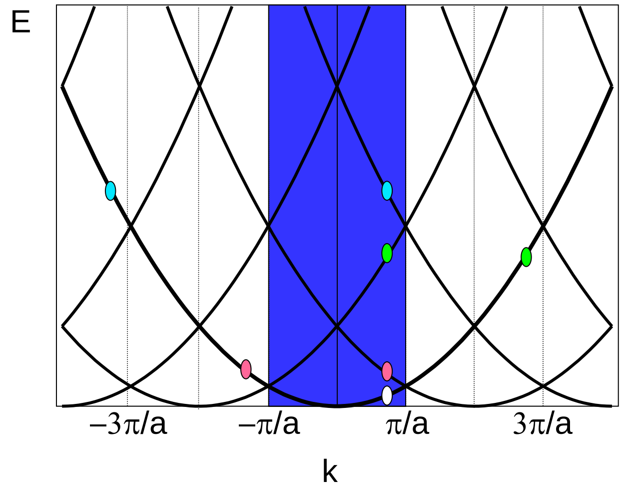
Dispersion relation must be periodic.... $E(k) = E(k + K_i)$



Nearly Free Electron Dispersion Relation

Dispersion relation must be periodic.... $E(k) = E(k + K_i)$

Expect all solutions to be represented within the Brillouin Zone (reduced zone)



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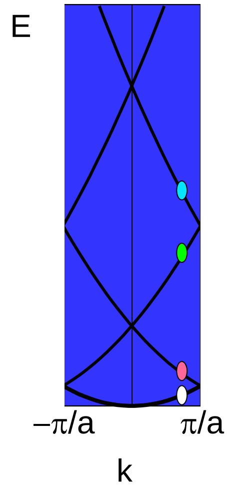

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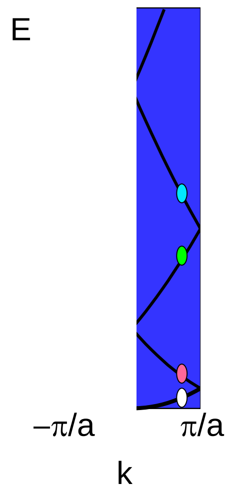
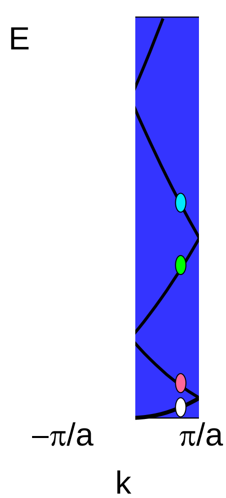
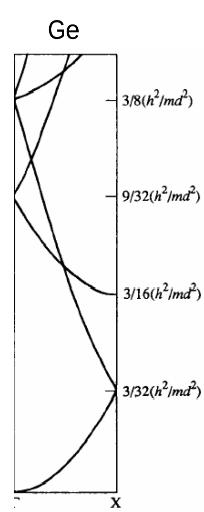


Nearly Free Electron Dispersion Relation

Extension to 3-D requires, translation by reciprocal lattice vectors in all directions... $E(\mathbf{k}) = \mathbf{E}(\mathbf{k} + \mathbf{K_i})$





Nearly Free Electron Dispersion Relation

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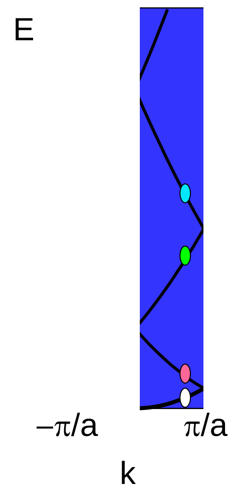
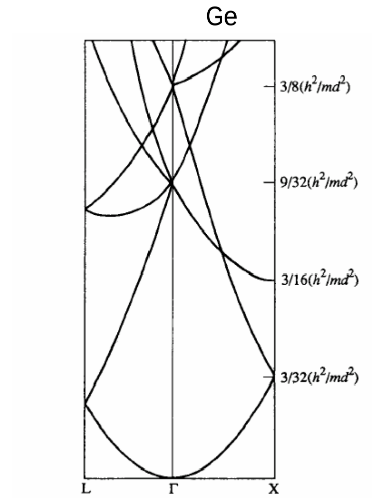




