

15.1 In the nearest-neighbor approximation we assume that the "hopping" matrix elements β are zero unless the two wells are adjacent. Hence the matrix representing the Hamiltonian for a linear chain of 3 wells is

$$H \doteq \begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{pmatrix}$$

Diagonalizing this Hamiltonian

$$\begin{vmatrix} \alpha - \lambda & \beta & 0 \\ \beta & \alpha - \lambda & \beta \\ 0 & \beta & \alpha - \lambda \end{vmatrix} = 0$$

$$(\alpha - \lambda)[(\alpha - \lambda)^2 - \beta^2] - \beta^2(\alpha - \lambda) = 0$$

$$(\alpha - \lambda)[(\alpha - \lambda)^2 - 2\beta^2] = 0 \Rightarrow \lambda = \alpha, \alpha \pm \sqrt{2}\beta$$

gives the energy eigenvalues

$$E_1 = \alpha - \sqrt{2}\beta$$

$$E_2 = \alpha$$

$$E_3 = \alpha + \sqrt{2}\beta$$

The eigenstates are

$$H|\psi_1\rangle = E_1|\psi_1\rangle$$

$$\begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = (\alpha - \sqrt{2}\beta) \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

$$\left. \begin{aligned} \alpha a + \beta b &= (\alpha - \sqrt{2}\beta)a \\ \beta a + \alpha b + \beta c &= (\alpha - \sqrt{2}\beta)b \\ \beta b + \alpha c &= (\alpha - \sqrt{2}\beta)c \end{aligned} \right\} |\psi_1\rangle \doteq \frac{1}{2} \begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix}$$

$$H|\psi_2\rangle = E_2|\psi_2\rangle$$

$$\begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \alpha \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

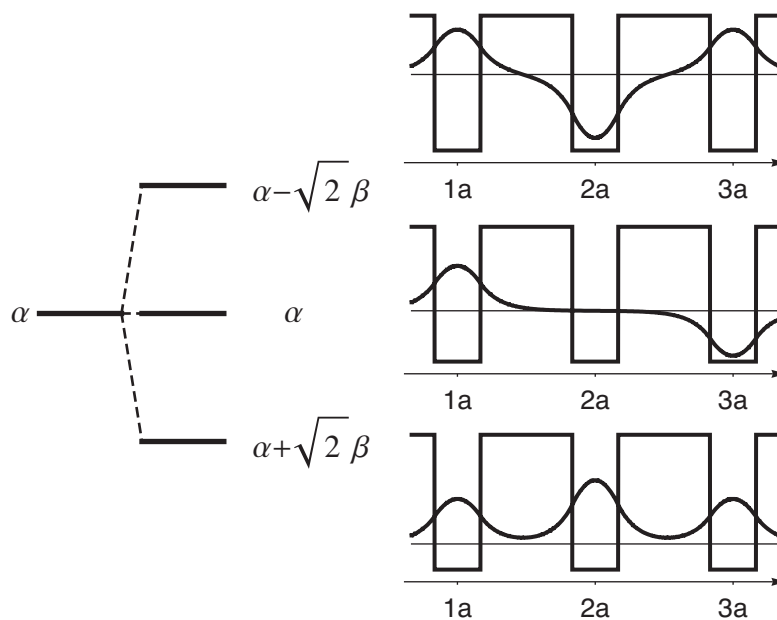
$$\left. \begin{aligned} \alpha a + \beta b &= \alpha a \\ \beta a + \alpha b + \beta c &= \alpha b \\ \beta b + \alpha c &= \alpha c \end{aligned} \right\} |\psi_2\rangle \doteq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

$$H|\psi_3\rangle = E_3|\psi_3\rangle$$

$$\begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = (\alpha + \sqrt{2}\beta) \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

$$\left. \begin{aligned} \alpha a + \beta b &= (\alpha + \sqrt{2}\beta)a \\ \beta a + \alpha b + \beta c &= (\alpha + \sqrt{2}\beta)b \\ \beta b + \alpha c &= (\alpha + \sqrt{2}\beta)c \end{aligned} \right\} |\psi_3\rangle \doteq \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}$$

These molecular states are shown below



15.2 For an N -well chain, the matrix representing the Hamiltonian is

$$H \doteq \begin{pmatrix} \alpha & \beta & 0 & 0 & \dots \\ \beta & \alpha & \beta & 0 & \dots \\ 0 & \beta & \alpha & \beta & \dots \\ 0 & 0 & \beta & \alpha & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

