6.730 Physics for Solid State Applications

Lecture 16: Nearly Free Electron Bands

Outline

- Fun: Application of 1-D Tight Binding
- Free Electron in Reduced Zone Representation
- Nearly Free Electron Bands
- Labeling Eigenvectors

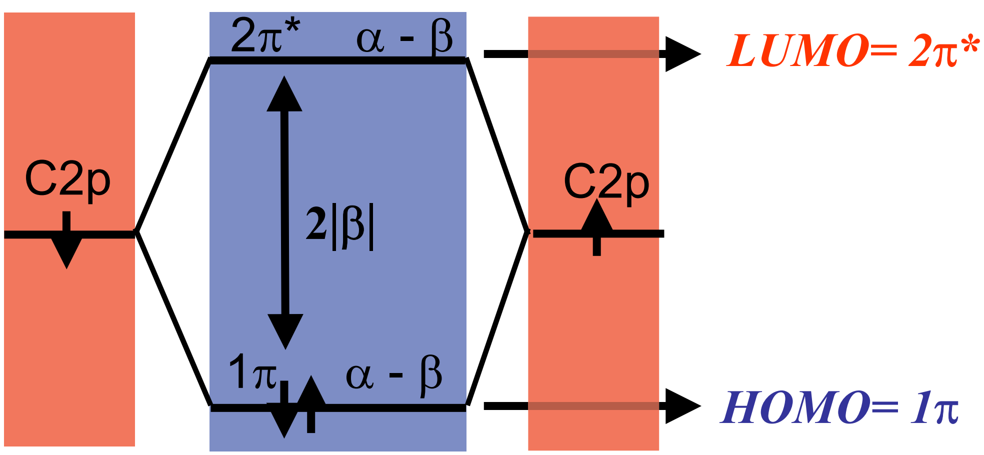
B. Ethene and frontier orbitals

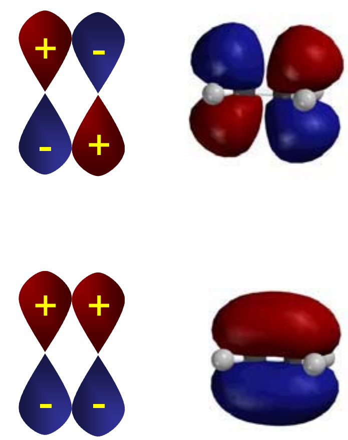
Ethene: $CH_2{=}CH_2$

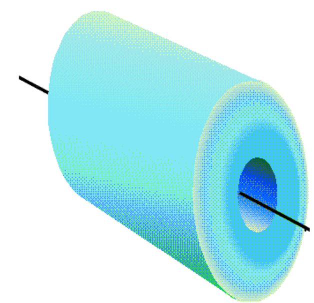
Within the Hückel approximation, the secular determinant becomes:

$$\begin{vmatrix} (\alpha - E) & \beta \\ \beta & (\alpha - E) \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0$$

$$\rightarrow \begin{cases} E_- = \alpha - \beta \rightarrow & \text{energy of the } \textit{Lowest Unoccupied Molecular Orbital (LUMO)} \\ E_+ = \alpha + \beta \rightarrow & \text{energy of the } \textit{Highest Occupied Molecular Orbital (HOMO)} \end{cases}$$







Sketch Calculated (Hartree-Fock level)

➔ HOMO and LUMO are the ***frontier orbitals*** of a molecule.

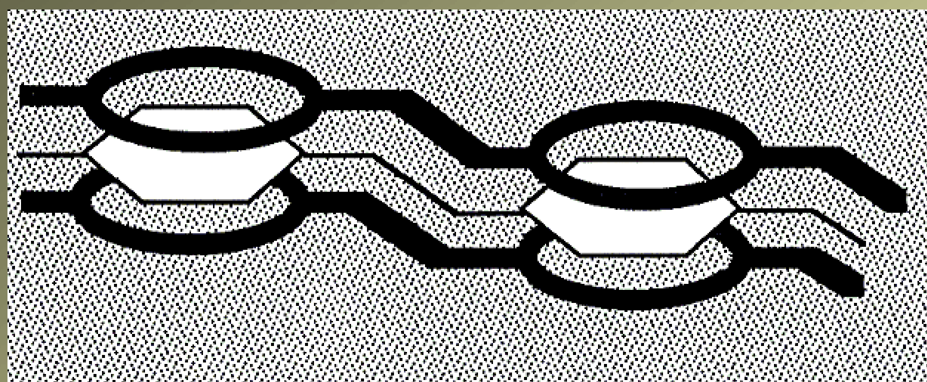
➔ those are important orbitals because they are largely responsible for many ***chemical*** and ***optical properties*** of the molecule.