LCAO and Nearly Free Electron Bandstructure

$$\psi_i(r) = \sum_{\alpha} \sum_{\mathbf{R}_n} c_{i,\alpha[\mathrm{R}_n]} \phi_\alpha(r - \mathbf{R}_n) \qquad \psi(r) = \sum_{\mathbf{R}} c_{\mathrm{k}} e^{i\mathbf{kr}}$$

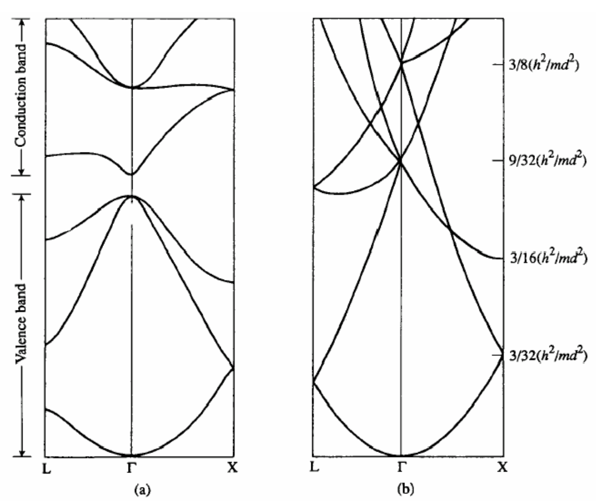


Fig. 7.6 Comparison between the LCAO bands for Ge, computed with an sp^3 basis, and the free electron bands. From Harrison (1980).

Finite Basis Set Expansion with Plane Waves

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_{\text{box}}}} e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{u}_{\mathbf{k}}(\mathbf{r})$$

Fourier series expansion of Bloch function

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_{\text{box}}}} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\{\mathbf{K_i}\}} \mathbf{u}_{\mathbf{k}}[\mathbf{K_i}] e^{i\mathbf{K_i}\cdot\mathbf{r}}$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\{\mathbf{K_i}\}} \mathbf{u}_{\mathbf{k}}[\mathbf{K_i}] \left(\frac{1}{\sqrt{V_{\text{box}}}} e^{i(\mathbf{k}+\mathbf{K_i})\cdot\mathbf{r}} \right)$$

Basis functions in expansion are...

$$\phi_{\ell}(\mathbf{r}) = \frac{1}{\sqrt{V_{\text{box}}}} e^{i(\mathbf{k}+\mathbf{K_i})\cdot\mathbf{r}}$$

Finite Basis Set Expansion with Plane Waves
Hamiltonian Matrix

$$\phi_{\ell}(\mathbf{r}) = \frac{1}{\sqrt{V_{\text{box}}}} e^{i(\mathbf{k}+\mathbf{K_i})\cdot\mathbf{r}}$$

$$E \begin{pmatrix} u_{\mathbf{k}}[\mathbf{K_0}] \\ u_{\mathbf{k}}[\mathbf{K_1}] \\ u_{\mathbf{k}}[\mathbf{K_2}] \\ u_{\mathbf{k}}[\mathbf{K_3}] \end{pmatrix} = \begin{pmatrix} H_{00} & H_{01} & H_{02} & H_{03} \\ H_{10} & H_{11} & H_{12} & H_{13} \\ H_{20} & H_{21} & H_{22} & H_{23} \\ H_{30} & H_{31} & H_{32} & H_{33} \end{pmatrix} \begin{pmatrix} u_{\mathbf{k}}[\mathbf{K_0}] \\ u_{\mathbf{k}}[\mathbf{K_1}] \\ u_{\mathbf{k}}[\mathbf{K_2}] \\ u_{\mathbf{k}}[\mathbf{K_3}] \end{pmatrix}$$

Basis functions are exactly orthogonal...overlaps are all zero.

$$\frac{1}{V_{\text{box}}} \int_{V_{\text{box}}} e^{-i(\mathbf{K_m}-\mathbf{K_n})\cdot\mathbf{r}}\, d^3\mathbf{r} = \delta_{\mathbf{K_m},\mathbf{K_n}}$$