To find the eigenvalues and eigenvectors in Mathematica, use the following commands:

```
Ndim = 5;
H = Table[0, {i, Ndim}, {j, Ndim}];
Do[H[[i, i]] =  $\alpha$ , {i, Ndim}];
Do[H[[i, i + 1]] =  $\beta$ , {i, Ndim - 1}];
Do[H[[i, i - 1]] =  $\beta$ , {i, 2, Ndim}];
H // MatrixForm
Eigenvalues[H]
Map[Normalize, Eigenvectors[H]]
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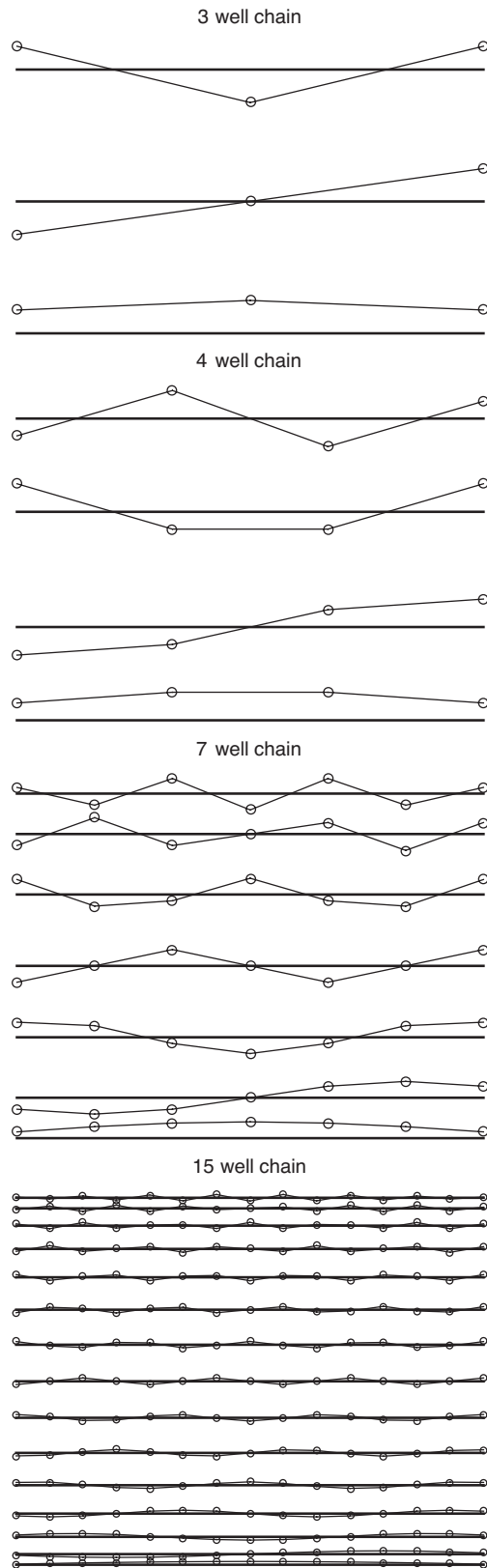
which produce the output

$$\begin{pmatrix} \alpha & \beta & 0 & 0 & 0 \\ \beta & \alpha & \beta & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & \beta & \alpha & \beta \\ 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

$$\{\alpha, \alpha - \beta, \alpha + \beta, \alpha - \sqrt{3}\beta, \alpha + \sqrt{3}\beta\}$$

$$\left\{ \begin{aligned} &\left\{ \frac{1}{\sqrt{3}}, 0, -\frac{1}{\sqrt{3}}, 0, \frac{1}{\sqrt{3}} \right\}, \\ &\left\{ -\frac{1}{2}, \frac{1}{2}, 0, -\frac{1}{2}, \frac{1}{2} \right\}, \\ &\left\{ -\frac{1}{2}, -\frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2} \right\}, \\ &\left\{ \frac{1}{2\sqrt{3}}, -\frac{1}{2}, \frac{1}{\sqrt{3}}, -\frac{1}{2}, \frac{1}{2\sqrt{3}} \right\}, \\ &\left\{ \frac{1}{2\sqrt{3}}, \frac{1}{2}, \frac{1}{\sqrt{3}}, \frac{1}{2}, \frac{1}{2\sqrt{3}} \right\} \end{aligned} \right\}$$

The following graphics show the energy levels arranged vertically and the amplitudes of each well state arranged horizontally



15.3 For the carbon dioxide molecule, the three atomic states are not identical. Rather, the middle state $|2\rangle$ associated with the carbon atom is different from the states $|1\rangle$ and $|3\rangle$ associated with the oxygen atoms. Hence the "on-site" energies of electrons on the isolated oxygen and carbon atoms are different. We label them α_o and α_c . The near neighbor hopping matrix element β describes the carbon-oxygen interaction. There is no oxygen-oxygen coupling. Hence the matrix representing the Hamiltonian for CO_2 is

$$H \doteq \begin{pmatrix} \alpha_o & \beta & 0 \\ \beta & \alpha_c & \beta \\ 0 & \beta & \alpha_o \end{pmatrix}$$

Diagonalizing this Hamiltonian

$$\begin{vmatrix} \alpha_o - \lambda & \beta & 0 \\ \beta & \alpha_c - \lambda & \beta \\ 0 & \beta & \alpha_o - \lambda \end{vmatrix} = 0$$

$$(\alpha_o - \lambda)[(\alpha_c - \lambda)(\alpha_o - \lambda) - \beta^2] - \beta^2(\alpha_o - \lambda) = 0$$

$$(\alpha_o - \lambda)[(\alpha_c - \lambda)(\alpha_o - \lambda) - 2\beta^2] = 0$$

$$\Rightarrow \lambda = \alpha_o, \frac{1}{2}(\alpha_c + \alpha_o) \pm \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2}$$

gives the energy eigenvalues

$$E_1 = \frac{1}{2}(\alpha_c + \alpha_o) - \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2}$$

$$E_2 = \alpha_o$$

$$E_3 = \frac{1}{2}(\alpha_c + \alpha_o) + \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2}$$

The eigenstates are

$$H|\psi_1\rangle = E_1|\psi_1\rangle$$

$$\begin{pmatrix} \alpha_o & \beta & 0 \\ \beta & \alpha_c & \beta \\ 0 & \beta & \alpha_o \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \left(\frac{1}{2}(\alpha_c + \alpha_o) - \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2} \right) \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

$$\left. \begin{aligned} \alpha_o a + \beta b &= \left(\frac{1}{2}(\alpha_c + \alpha_o) - \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2} \right) a \\ \beta a + \alpha_c b + \beta c &= \left(\frac{1}{2}(\alpha_c + \alpha_o) - \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2} \right) b \\ \beta b + \alpha_o c &= \left(\frac{1}{2}(\alpha_c + \alpha_o) - \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2} \right) c \end{aligned} \right\} |\psi_1\rangle \doteq \frac{1}{\sqrt{2 + \gamma_-^2}} \begin{pmatrix} 1 \\ \gamma_- \\ 1 \end{pmatrix}$$