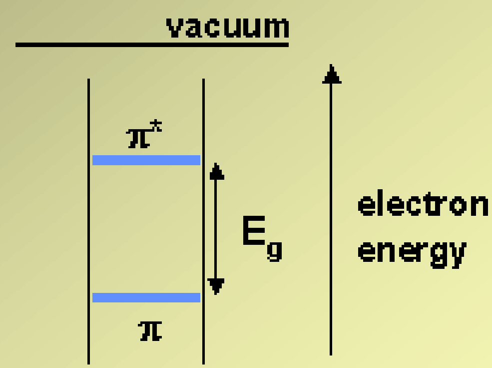
Courtesy of Crispin Xavier Dept. of Physics, Linköping University

Note: The π orbitals together give rise to an cylindrical distribution of charge. Electrons can circulate around this torus can create magnetic effect detected in NMR

CP Energy Bands

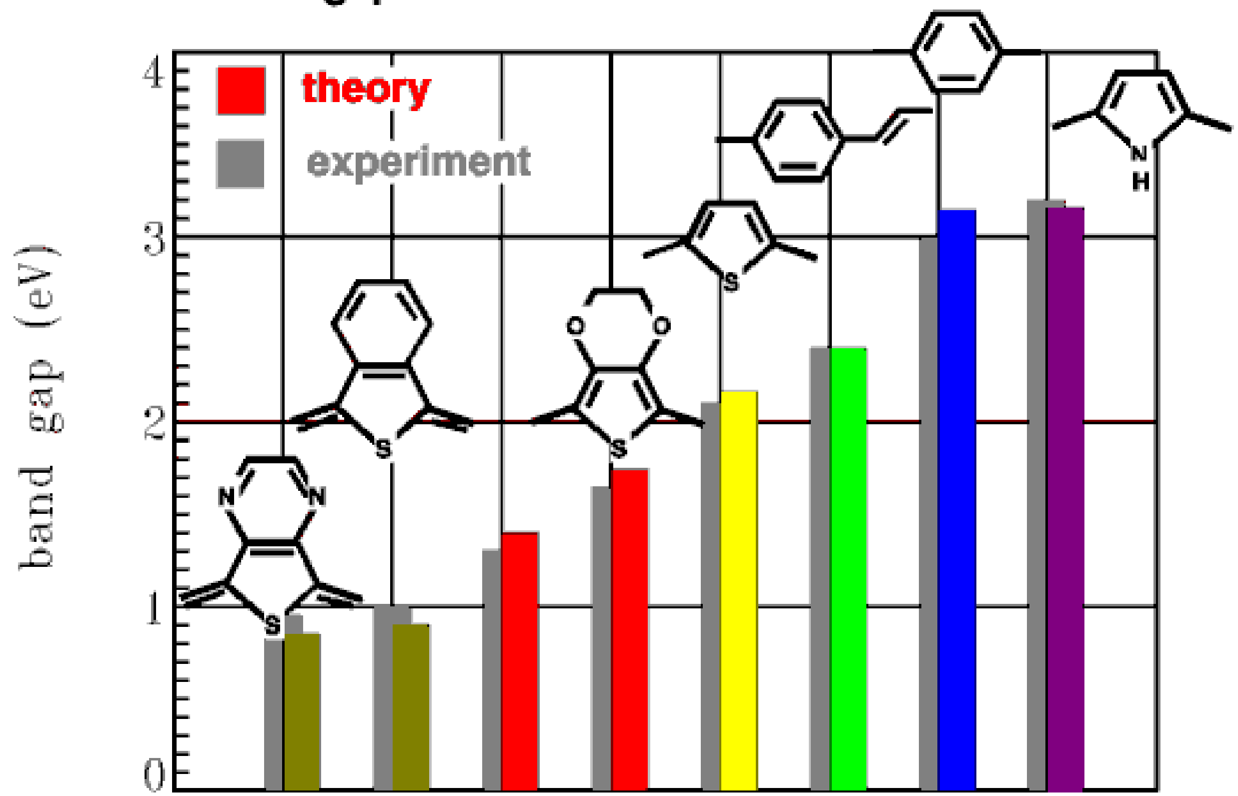
- The delocalised π-electron system thus confers semiconducting properties to the CP with π-bonding (valence) and π^*-antibonding (conduction) bands.





- For intrinsically pure CP films, the band-gap between the π and π^* bands is expected to be essentially free of defect and dangling-bond states. Surface state densities should also be minimal since chemical bonds at the surface of an organic semiconductor are identical to those in the bulk