Finite Basis Set Expansion with Plane Waves

Hamiltonian Matrix

$$E\begin{pmatrix} u_{\mathbf{k}}[\mathbf{K_0}] \\ u_{\mathbf{k}}[\mathbf{K_1}] \\ u_{\mathbf{k}}[\mathbf{K_2}] \\ u_{\mathbf{k}}[\mathbf{K_3}] \end{pmatrix} = \begin{pmatrix} H_{00} & H_{01} & H_{02} & H_{03} \\ H_{10} & H_{11} & H_{12} & H_{13} \\ H_{20} & H_{21} & H_{22} & H_{23} \\ H_{30} & H_{31} & H_{32} & H_{33} \end{pmatrix} \begin{pmatrix} u_{\mathbf{k}}[\mathbf{K_0}] \\ u_{\mathbf{k}}[\mathbf{K_1}] \\ u_{\mathbf{k}}[\mathbf{K_2}] \\ u_{\mathbf{k}}[\mathbf{K_3}] \end{pmatrix}$$

$$H_{m,n} = \left\langle \frac{e^{i(\mathbf{k}+\mathbf{K_m})\cdot\mathbf{r}}}{\sqrt{V_{\text{box}}}} \middle| \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}) \middle| \frac{e^{i(\mathbf{k}+\mathbf{K_n})\cdot\mathbf{r}}}{\sqrt{V_{\text{box}}}} \right\rangle$$

$$H_{m,n} = \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_n})^2 \delta_{\mathbf{K_m},\mathbf{K_n}} + \mathbf{V}[\mathbf{K_m}-\mathbf{K_n}]$$

Fourier Series coefficients for the lattice potential...

$$V[\mathbf{K_m}-\mathbf{K_n}] = \frac{\mathbf{1}}{\mathbf{V_{WSC}}} \int_{\mathbf{V_{WSC}}} \mathbf{e}^{-\mathbf{i}(\mathbf{K_m}-\mathbf{K_n})\cdot\mathbf{r}}\, \mathbf{V}(\mathbf{r})\mathbf{d}^3\mathbf{r}$$

Finite Basis Set Expansion with Plane Waves

Hamiltonian Matrix

$$H_{m,n} = \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_n})^2 \delta_{\mathbf{K_m},\mathbf{K_n}} + \mathbf{V}[\mathbf{K_m}-\mathbf{K_n}]$$

$$E_n(\mathbf{k})\begin{pmatrix} u_{\mathbf{k,n}}[\mathbf{K_0}] \\ u_{\mathbf{k,n}}[\mathbf{K_1}] \\ u_{\mathbf{k,n}}[\mathbf{K_2}] \\ u_{\mathbf{k,n}}[\mathbf{K_3}] \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_0})^2+\mathbf{V}[0] & V[\mathbf{K_0}-\mathbf{K_1}] & V[\mathbf{K_0}-\mathbf{K_2}] & V[\mathbf{K_0}-\mathbf{K_3}] \\ V[\mathbf{K_1}-\mathbf{K_0}] & \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_1})^2+\mathbf{V}[0] & V[\mathbf{K_1}-\mathbf{K_2}] & V[\mathbf{K_1}-\mathbf{K_3}] \\ V[\mathbf{K_2}-\mathbf{K_0}] & V[\mathbf{K_2}-\mathbf{K_1}] & \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_2})^2+\mathbf{V}[0] & V[\mathbf{K_2}-\mathbf{K_3}] \\ V[\mathbf{K_3}-\mathbf{K_0}] & V[\mathbf{K_3}-\mathbf{K_1}] & V[\mathbf{K_3}-\mathbf{K_2}] & \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_3})^2+\mathbf{V}[0] \end{pmatrix} \begin{pmatrix} u_{\mathbf{k,n}}[\mathbf{K_0}] \\ u_{\mathbf{k,n}}[\mathbf{K_1}] \\ u_{\mathbf{k,n}}[\mathbf{K_2}] \\ u_{\mathbf{k,n}}[\mathbf{K_3}] \end{pmatrix}$$