$$\begin{aligned}
 H|\psi_2\rangle &= E_2|\psi_2\rangle \\
 \begin{pmatrix} \alpha_o & \beta & 0 \\ \beta & \alpha_c & \beta \\ 0 & \beta & \alpha_o \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} &= \alpha_o \begin{pmatrix} a \\ b \\ c \end{pmatrix} \\
 \left. \begin{aligned} \alpha_o a + \beta b &= \alpha_o a \\ \beta a + \alpha_c b + \beta c &= \alpha_o b \\ \beta b + \alpha_o c &= \alpha_o c \end{aligned} \right\} |\psi_2\rangle &\doteq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}
 \end{aligned}$$

This molecular state is a superposition of oxygen states only, and the energy is the same as the energy of the atomic oxygen state.

$$\begin{aligned}
 H|\psi_3\rangle &= E_3|\psi_3\rangle \\
 \begin{pmatrix} \alpha_o & \beta & 0 \\ \beta & \alpha_c & \beta \\ 0 & \beta & \alpha_o \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} &= \left(\frac{1}{2}(\alpha_c + \alpha_o) + \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2} \right) \begin{pmatrix} a \\ b \\ c \end{pmatrix} \\
 \left. \begin{aligned} \alpha_o a + \beta b &= \left(\frac{1}{2}(\alpha_c + \alpha_o) + \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2} \right) a \\ \beta a + \alpha_c b + \beta c &= \left(\frac{1}{2}(\alpha_c + \alpha_o) + \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2} \right) b \\ \beta b + \alpha_o c &= \left(\frac{1}{2}(\alpha_c + \alpha_o) + \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2} \right) c \end{aligned} \right\} |\psi_3\rangle &\doteq \frac{1}{\sqrt{2 + \gamma_+^2}} \begin{pmatrix} 1 \\ \gamma_+ \\ 1 \end{pmatrix}
 \end{aligned}$$

Where the parameters γ_{\pm} are

$$\gamma_{\pm} = \frac{\frac{1}{2}(\alpha_c - \alpha_o) \pm \frac{1}{2}\sqrt{(\alpha_c - \alpha_o)^2 + 8\beta^2}}{\beta}$$

Molecular states 1 and 3 are superpositions of oxygen states (in equal proportion) and of the carbon state, and the energies are equally displaced from the average energy of the carbon and oxygen states.

15.4 The extension of the Hamiltonian in Fig. 15.10 to 3 wells is

$$H_B \doteq \begin{pmatrix} \alpha_g & \beta_g & 0 & 0 & \beta_{ge} & 0 \\ \beta_g & \alpha_g & \beta_g & \beta_{ge} & 0 & \beta_{ge} \\ 0 & \beta_g & \alpha_g & 0 & \beta_{ge} & 0 \\ 0 & \beta_{ge} & 0 & \alpha_e & \beta_e & 0 \\ \beta_{ge} & 0 & \beta_{ge} & \beta_e & \alpha_e & \beta_e \\ 0 & \beta_{ge} & 0 & 0 & \beta_e & \alpha_e \end{pmatrix} \begin{matrix} |1g\rangle \\ |2g\rangle \\ |3g\rangle \\ |1e\rangle \\ |2e\rangle \\ |3e\rangle \end{matrix}$$

We express the energy eigenvalue equation $H|\psi\rangle = E|\psi\rangle$ as

$$\begin{pmatrix} \alpha_g & \beta_g & 0 & 0 & \beta_{ge} & 0 \\ \beta_g & \alpha_g & \beta_g & \beta_{ge} & 0 & \beta_{ge} \\ 0 & \beta_g & \alpha_g & 0 & \beta_{ge} & 0 \\ 0 & \beta_{ge} & 0 & \alpha_e & \beta_e & 0 \\ \beta_{ge} & 0 & \beta_{ge} & \beta_e & \alpha_e & \beta_e \\ 0 & \beta_{ge} & 0 & 0 & \beta_e & \alpha_e \end{pmatrix} \begin{pmatrix} c_{1g} \\ c_{2g} \\ c_{3g} \\ c_{1e} \\ c_{2e} \\ c_{3e} \end{pmatrix} = E \begin{pmatrix} c_{1g} \\ c_{2g} \\ c_{3g} \\ c_{1e} \\ c_{2e} \\ c_{3e} \end{pmatrix}$$

For an N -well system, this leads to the equations

$$\begin{aligned} \alpha_g c_{1g} + \beta_g c_{2g} + \beta_{ge} c_{2e} &= E c_{1g} \\ \beta_g c_{1g} + \alpha_g c_{2g} + \beta_g c_{3g} + \beta_{ge} c_{1e} + \beta_{ge} c_{3e} &= E c_{2g} \\ \beta_g c_{2g} + \alpha_g c_{3g} + \beta_g c_{4g} + \beta_{ge} c_{2e} + \beta_{ge} c_{4e} &= E c_{3g} \\ &\vdots \\ \alpha_e c_{1e} + \beta_e c_{2e} + \beta_{ge} c_{2g} &= E c_{1e} \\ \beta_e c_{1e} + \alpha_e c_{2e} + \beta_e c_{3e} + \beta_{ge} c_{1g} + \beta_{ge} c_{3g} &= E c_{2e} \\ \beta_e c_{2e} + \alpha_e c_{3e} + \beta_e c_{4e} + \beta_{ge} c_{2g} + \beta_{ge} c_{4g} &= E c_{3e} \\ &\vdots \end{aligned}$$

