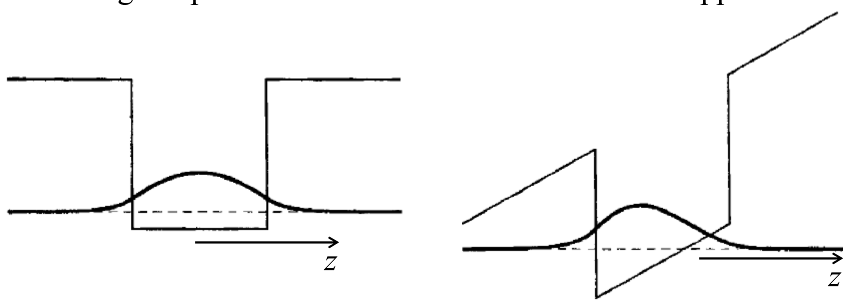
NEARLY FREE ELECTRON MODEL

Perturbation Theory

Rectangular potential well   Potential well with applied field



- A perturbed potential well may not be solved exactly.
- Usually, we need
  - First order correction in the wavefunctions
  - Second order correction in the energy values

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Energy and Wavefunctions

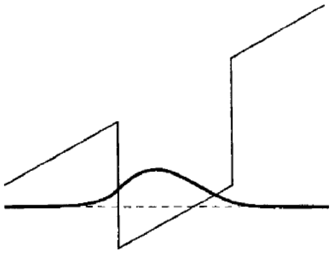
$$\hat{H} = \hat{H}_0 + \hat{V}$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots$$

$$\psi_n = \psi_n^{(0)} + \psi_n^{(1)} + \psi_n^{(2)} + \cdots$$

$$E_n = \varepsilon_n + V_{nn} + \sum_{k,k\neq n} \frac{|V_{kn}|^2}{\varepsilon_n - \varepsilon_k} + \cdots$$

$$\psi_n = \phi_n + \sum_{k,k\neq n} \frac{V_{kn}}{\varepsilon_n - \varepsilon_k}\phi_k + \cdots$$



Free Electron Model

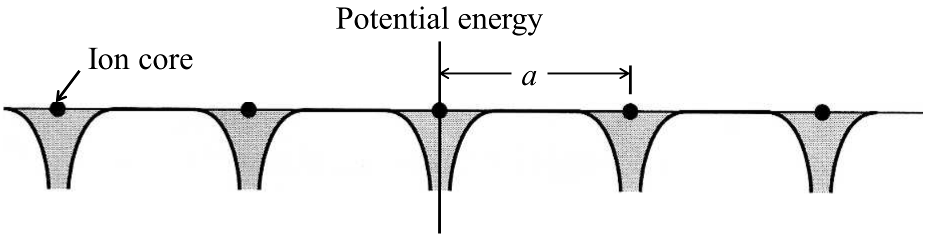
- Allowed energy values of free electons

$$\varepsilon_0(k) = \frac{\hbar^2 k^2}{2m_0}$$

- The free electron wavefunctions

$$\psi_k(x) = \frac{1}{\sqrt{L}} e^{ikx}$$

Periodic Potential: Perturbation



- Free electrons are perturbed only weakly by the periodic potential of the ion cores.
- Periodic potential: $V(x) = \sum_{n=-\infty}^{\infty} V_n e^{2\pi inx/a} = \sum_{n=-\infty} V_n e^{iG_n x}$
- G_n is the reciprocal lattice vector: $G_n = \frac{2\pi}{a} n$

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New Energy

- Effect on the energies can be found using the perturbation theory

$$E(k) \approx \varepsilon_0(k) + V_{kk} + \sum_{k',k'\neq k} \frac{|V_{k'k}|^2}{\varepsilon_0(k) - \varepsilon_0(k')}$$