Band gaps



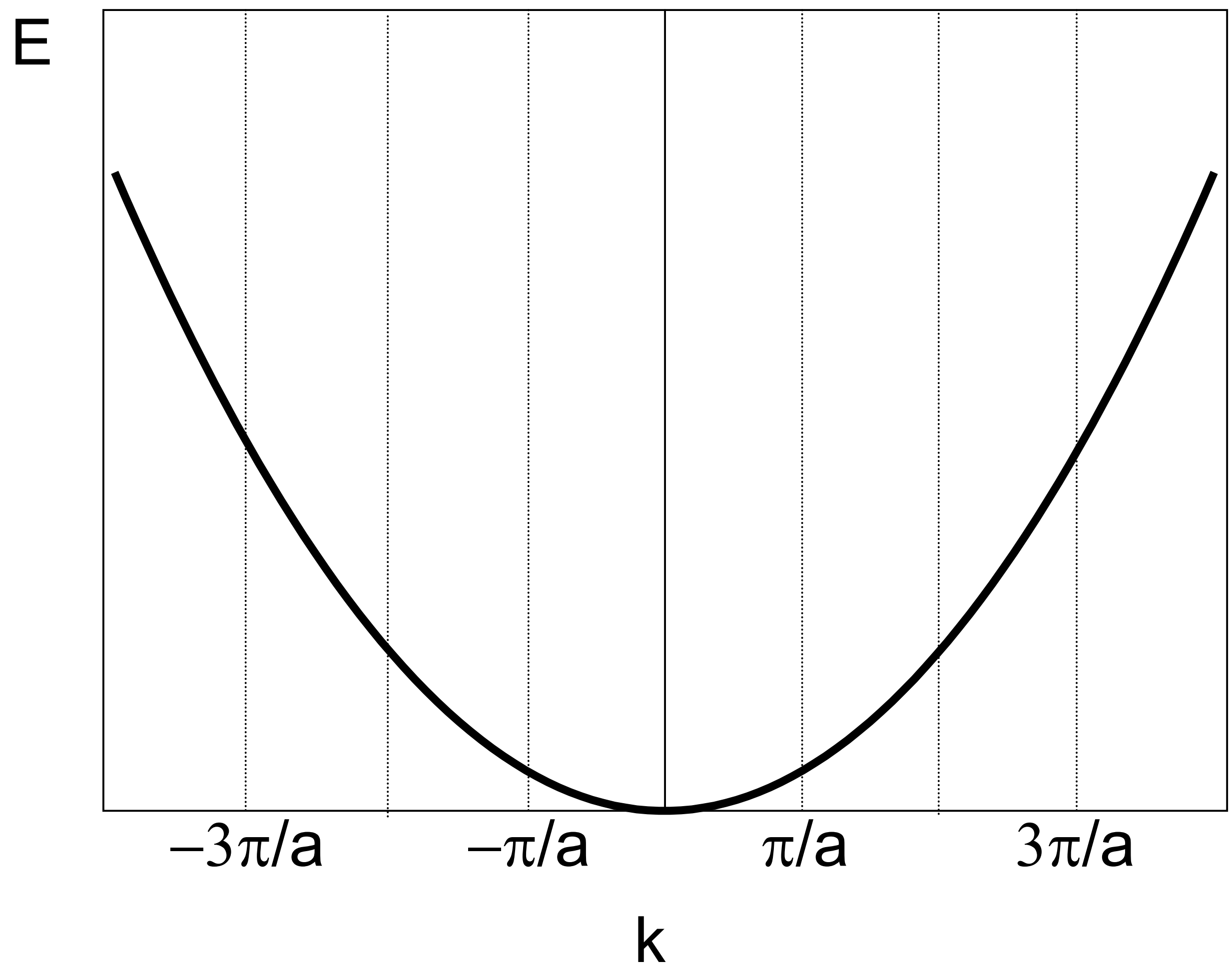
LCAO and Nearly Free Electron Bandstructure