We ignore the endpoint equations to find the general equations

$$\begin{aligned} \beta_g c_{p-1,g} + \alpha_g c_{pg} + \beta_g c_{p+1,g} + \beta_{ge} c_{p-1,e} + \beta_{ge} c_{p+1,e} &= E c_{pg} \\ \beta_e c_{p-1,e} + \alpha_e c_{pe} + \beta_e c_{p+1,e} + \beta_{ge} c_{p-1,g} + \beta_{ge} c_{p+1,g} &= E c_{pe} \end{aligned}$$

We use the technique of normal mode solutions to solve these equations for the coefficients and the energies. We assume

$$c_{pg} = Ae^{ipka}$$

$$c_{pe} = Be^{ipka}$$

This gives

$$\beta_g Ae^{i(p-1)ka} + (\alpha_g - E)Ae^{ipka} + \beta_g Ae^{i(p+1)ka} + \beta_{ge} Be^{i(p-1)ka} + \beta_{ge} Be^{i(p+1)ka} = 0$$

$$\beta_e Be^{i(p-1)ka} + (\alpha_e - E)Be^{ipka} + \beta_e Be^{i(p+1)ka} + \beta_{ge} Ae^{i(p-1)ka} + \beta_{ge} Ae^{i(p+1)ka} = 0$$

Factor out e^{ipka} to obtain

$$\beta_g Ae^{-ika} + (\alpha_g - E)A + \beta_g Ae^{ika} + \beta_{ge} Be^{-ika} + \beta_{ge} Be^{ika} = 0$$

$$\beta_e Be^{-ika} + (\alpha_e - E)B + \beta_e Be^{ika} + \beta_{ge} Ae^{-ika} + \beta_{ge} Ae^{ika} = 0$$

Use the Euler relation to get

$$(\alpha_g + 2\beta_g \cos(ka) - E)A + 2\beta_{ge} B \cos(ka) = 0$$

$$(\alpha_e + 2\beta_e \cos(ka) - E)B + 2\beta_{ge} A \cos(ka) = 0$$

From the single state example, we recognize that

$$f_g(k) = \alpha_g + 2\beta_g \cos(ka)$$

$$f_e(k) = \alpha_e + 2\beta_e \cos(ka)$$

are the dispersion relations that we would have obtained if we had considered either the ground or excited states alone (or with no interaction). Using these equations to simplify the notation, we solve the two equations from the energy:

$$(f_g(k) - E)A + 2\beta_{ge} B \cos(ka) = 0 \Rightarrow B = -\frac{(f_g(k) - E)}{2\beta_{ge} \cos(ka)} A$$

$$-(f_e(k) - E)\frac{(f_g(k) - E)}{2\beta_{ge} \cos(ka)} + 2\beta_{ge} \cos(ka) = 0$$

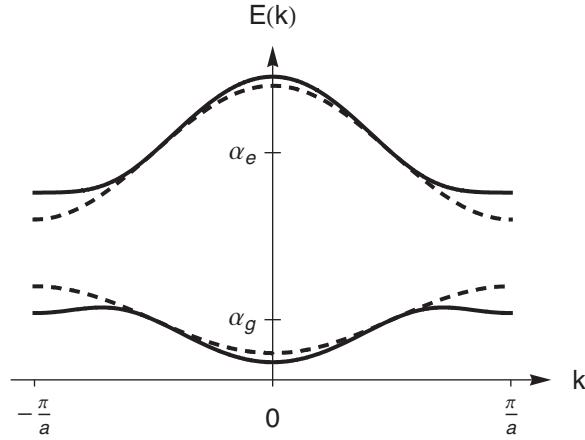
$$E^2 - E(f_g(k) + f_e(k)) - 4\beta_{ge}^2 \cos^2(ka) + f_g(k)f_e(k) = 0$$

Solving the quadratic equation for the energy yields

$$E_1(k) = \frac{1}{2}[f_g(k) + f_e(k)] + \sqrt{\frac{1}{4}[f_g(k) - f_e(k)]^2 + 4\beta_{ge}^2 \cos^2(ka)}$$

$$E_2(k) = \frac{1}{2}[f_g(k) + f_e(k)] - \sqrt{\frac{1}{4}[f_g(k) - f_e(k)]^2 + 4\beta_{ge}^2 \cos^2(ka)}$$

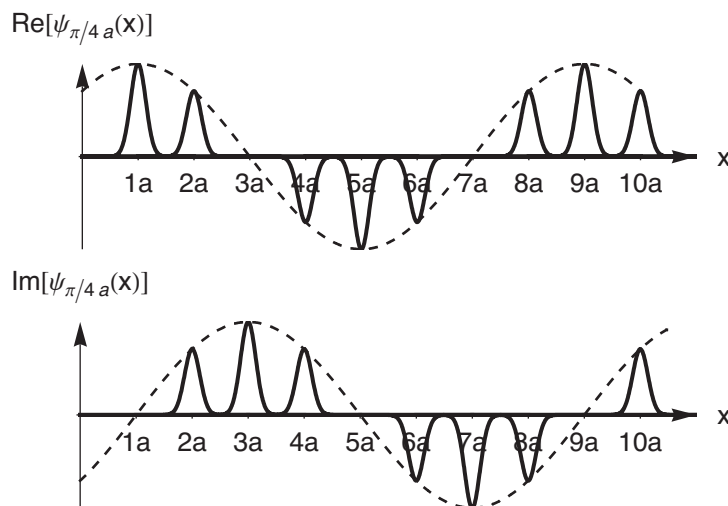
The plot below gives the dispersion relation, showing that the non-interacting dispersion relations (dashed lines from Fig. 15.11) are pushed apart by the interaction.



15.5 a) For $k = \pi/4a$, the molecular wave function is

$$\begin{aligned}
 \psi_{\pi/4a}(x) &= \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{in\pi/4} \phi_n(x) \\
 &= \frac{e^{i\pi/4}}{\sqrt{N}} [\phi_1(x) + e^{i\pi/4} \phi_2(x) + e^{i\pi/2} \phi_3(x) + e^{i3\pi/4} \phi_4(x) + e^{i\pi} \phi_5(x) + e^{i5\pi/4} \phi_6(x) \dots] \\
 &= \frac{e^{i\pi/4}}{\sqrt{N}} [\phi_1(x) + e^{i\pi/4} \phi_2(x) + i\phi_3(x) + ie^{i\pi/4} \phi_4(x) - \phi_5(x) - e^{i\pi/4} \phi_6(x) \dots] \\
 &= \frac{e^{i\pi/4}}{\sqrt{N}} [\phi_1(x) + \frac{1}{\sqrt{2}} \phi_2(x) - \frac{1}{\sqrt{2}} \phi_4(x) - \phi_5(x) - \frac{1}{\sqrt{2}} \phi_6(x) \dots] \\
 &\quad + \frac{ie^{i\pi/4}}{\sqrt{N}} [\frac{1}{\sqrt{2}} \phi_2(x) + \phi_3(x) + \frac{1}{\sqrt{2}} \phi_4(x) - \frac{1}{\sqrt{2}} \phi_6(x) \dots]
 \end{aligned}$$

As in the textbook examples, the patterns of the real and imaginary parts are the same $(0, \frac{1}{\sqrt{2}}, 1, \frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}, -1, \frac{1}{\sqrt{2}}, 0, \dots)$ with a repeat distance in this case of 8 cells. Hence the wave function has a wavelength corresponding to $2\pi/k = 8a$ as evident below:



The energy of the state is determined by the dispersion relation

$$E(k) = \alpha + 2\beta \cos(ka)$$

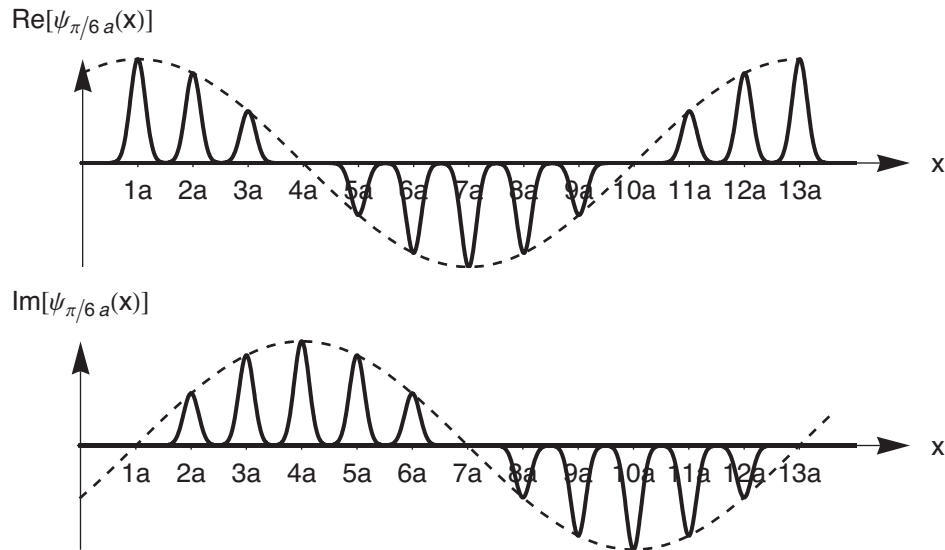
For $k = \pi/4a$, the energy is

$$E(\pi/4a) = \alpha + 2\beta \cos(\pi/4) = \alpha + 2\beta(1/\sqrt{2}) = \alpha + \sqrt{2}\beta$$

b) Repeat for $k = \pi/6a$. The molecular wave function is

$$\begin{aligned} \psi_{\pi/6a}(x) &= \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{in\pi/6} \varphi_n(x) \\ &= \frac{e^{i\pi/6}}{\sqrt{N}} [\varphi_1(x) + e^{i\pi/6} \varphi_2(x) + e^{i\pi/3} \varphi_3(x) + e^{i\pi/2} \varphi_4(x) + e^{i2\pi/3} \varphi_5(x) + e^{i5\pi/6} \varphi_6(x) \dots] \\ &= \frac{e^{i\pi/6}}{\sqrt{N}} [\varphi_1(x) + e^{i\pi/6} \varphi_2(x) + e^{i\pi/3} \varphi_3(x) + i\varphi_4(x) + ie^{i\pi/6} \varphi_5(x) + ie^{i\pi/3} \varphi_6(x) \dots] \\ &= \frac{e^{i\pi/6}}{\sqrt{N}} [\varphi_1(x) + \frac{\sqrt{3}}{2} \varphi_2(x) + \frac{1}{2} \varphi_3(x) - \frac{1}{2} \varphi_5(x) - \frac{\sqrt{3}}{2} \varphi_6(x) \dots] \\ &\quad + \frac{ie^{i\pi/6}}{\sqrt{N}} [\frac{1}{2} \varphi_2(x) + \frac{\sqrt{3}}{2} \varphi_3(x) + \varphi_4(x) + \frac{\sqrt{3}}{2} \varphi_5(x) + \frac{1}{2} \varphi_6(x) \dots] \end{aligned}$$

As in the textbook examples, the patterns of the real and imaginary parts are the same $(0, \frac{1}{2}, \frac{\sqrt{3}}{2}, 1, \frac{\sqrt{3}}{2}, \frac{1}{2}, 0, -\frac{1}{2}, -\frac{\sqrt{3}}{2}, -1, -\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0, \dots)$ with a repeat distance in this case of 12 cells. Hence the wave function has a wavelength corresponding to $2\pi/k = 12a$ as evident below:



The energy of the state is determined by the dispersion relation

$$E(k) = \alpha + 2\beta \cos(ka)$$

For $k = \pi/6a$, the energy is

$$E(\pi/6a) = \alpha + 2\beta \cos(\pi/6) = \alpha + 2\beta(\sqrt{3}/2) = \alpha + \sqrt{3}\beta$$

c) Repeat for $k = \pi/6a + 2\pi/a = 13\pi/6a$. The molecular wave function is

$$\begin{aligned}\psi_{13\pi/6a}(x) &= \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{in13\pi/6} \varphi_n(x) \\ &= \frac{e^{i13\pi/6}}{\sqrt{N}} [\varphi_1(x) + e^{i13\pi/6} \varphi_2(x) + e^{i13\pi/3} \varphi_3(x) + e^{i13\pi/2} \varphi_4(x) + e^{i26\pi/3} \varphi_5(x) + e^{i65\pi/6} \varphi_6(x) \dots] \\ &= \frac{e^{i13\pi/6}}{\sqrt{N}} [\varphi_1(x) + e^{i\pi/6} \varphi_2(x) + e^{i\pi/3} \varphi_3(x) + e^{i\pi/2} \varphi_4(x) + e^{i2\pi/3} \varphi_5(x) + e^{i5\pi/6} \varphi_6(x) \dots] \\ &= \frac{e^{i\pi/6}}{\sqrt{N}} [\varphi_1(x) + e^{i\pi/6} \varphi_2(x) + e^{i\pi/3} \varphi_3(x) + i\varphi_4(x) + ie^{i\pi/6} \varphi_5(x) + ie^{i\pi/3} \varphi_6(x) \dots] \\ &= \frac{e^{i\pi/6}}{\sqrt{N}} [\varphi_1(x) + \frac{\sqrt{3}}{2} \varphi_2(x) + \frac{1}{2} \varphi_3(x) - \frac{1}{2} \varphi_5(x) - \frac{\sqrt{3}}{2} \varphi_6(x) \dots] \\ &\quad + \frac{ie^{i\pi/6}}{\sqrt{N}} [\frac{1}{2} \varphi_2(x) + \frac{\sqrt{3}}{2} \varphi_3(x) + \varphi_4(x) + \frac{\sqrt{3}}{2} \varphi_5(x) + \frac{1}{2} \varphi_6(x) \dots]\end{aligned}$$

In the third line above, we reduced each phase by an integer multiple of 2π . The final result is that the wave function is identical to the $k = \pi/6a$ case in (b). Hence, the second Brillouin zone is equivalent to the first zone.

15.6 The integral is

$$E_{TOT} = \int_{E_{\min}}^{E_{\max}} E g(E) dE$$

The total energy of a system is found by adding the energies of the component states. $g(E)$ is the number of states per unit energy interval, so $g(E)dE$ represents the number of states in an energy interval dE , and those states each have energy E . The integral performs the sum.

Using Eq. (15.45) for the density of states, we get