- The matrix element:

$$V_{kk} = V_0 \rightarrow \quad E(k) \approx \varepsilon_0(k) + \sum_{k',k'\neq k} \frac{|V_{k'k}|^2}{\varepsilon_0(k) - \varepsilon_0(k')}$$

$$V_{k'k} = \int \phi_{k'}^*(x) V(x) \phi_k(x) dx = \sum_n V_n \frac{1}{L} \int_0^L e^{-ik'x} e^{iG_n x} e^{ikx} dx$$

- The integral vanishes unless the total wavenumber is zero:

$$k' = k + G_n$$

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New Wavefunction

$$\psi_k = \phi_k + \sum_{n,n\neq 0} \frac{V_{k+G_n,k}\,\phi_{k+G_n}}{\varepsilon_0(k)-\varepsilon_0(k+G_n)} = e^{ikx}\left[1+\sum_{n,n\neq 0}\frac{V_n e^{iG_n x}}{\varepsilon_0(k)-\varepsilon_0(k+G_n)}\right]$$

- The function inside the square brackets is a Fourier series and is consequently periodic. We have therefore proved Bloch's theorem, which states that the wavefunction in a crystal can be written in the form of a plane wave multiplied by a function with the period of the lattice.
- The wavefunction also satisfies the obvious check that it reverts to a simple plane wave in an empty lattice where $V(x) = 0$.

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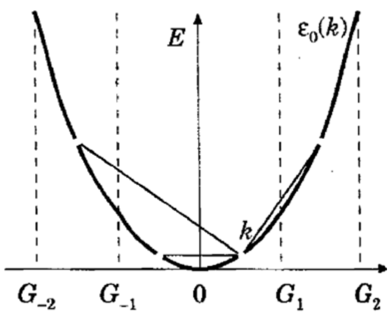
Degeneracy



$$k' = k + G_n \qquad \varepsilon_0(k) = \varepsilon_0(-k)$$

$$k = -\frac{1}{2}G_n, \qquad k = \frac{n\pi}{a}, \qquad n = \pm 1, \pm 2, \ldots$$

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Schrodinger Equation

$$\psi = a_k \phi_k(x) + a_{k+G_n} \phi_{k+G_n}(x)$$

$$\begin{pmatrix} \varepsilon_0(k) & V_n \\ V_n & \varepsilon_0(k+G_n) \end{pmatrix} \begin{pmatrix} a_k \\ a_{k+G_n} \end{pmatrix} = E(k) \begin{pmatrix} a_k \\ a_{k+G_n} \end{pmatrix}$$

$$\det \begin{vmatrix} E(k) - \varepsilon_0(k) & -V_n \\ -V_n & E(k) - \varepsilon_0(k+G_n) \end{vmatrix} = 0$$

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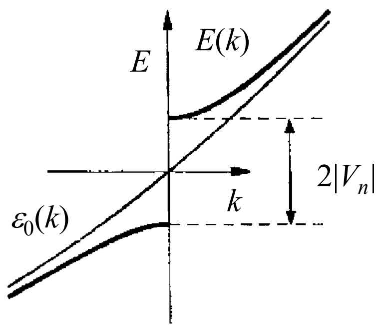
Solution

$$E(k) = \frac{\varepsilon_0(k) + \varepsilon_0(k+G_n)}{2} \pm \sqrt{\left[\frac{\varepsilon_0(k) - \varepsilon_0(k+G_n)}{2}\right]^2 + V_n^2}$$



$$k = -\frac{1}{2} G_n$$

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k Away from $-G_n/2$

$$|\varepsilon_0(k)-\varepsilon_0(k+G_n)| \gg |V_n|$$

$$E(k)=\frac{\varepsilon_0(k)+\varepsilon_0(k+G_n)}{2}\pm\sqrt{[\varepsilon_0(k)-\varepsilon_0(k+G_n)]^2/4+|V_n|^2}$$

$$=\frac{\varepsilon_0(k)+\varepsilon_0(k+G_n)}{2}\pm\frac{\varepsilon_0(k)-\varepsilon_0(k+G_n)}{2}\sqrt{1+\frac{|V_n|^2}{[\varepsilon_0(k)-\varepsilon_0(k+G_n)]^2/4}}$$