Infinite Basis Set Expansion with Plane Waves

Hamiltonian Matrix

$$\begin{bmatrix} \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \lambda(k+K_{-3})^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} & V_{-6} & V_{-7} \\ V_1 & \lambda(k+K_{-2})^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} & V_{-6} \\ V_2 & V_1 & \lambda(k+K_{-1})^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} \\ V_3 & V_2 & V_1 & \lambda(k+K_0)^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} \\ V_4 & V_3 & V_2 & V_1 & \lambda(k+K_1)^2+V_0 & V_{-1} & V_{-2} & V_{-3} \\ V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(k+K_2)^2+V_0 & V_{-1} & V_{-2} \\ V_6 & V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(k+K_3)^2+V_0 & V_{-1} \\ V_7 & V_6 & V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(k+K_4)^2+V_0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \begin{pmatrix} \vdots \\ u_{k,n}[K_{-3}] \\ u_{k,n}[K_{-2}] \\ u_{k,n}[K_{-1}] \\ u_{k,n}[K_0] \\ u_{k,n}[K_1] \\ u_{k,n}[K_2] \\ u_{k,n}[K_3] \\ u_{k,n}[K_4] \\ \vdots \end{pmatrix} = E_n(\mathbf{k}) \begin{pmatrix} \vdots \\ u_{k,n}[K_{-3}] \\ u_{k,n}[K_{-2}] \\ u_{k,n}[K_{-1}] \\ u_{k,n}[K_0] \\ u_{k,n}[K_1] \\ u_{k,n}[K_2] \\ u_{k,n}[K_3] \\ u_{k,n}[K_4] \\ \vdots \end{pmatrix}$$

$$\psi_{\mathbf{k,n}}(\mathbf{r}) = \sum_{\{\mathbf{K_i}\}} \mathbf{u_{k,n}}[\mathbf{K_i}] \left(\frac{\mathbf{1}}{\sqrt{V_{\text{box}}}} \mathbf{e}^{\mathbf{i}(\mathbf{k}+\mathbf{K_i})\cdot\mathbf{r}} \right)$$

$$a_{\mathbf{k,n}}(\mathbf{q}) = \sum_{\mathbf{K_i}} \frac{\mathbf{1}}{\sqrt{V_{\text{box}}}} \mathbf{u_{k,n}}[\mathbf{K_i}] \delta(\mathbf{q} - (\mathbf{k}+\mathbf{K_i}))$$

Infinite Basis Set Expansion with Plane Waves

Hamiltonian Matrix

$$H_{m,n} = \frac{\hbar^2}{2m} (\mathbf{k}+\mathbf{K_n})^2 \delta_{\mathbf{K_m},\mathbf{K_n}} + \mathbf{V}[\mathbf{K_m} - \mathbf{K_n}]$$

$$\begin{bmatrix} \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \lambda(k+K_{-3})^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} & V_{-6} & V_{-7} \\ V_1 & \lambda(k+K_{-2})^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} & V_{-6} \\ V_2 & V_1 & \lambda(k+K_{-1})^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} \\ V_3 & V_2 & V_1 & \lambda(k+K_0)^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} \\ V_4 & V_3 & V_2 & V_1 & \lambda(k+K_1)^2+V_0 & V_{-1} & V_{-2} & V_{-3} \\ V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(k+K_2)^2+V_0 & V_{-1} & V_{-2} \\ V_6 & V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(k+K_3)^2+V_0 & V_{-1} \\ V_7 & V_6 & V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(k+K_4)^2+V_0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}$$

$$\lambda = \hbar^2/2m \qquad V[\mathbf{K_m} - \mathbf{K_n}] = \mathbf{V_{m-n}}$$

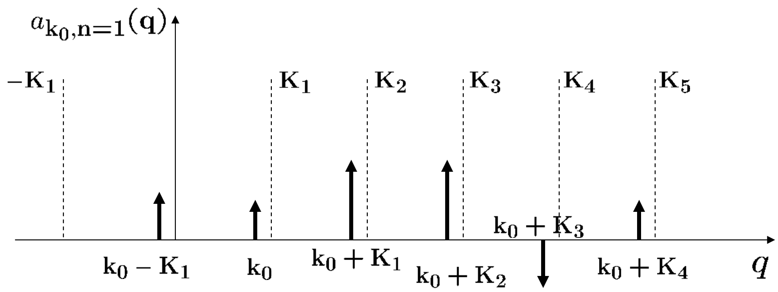
Eigenvectors for Nearly Free Electron Bands

$$\psi_{\mathbf{k},\mathbf{n}}(\mathbf{r}) = \sum_{\{\mathbf{K_i}\}} \mathbf{u}_{\mathbf{k},\mathbf{n}}[\mathbf{K_i}] \left(\frac{1}{\sqrt{V_{\text{box}}}} \mathbf{e}^{\mathbf{i}(\mathbf{k}+\mathbf{K_i})\cdot\mathbf{r}} \right)$$