$$E_{TOT} = \int_{E_{\min}}^{E_{\max}} E g(E) dE = \int_{E_{\min}}^{E_{\max}} E \frac{L}{2\pi\beta a \sin(ka)} dE = \frac{L}{2\pi\beta a} \int_{E_{\min}}^{E_{\max}} \frac{E}{\sin(ka)} dE$$

Because $g(E)$ is a function of E rather than k , we must express k in terms of E to do the integral. Use

$$\begin{aligned}E &= \alpha + 2\beta \cos(ka) \\ \sin(ka) &= \sqrt{1 - \cos^2(ka)} = \sqrt{1 - \left(\frac{E - \alpha}{2\beta}\right)^2}\end{aligned}$$

to get

$$\begin{aligned}
E_{TOT} &= \frac{L}{2\pi\beta a} \int_{E_{\min}}^{E_{\max}} \frac{E}{\sqrt{1 - \left(\frac{E - \alpha}{2\beta}\right)^2}} dE \\
&= \frac{L}{2\pi\beta a} \left[2\alpha\beta \sin^{-1}\left(\frac{E - \alpha}{2\beta}\right) - 2\beta^2 \sqrt{\frac{4\beta^2 - (E - \alpha)^2}{\beta^2}} \right]_{\alpha - 2\beta}^{\alpha + 2\beta} \\
&= \frac{L}{2\pi\beta a} [2\pi\alpha\beta] = \frac{L\alpha}{a} = \frac{Na\alpha}{a} = N\alpha
\end{aligned}$$

15.7 a) For a free particle, the relation between E and k is

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

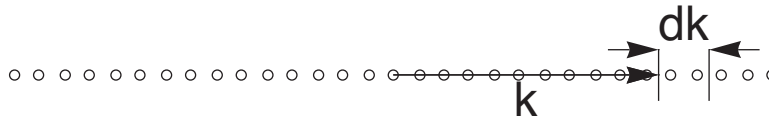
Using Eq. (15.43), the density of states in energy space in one dimension is

$$g(E) = \frac{L}{\pi} \frac{dk}{dE} = \frac{L}{\pi} \left(\frac{dE}{dk} \right)^{-1} = \frac{L}{\pi} \left(\frac{\hbar^2 k}{m} \right)^{-1} = \frac{mL}{\pi \hbar^2 k}$$

Writing this in terms of the energy, we get

$$g(E) = \frac{mL}{\pi \hbar^2 k} = \frac{mL}{\pi \hbar^2} \sqrt{\frac{\hbar^2}{2mE}} = \frac{L}{\pi \hbar} \sqrt{\frac{m}{2E}}$$

b) To find the density of states in energy space in two dimensions, go back and revisit the argument in Section 15.7. The number of states in a region of size dk in k space is the density $g_k(k)$ times dk . We can calculate the number of states by dividing the volume of the region by the volume per state. In one dimension, the volume of the region is dk and the volume per state is $2\pi/Na$ (See Fig. 15.9 and below)



so the number of states is

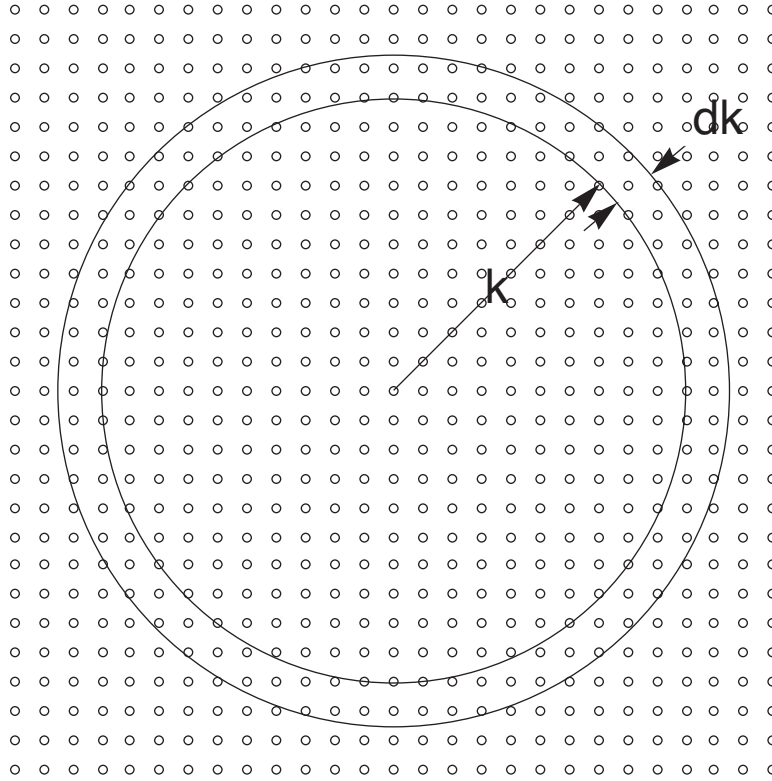
$$g_k(k)dk = \frac{dk}{2\pi/Na} = \frac{Na}{2\pi} dk$$

and the density in k space is

$$g_k(k) = \frac{L}{2\pi}$$

as we found in Eq. (15.41), where $L = Na$ is the length (1 dimensional volume) of the chain of wells.

In two dimensions, the volume of the annular region of width dk is $2\pi k dk$ and the volume per state is $(2\pi/Na)^2$



so the number of states is

$$g_k(k)dk = \frac{2\pi k dk}{(2\pi/Na)^2} = \frac{(Na)^2}{2\pi} k dk$$

and the density in k space is

$$g_k(k) = \frac{L^2}{2\pi} k$$

To find the energy density of states, use Eq. (15.43):

$$g(E) = 2g_k(k) \frac{dk}{dE} = 2 \frac{L^2}{2\pi} k \frac{dk}{dE} = \frac{L^2}{\pi} k \left(\frac{dE}{dk} \right)^{-1} = \frac{L^2}{\pi} k \left(\frac{\hbar^2 k}{m} \right)^{-1} = \frac{mL^2}{\pi \hbar^2}$$

This is a constant, independent of the energy.

15.8 The well parameter z_0 is (note that when using the equations from Chapter 5, we must use $b/2$ for the well half-width, which was a in Chapter 5)

$$z_0 = \sqrt{\frac{2mV_0(b/2)^2}{\hbar^2}} = \sqrt{\frac{2(511\text{keV})1\text{eV}(0.35\text{nm}/2)^2}{(1240\text{eVnm}/2\pi)^2}} = 0.897$$

This parameter is less than $\pi/2$, so there is only one solution to the transcendental equation determining the energy eigenvalues (see Fig. 5.16)

$$z \tan(z) = \sqrt{z_0^2 - z^2} \rightarrow z = 0.691$$

Hence the bound state energy is

$$E_g = \frac{\hbar^2 z^2}{2ma^2} = \frac{z^2}{z_0^2} V_0 = 0.594 eV$$

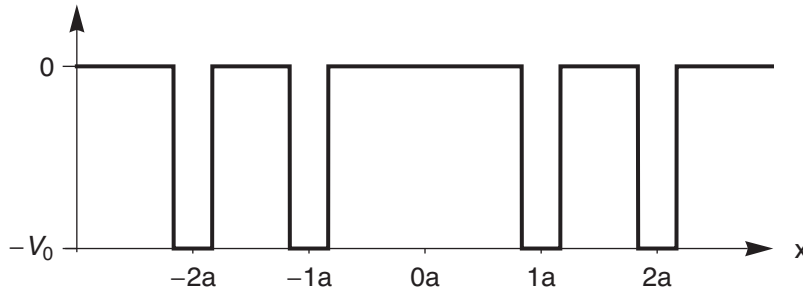
The matrix elements that we need to determine α and β are

$$\langle n | V' | n \rangle = \alpha - E_g = \int_{-\infty}^{\infty} \varphi_n^*(x) V'(x) \varphi_n(x) dx$$

and