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

$$\psi(r) = \sum_{\mathbf{R}} c_{\mathbf{k}} e^{i\mathbf{kr}}$$

Free Electron Dispersion Relation

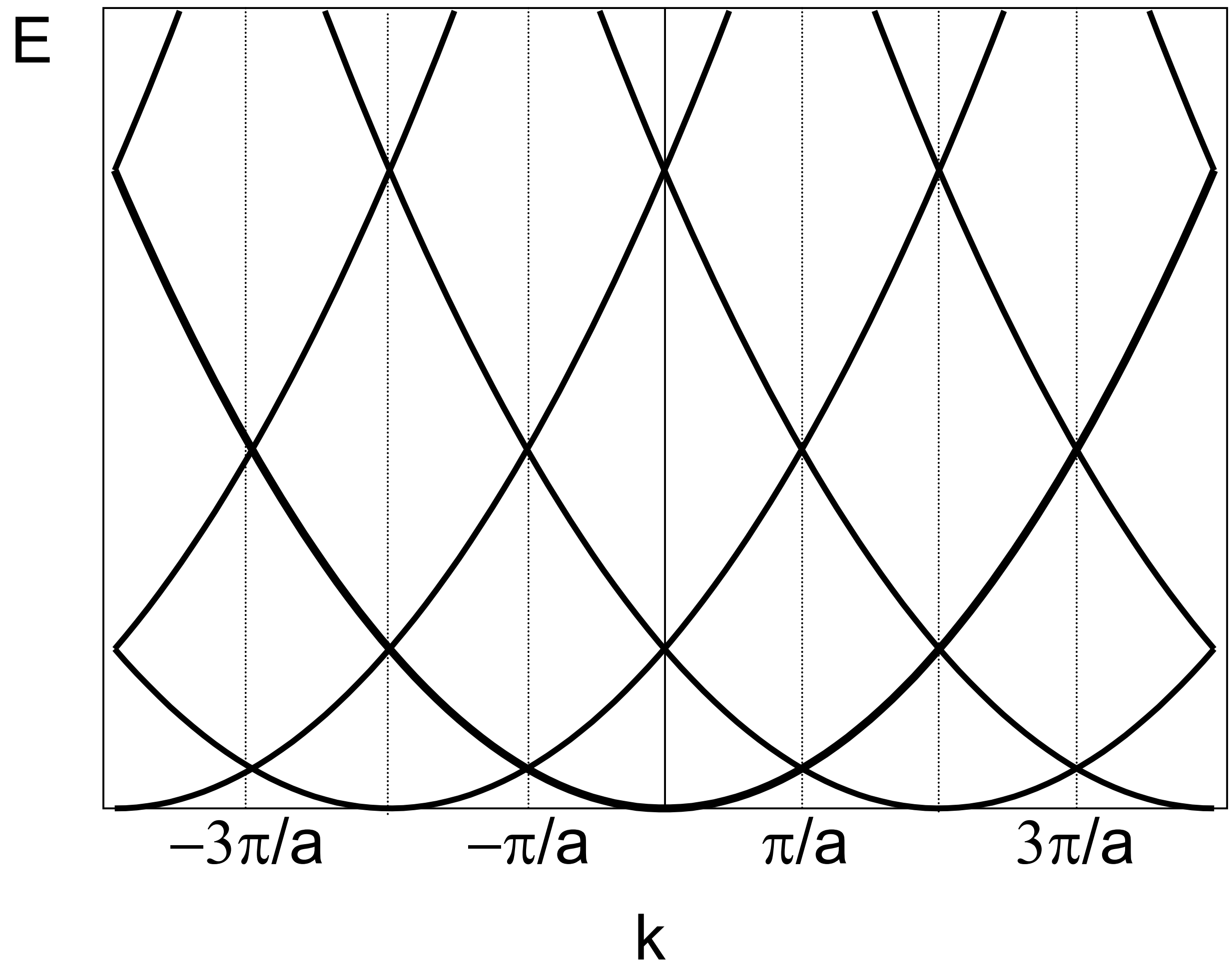
$$E = \frac{\hbar^2 k^2}{2m}$$



Nearly Free Electron Dispersion Relation

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

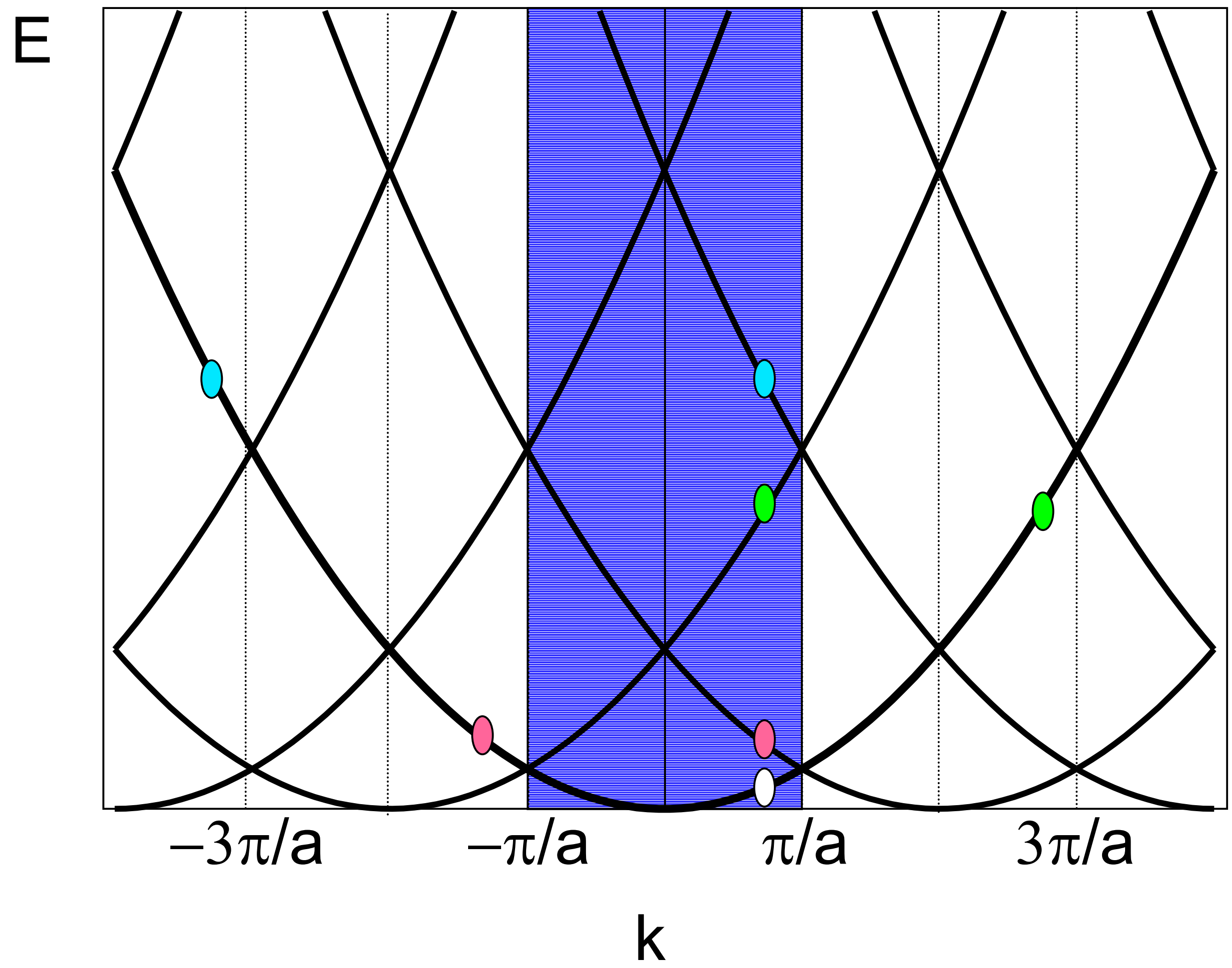
Dispersion relation must be periodic…. $E(k) = E(k + K_i)$