Fourier transform

$$a_{\mathbf{k},\mathbf{n}}(\mathbf{q}) = \sum_{\mathbf{K_i}} \frac{1}{\sqrt{V_{\text{box}}}} \mathbf{u}_{\mathbf{k},\mathbf{n}}[\mathbf{K_i}]\delta(\mathbf{q}-(\mathbf{k}+\mathbf{K_i}))$$

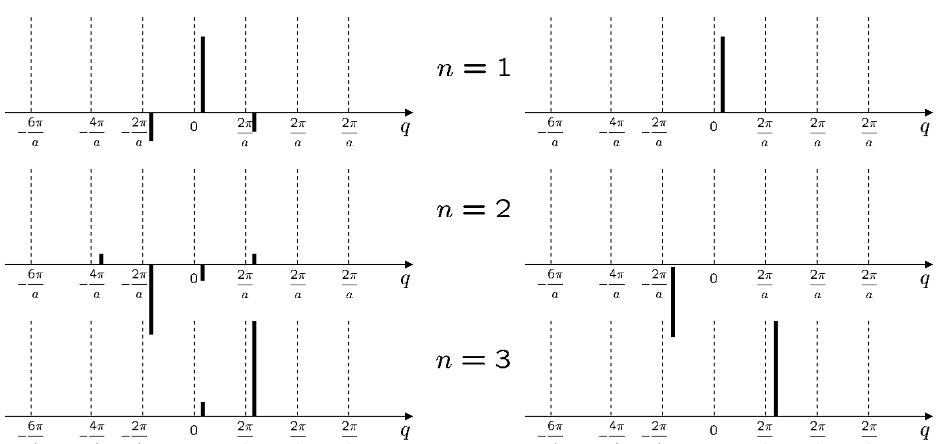
Sample eigenvector...



Eigenvectors for Nearly Free Electron Bands

$a_{\mathbf{k},\mathbf{n}}(\mathbf{q}) \qquad \mathbf{k} = \frac{\pi}{\mathbf{2a}}$

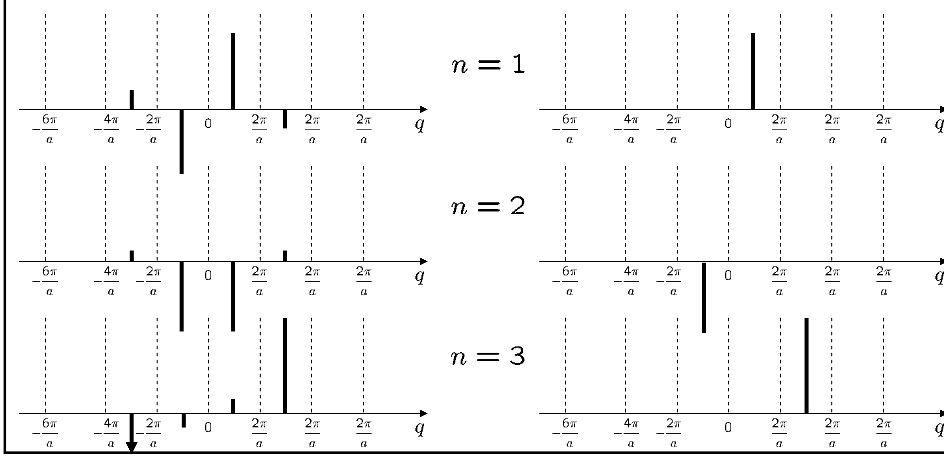
$V[\mathbf{K_m}-\mathbf{K_n}] \neq \mathbf{0}$ $\qquad$ $V[\mathbf{K_m}-\mathbf{K_n}] = \mathbf{0}$



Eigenvectors for Nearly Free Electron Bands

$a_{\mathbf{k},\mathbf{n}}(\mathbf{q}) \qquad \mathbf{k} = \frac{\pi}{\mathbf{a}}$

$V[\mathbf{K_m} - \mathbf{K_n}] \neq \mathbf{0}$ $\qquad$ $V[\mathbf{K_m} - \mathbf{K_n}] = \mathbf{0}$



Eigenvectors for Nearly Free Electron Bands

$a_{\mathbf{k},\mathbf{n}}(\mathbf{q}) \qquad \mathbf{k} = \mathbf{0}$

$V[\mathbf{K_m} - \mathbf{K_n}] \neq \mathbf{0}$ $\qquad$ $V[\mathbf{K_m} - \mathbf{K_n}] = \mathbf{0}$