$$\beta = \langle n | V' | n \pm 1 \rangle = \int_{-\infty}^{\infty} \varphi_n^*(x) V'(x) \varphi_{n \pm 1}(x) dx$$

Let's set $n = 0$ for concreteness. Hence $V'(x)$ looks like:



The normalized wave function for an even parity state in a finite well was found in Problem 5.16:

$$\varphi_{\text{even}}(x) = \frac{1}{\sqrt{\frac{b}{2} + \frac{1}{q}}} \begin{cases} \cos(kb/2) e^{qb/2} e^{qx} & x < -b/2 \\ \cos(kx) & -b/2 \leq x \leq b/2 \\ \cos(kb/2) e^{qb/2} e^{-qx} & x > b/2 \end{cases}$$

For the first matrix element we get

$$\begin{aligned}
\langle 0|V'|0\rangle &= \int_{-\infty}^{\infty} \varphi_0^*(x) V'(x) \varphi_0(x) dx = 2 \int_0^{\infty} V'(x) |\varphi_0(x)|^2 dx \\
&= 2 \sum_{n=1}^{\infty} \int_{na-b/2}^{na+b/2} (-V_0) |\varphi_0(x)|^2 dx = -2V_0 \sum_{n=1}^{\infty} \int_{na-b/2}^{na+b/2} \frac{e^{qb} \cos^2(kb/2)}{\left(\frac{b}{2} + \frac{1}{q}\right)} e^{-2qx} dx \\
&= -\frac{2V_0 e^{qb} \cos^2(kb/2)}{\left(\frac{b}{2} + \frac{1}{q}\right)} \sum_{n=1}^{\infty} \left[\frac{e^{-2qx}}{-2q} \right]_{na-b/2}^{na+b/2} \\
&= -\frac{2V_0 e^{qb} \cos^2(kb/2)}{\left(\frac{b}{2} + \frac{1}{q}\right)} \sum_{n=1}^{\infty} \left[\frac{e^{-2q(na-b/2)} - e^{-2q(na+b/2)}}{2q} \right] \\
&= -\frac{V_0 \cos^2(kb/2)}{\left(\frac{qb}{2} + 1\right)} \sum_{n=1}^{\infty} e^{-2qna} (e^{2qb} - 1)
\end{aligned}$$

The wave vector relations are [see Eq. (5.87)]

$$\begin{aligned}
qb/2 &= \sqrt{z_0^2 - z^2} = z \tan z \\
kb/2 &= z
\end{aligned}$$

For this chain, $a = 3b$. It is convenient to write everything in terms of the single parameter z , giving the result

$$\langle 0|V'|0\rangle = -\frac{V_0 \cos^2 z}{(z \tan z + 1)} (e^{4z \tan z} - 1) \sum_{n=1}^{\infty} e^{-12nz \tan z} = -\frac{V_0 \cos^2 z}{(1 + z \tan z)} \frac{(e^{4z \tan z} - 1)}{(e^{12z \tan z} - 1)}$$

For our well, we get

$$\alpha - E_g = \langle 0|V'|0\rangle = -0.0035 \text{ eV}$$

giving

$$\alpha = E_g + \langle 0|V'|0\rangle = 0.590 \text{ eV}$$

The hopping matrix elements are

$$\begin{aligned}
\beta &= \langle 0|V'|1\rangle = \int_{-\infty}^{\infty} \varphi_0^*(x) V'(x) \varphi_1(x) dx \\
&= \sum_{n=-1}^{-\infty} \int_{na-b/2}^{na+b/2} (-V_0) \varphi_0^*(x) \varphi_1(x) dx + \sum_{n=1}^{\infty} \int_{na-b/2}^{na+b/2} (-V_0) \varphi_0^*(x) \varphi_1(x) dx
\end{aligned}$$

Both wave functions are decaying exponentials except in the well at $n = 1$. Using the wave functions given above, we get

$$\begin{aligned}
\beta &= \langle 0|V'|1\rangle = \int_{-\infty}^{\infty} \phi_0^*(x) V'(x) \phi_1(x) dx \\
&= \sum_{n=-1}^{-\infty} \int_{na-b/2}^{na+b/2} (-V_0) \phi_0^*(x) \phi_1(x) dx + \sum_{n=1}^{\infty} \int_{na-b/2}^{na+b/2} (-V_0) \phi_0^*(x) \phi_1(x) dx \\
&= -V_0 \frac{1}{\left(\frac{b}{2} + \frac{1}{q}\right)} \left\{ \begin{aligned} &e^{qb} \cos^2(kb/2) \sum_{n=-1}^{-\infty} \int_{na-b/2}^{na+b/2} e^{qx} e^{q(x-a)} dx \\ &+ \int_{a-b/2}^{a+b/2} e^{-qx} \cos[k(x-a)] dx \\ &+ e^{qb} \cos^2(kb/2) \sum_{n=2}^{\infty} \int_{na-b/2}^{na+b/2} e^{-qx} e^{-q(x-a)} dx \end{aligned} \right\}
\end{aligned}$$

The two sums must be equal, so we get

$$\begin{aligned}
\beta &= -V_0 \frac{1}{\left(\frac{b}{2} + \frac{1}{q}\right)} \left\{ \begin{aligned} &2e^{qb} \cos^2(kb/2) e^{-qa} \sum_{n=-1}^{-\infty} \left[\frac{e^{2qx}}{2q} \right]_{na-b/2}^{na+b/2} \\ &+ \left[e^{-qx} \frac{k \sin[k(x-a)] - q \cos[k(x-a)]}{q^2 + k^2} \right]_{a-b/2}^{a+b/2} \end{aligned} \right\} \\
&= -V_0 \frac{1}{\left(\frac{b}{2} + \frac{1}{q}\right)} \left\{ \begin{aligned} &\frac{\cos^2(kb/2) e^{-qa} (e^{2qb} - 1)}{q} \sum_{n=-1}^{-\infty} e^{2qna} \\ &+ \frac{2qe^{-qa}}{q^2 + k^2} \left[\frac{k}{q} \cosh\left(\frac{qb}{2}\right) \sin\left(\frac{kb}{2}\right) + \sinh\left(\frac{qb}{2}\right) \cos\left(\frac{kb}{2}\right) \right] \end{aligned} \right\}