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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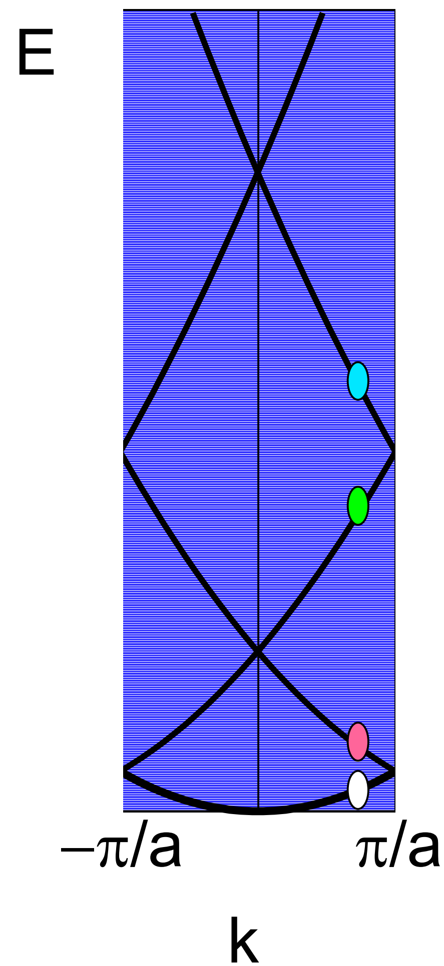

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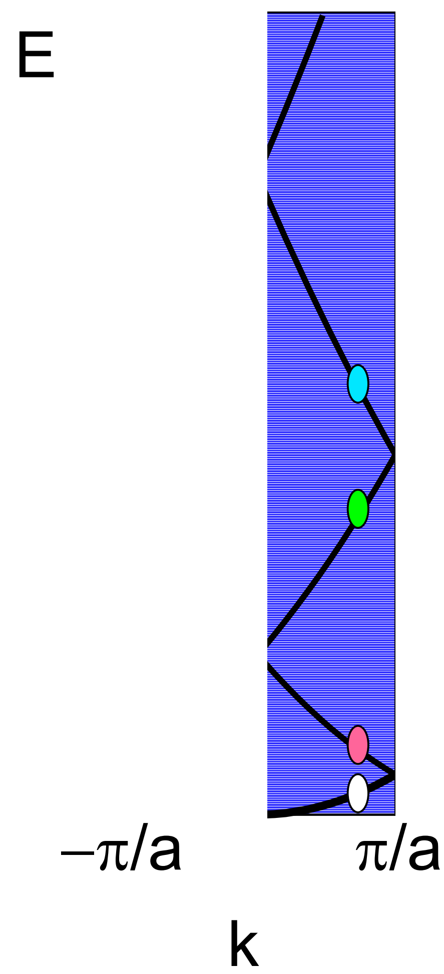
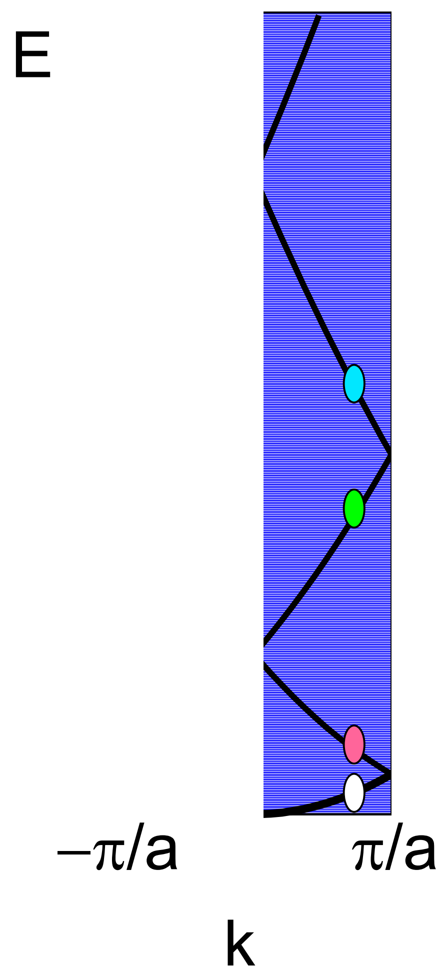
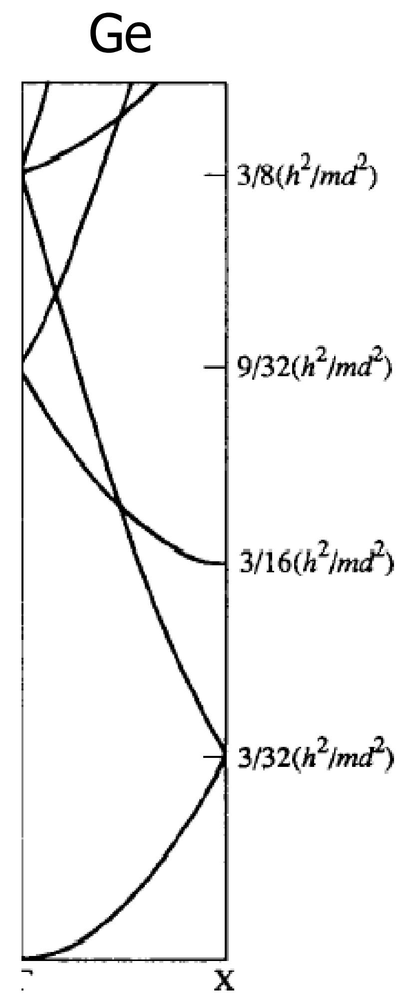