$$=\frac{\varepsilon_0(k)+\varepsilon_0(k+G_n)}{2}\pm\frac{\varepsilon_0(k)-\varepsilon_0(k+G_n)}{2}\left[1+\frac{1}{2}\frac{|V_n|^2}{[\varepsilon_0(k)-\varepsilon_0(k+G_n)]^2/4}\right]$$

$$=\frac{\varepsilon_0(k)+\varepsilon_0(k+G_n)}{2}\pm\left[\frac{\varepsilon_0(k)-\varepsilon_0(k+G_n)}{2}+\frac{|V_n|^2}{\varepsilon_0(k)-\varepsilon_0(k+G_n)}\right]$$

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k Away from $-G_n/2$

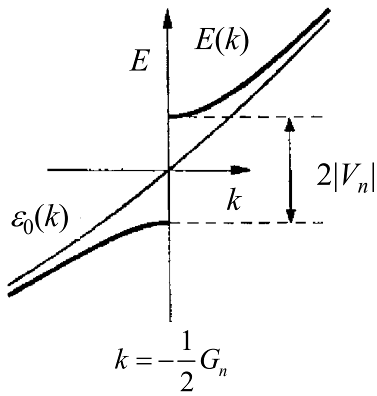
$$E(k)=\frac{\varepsilon_0(k)+\varepsilon_0(k+G_n)}{2}\pm\left[\frac{\varepsilon_0(k)-\varepsilon_0(k+G_n)}{2}+\frac{|V_n|^2}{\varepsilon_0(k)-\varepsilon_0(k+G_n)}\right]$$

- Taking the positive sign

$$E(k)\approx\varepsilon_0(k)+\frac{|V_n|^2}{\varepsilon_0(k)-\varepsilon_0(k+G_n)}$$

- Taking the negative sign

$$E(k+G_n)\approx\varepsilon_0(k+G_n)+\frac{|V_n|^2}{\varepsilon_0(k+G_n)-\varepsilon_0(k)}$$



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$k \to -G_n/2$

$$\left|\varepsilon_0(k) - \varepsilon_0(k+G_n)\right| \ll |V_n|$$

$$E(k) = \frac{\varepsilon_0(k)+\varepsilon_0(k+G_n)}{2} \pm \sqrt{\left[\varepsilon_0(k)-\varepsilon_0(k+G_n)\right]^2/4+|V_n|^2}$$

$$= \frac{\varepsilon_0(k)+\varepsilon_0(k+G_n)}{2} \pm |V_n|\sqrt{1+\left[\frac{\varepsilon_0(k)-\varepsilon_0(k+G_n)}{2|V_n|}\right]^2}$$

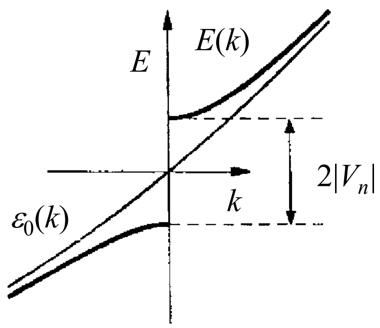
$$= \frac{\varepsilon_0(k)+\varepsilon_0(k+G_n)}{2} \pm |V_n|\left[1+\frac{1}{2}\left[\frac{\varepsilon_0(k)-\varepsilon_0(k+G_n)}{2|V_n|}\right]^2\right]$$

$$= \frac{\varepsilon_0(k)+\varepsilon_0(k+G_n)}{2} \pm \left[|V_n|+\frac{\varepsilon_0(k)-\varepsilon_0(k+G_n)}{8|V_n|}\right]$$

$k = -G_n/2$

$$E\left(k=-\frac{1}{2}G_n\right) = \varepsilon_0\left(-\frac{1}{2}G_n\right) \pm |V_n|$$

- A gap of width $2|V_n|$ has opened up at $k = -\frac{1}{2}G_n$



$k = -\frac{1}{2}G_n$