Nearly Free Electron Dispersion Relation

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

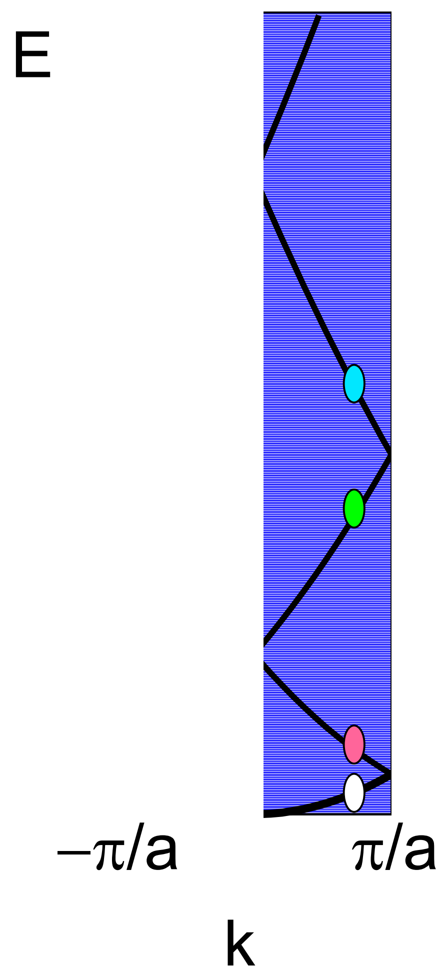




Nearly Free Electron Dispersion Relation

Extension to 3-D requires, translation by reciprocal lattice vectors in all directions…

$$E(\mathbf{k}) = \mathbf{E}(\mathbf{k} + \mathbf{K_i})$$



Ge

LCAO and Nearly Free Electron Bandstructure

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

Finite Basis Set Expansion with Plane Waves

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

Fourier series expansion of Bloch function

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

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

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

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

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

Basis functions are exactly orthogonal…overlaps are all zero.

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

Finite Basis Set Expansion with Plane Waves

Hamiltonian Matrix

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

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

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

Fourier Series coefficients for the lattice potential…

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

Finite Basis Set Expansion with Plane Waves
Hamiltonian Matrix

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

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

Infinite Basis Set Expansion with Plane Waves

Hamiltonian Matrix

$$\begin{bmatrix} \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \lambda(\mathrm{k}+\mathrm{K}_{-3})^2+\mathrm{V}_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} & V_{-6} & V_{-7} \\ V_1 & \lambda(\mathrm{k}+\mathrm{K}_{-2})^2+\mathrm{V}_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} & V_{-6} \\ V_2 & V_1 & \lambda(\mathrm{k}+\mathrm{K}_{-1})^2+\mathrm{V}_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} \\ V_3 & V_2 & V_1 & \lambda(\mathrm{k}+\mathrm{K}_0)^2+\mathrm{V}_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} \\ V_4 & V_3 & V_2 & V_1 & \lambda(\mathrm{k}+\mathrm{K}_1)^2+\mathrm{V}_0 & V_{-1} & V_{-2} & V_{-3} \\ V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(\mathrm{k}+\mathrm{K}_2)^2+\mathrm{V}_0 & V_{-1} & V_{-2} \\ V_6 & V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(\mathrm{k}+\mathrm{K}_3)^2+\mathrm{V}_0 & V_{-1} \\ V_7 & V_6 & V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(\mathrm{k}+\mathrm{K}_4)^2+\mathrm{V}_0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \begin{pmatrix} \vdots \\ u_{\mathrm{k,n}}[\mathrm{K}_{-3}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{-2}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{-1}] \\ u_{\mathrm{k,n}}[\mathrm{K}_0] \\ u_{\mathrm{k,n}}[\mathrm{K}_1] \\ u_{\mathrm{k,n}}[\mathrm{K}_2] \\ u_{\mathrm{k,n}}[\mathrm{K}_3] \\ u_{\mathrm{k,n}}[\mathrm{K}_4] \\ \vdots \end{pmatrix} = E_n(\mathrm{k}) \begin{pmatrix} \vdots \\ u_{\mathrm{k,n}}[\mathrm{K}_{-3}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{-2}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{-1}] \\ u_{\mathrm{k,n}}[\mathrm{K}_0] \\ u_{\mathrm{k,n}}[\mathrm{K}_1] \\ u_{\mathrm{k,n}}[\mathrm{K}_2] \\ u_{\mathrm{k,n}}[\mathrm{K}_3] \\ u_{\mathrm{k,n}}[\mathrm{K}_4] \\ \vdots \end{pmatrix}$$

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

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

Infinite Basis Set Expansion with Plane Waves

Hamiltonian Matrix

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

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

$$\lambda = \hbar^2/2m$$

$$V[\mathbf{K_m} - \mathbf{K_n}] = \mathbf{V_{m-n}}$$

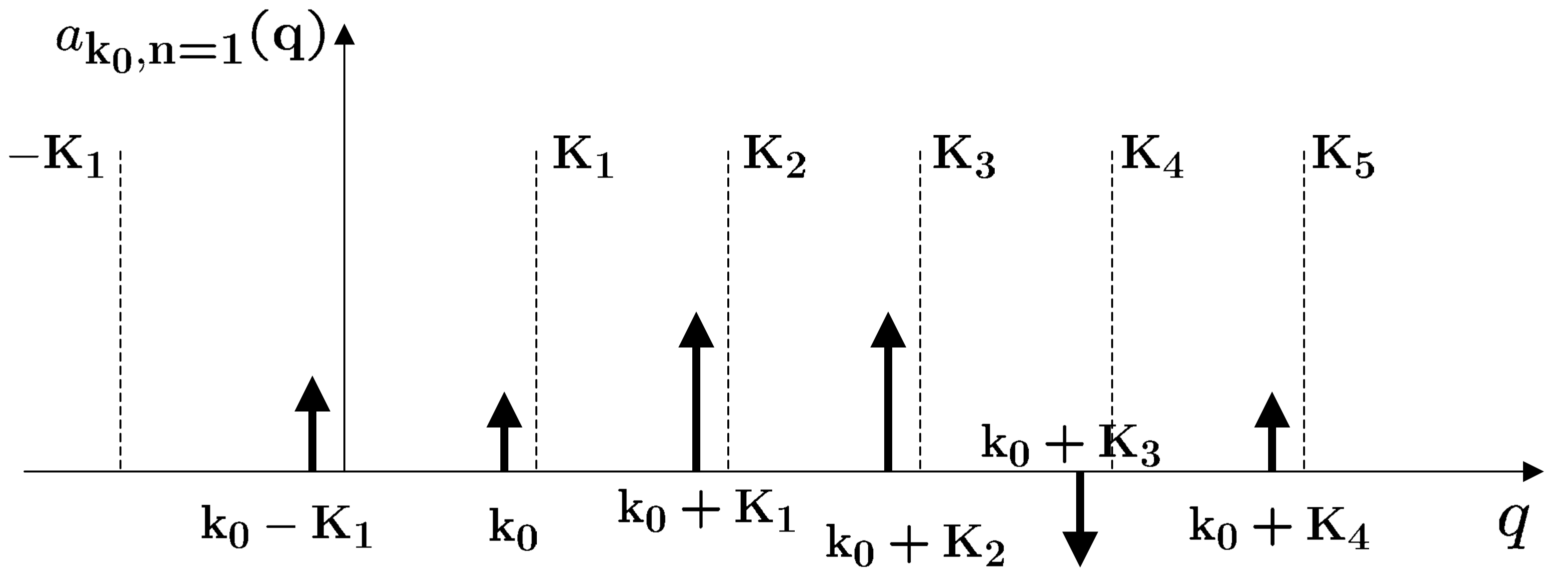
Eigenvectors for Nearly Free Electron Bands

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

Fourier transform

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

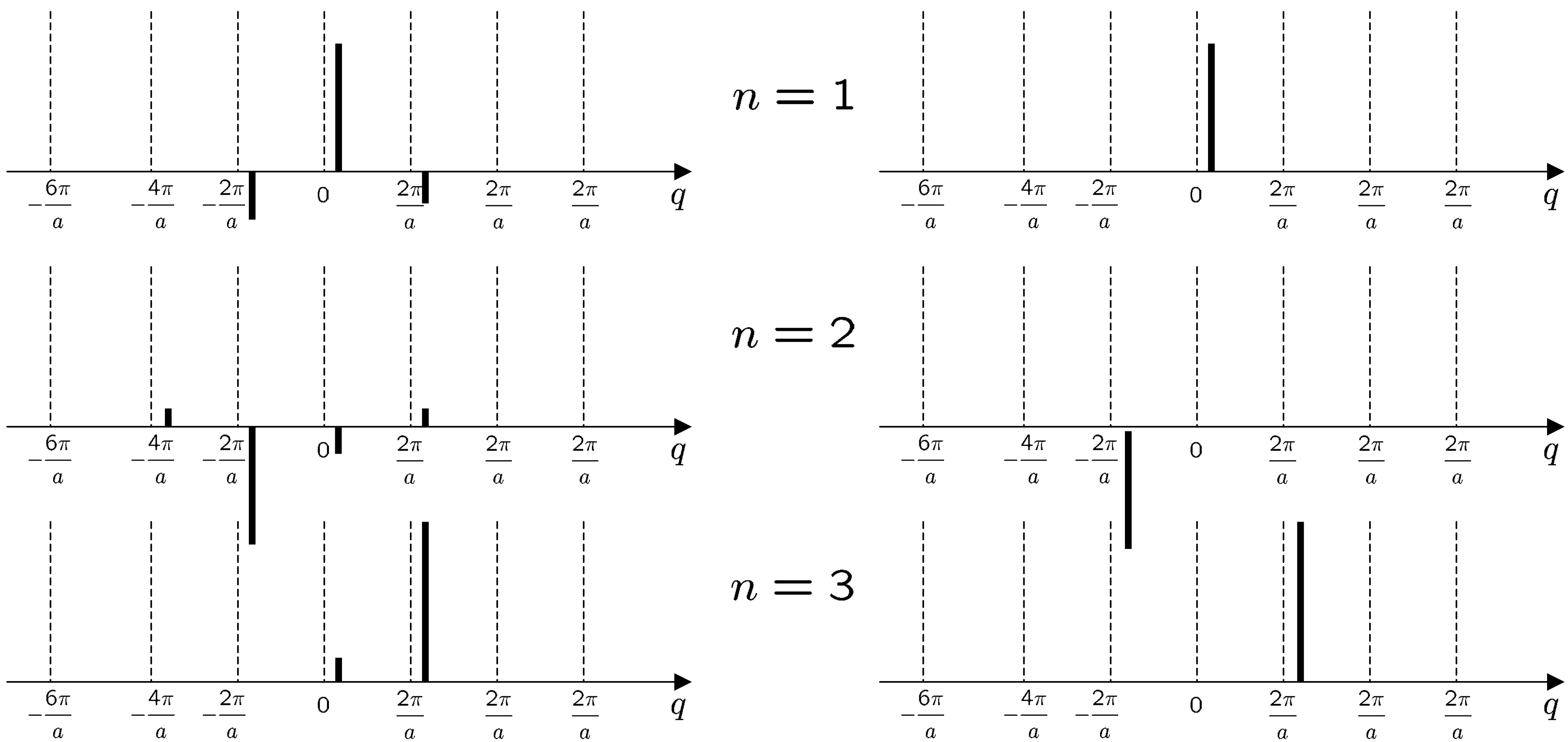
Sample eigenvector…



Eigenvectors for Nearly Free Electron Bands

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

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



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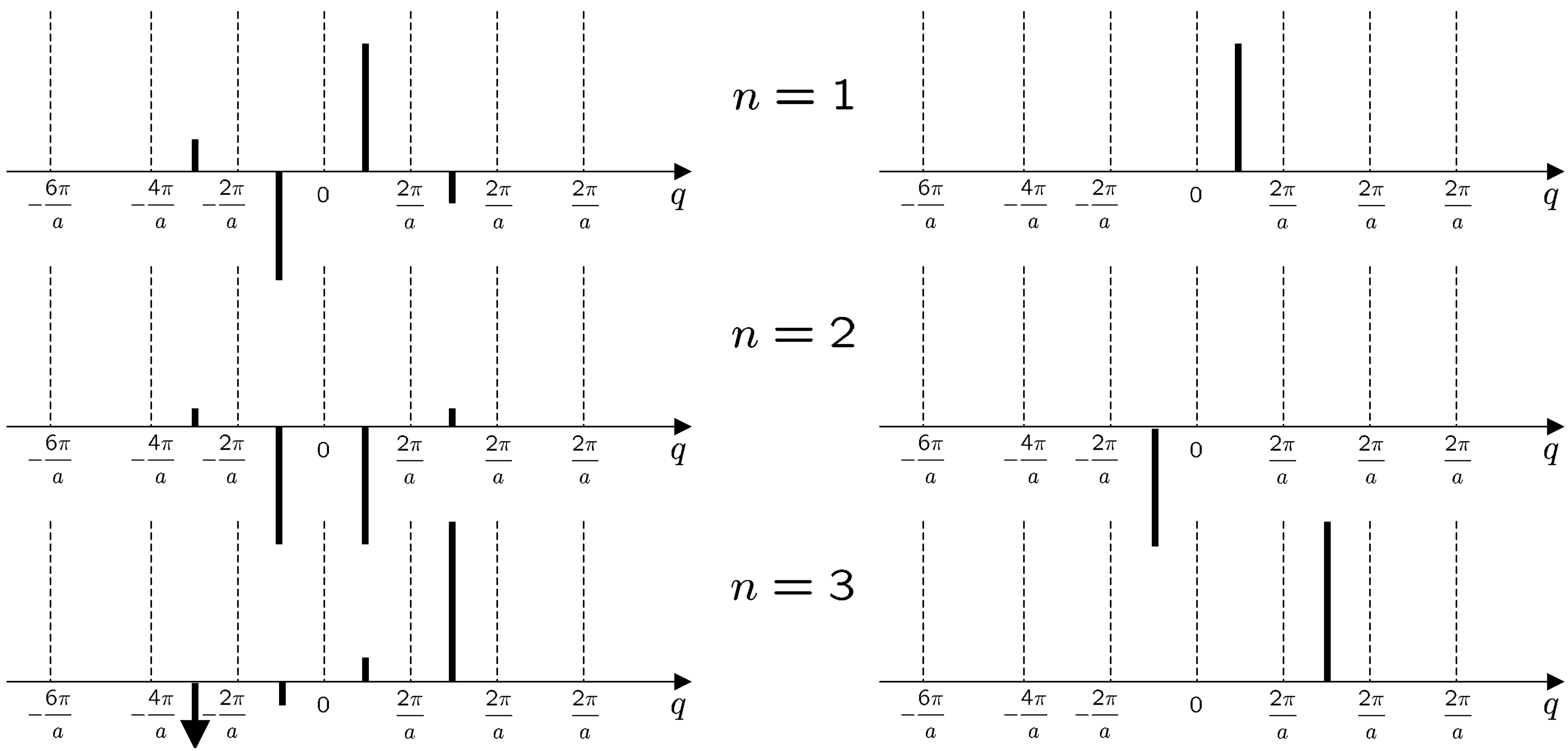
$$a_{\mathbf{k},\mathbf{n}}(\mathbf{q}) \qquad \mathbf{k} = \frac{\pi}{\mathbf{a}}$$

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



Eigenvectors for Nearly Free Electron Bands

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

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