\end{aligned}$$

Using the wave vector relations gives

$$\begin{aligned}
\beta &= -V_0 \frac{1}{(1 + z \tan z)} \left\{ \begin{aligned} &\cos^2 z e^{-6z \tan z} (e^{4z \tan z} - 1) \sum_{n=1}^{\infty} e^{-12nz \tan z} \\ &+ 2e^{-5z \tan z} \sin^2 z \cos^2 z [\cosh(z \tan z) + \sinh(z \tan z)] \end{aligned} \right\} \\
&= -V_0 \frac{\cos^2 z e^{-6z \tan z}}{(1 + z \tan z)} \left\{ \begin{aligned} &\frac{(e^{4z \tan z} - 1)}{(e^{12z \tan z} - 1)} + 2e^{2z \tan z} \sin^2 z \end{aligned} \right\}
\end{aligned}$$

For our well, we get

$$\beta = \langle 0|V'|1\rangle = -0.031 \text{ eV}$$

15.9 The Kronig-Penney model leads to the equations

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ e^{-iqb} & e^{iqb} & -e^{-ika} e^{i\kappa(a-b)} & -e^{-ika} e^{-i\kappa(a-b)} \\ q & -q & -\kappa & \kappa \\ qe^{-iqb} & -qe^{iqb} & -\kappa e^{-ika} e^{i\kappa(a-b)} & \kappa e^{-ika} e^{-i\kappa(a-b)} \end{pmatrix} \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = 0$$

To simplify the algebra, reorder the rows:

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ q & -q & -\kappa & \kappa \\ e^{-iqb} & e^{iqb} & -e^{-ika} e^{i\kappa(a-b)} & -e^{-ika} e^{-i\kappa(a-b)} \\ qe^{-iqb} & -qe^{iqb} & -\kappa e^{-ika} e^{i\kappa(a-b)} & \kappa e^{-ika} e^{-i\kappa(a-b)} \end{pmatrix} \begin{pmatrix} A \\ C \\ B \\ D \end{pmatrix} = 0$$

There are non-trivial solutions to this set of equations only if the determinant of the 4 x 4 matrix is zero. The characteristic equation is

$$\begin{aligned} & -q(-2\kappa e^{-i2ka}) + \kappa(\kappa e^{-ika} e^{iqb} e^{-i\kappa(a-b)} - qe^{-ika} e^{iqb} e^{-i\kappa(a-b)}) + \kappa(-\kappa e^{-ika} e^{iqb} e^{i\kappa(a-b)} - qe^{-ika} e^{iqb} e^{i\kappa(a-b)}) \\ & -q(-2\kappa e^{-i2ka}) - \kappa(\kappa e^{-ika} e^{-iqb} e^{-i\kappa(a-b)} + qe^{-ika} e^{-iqb} e^{-i\kappa(a-b)}) - \kappa(-\kappa e^{-ika} e^{-iqb} e^{i\kappa(a-b)} + qe^{-ika} e^{-iqb} e^{i\kappa(a-b)}) \\ & -q(\kappa e^{-ika} e^{iqb} e^{-i\kappa(a-b)} - qe^{-ika} e^{iqb} e^{-i\kappa(a-b)}) - q(\kappa e^{-ika} e^{-iqb} e^{-i\kappa(a-b)} + qe^{-ika} e^{-iqb} e^{-i\kappa(a-b)}) - \kappa(-2q) \\ & + q(-\kappa e^{-ika} e^{iqb} e^{i\kappa(a-b)} - qe^{-ika} e^{iqb} e^{i\kappa(a-b)}) + q(-\kappa e^{-ika} e^{-iqb} e^{i\kappa(a-b)} + qe^{-ika} e^{-iqb} e^{i\kappa(a-b)}) - \kappa(-2q) = 0 \end{aligned}$$

Convert the qb terms to trig functions:

$$\begin{aligned} & 4\kappa q e^{-i2ka} + 4\kappa q \\ & + e^{-ika} \left\{ \begin{aligned} & 2i\kappa^2 e^{-i\kappa(a-b)} \sin qb - 2i\kappa^2 e^{i\kappa(a-b)} \sin qb + 2iq^2 e^{-i\kappa(a-b)} \sin qb - 2iq^2 e^{i\kappa(a-b)} \sin qb \\ & - 4q\kappa e^{-i\kappa(a-b)} \cos qb - 4q\kappa e^{i\kappa(a-b)} \cos qb \end{aligned} \right\} = 0 \end{aligned}$$

Then convert the κ terms to trig functions:

$$\begin{aligned} & e^{-ika} (4\kappa q e^{-ika} + 4\kappa q e^{ika}) \\ & + e^{-ika} \left\{ \begin{aligned} & 4\kappa^2 \sin qb \sin(\kappa(a-b)) + 4q^2 \sin qb \sin(\kappa(a-b)) \\ & - 8q\kappa \cos qb \cos(\kappa(a-b)) \end{aligned} \right\} = 0 \end{aligned}$$

Finally, convert the ka term to trig functions and divide out the e^{-ika} term to get

$$8\kappa q \cos ka + 4(\kappa^2 + q^2) \sin qb \sin(\kappa(a-b)) - 8q\kappa \cos qb \cos(\kappa(a-b)) = 0$$

The dispersion relation is thus

$$\cos qb \cos(\kappa(a-b)) - \frac{(\kappa^2 + q^2)}{2q\kappa} \sin qb \sin(\kappa(a-b)) = \cos ka$$

b) If κ is imaginary, then we have the equations

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ q & -q & -i|\kappa| & i|\kappa| \\ e^{-iqb} & e^{iqb} & -e^{-ika} e^{-|\kappa|(a-b)} & -e^{-ika} e^{|\kappa|(a-b)} \\ qe^{-iqb} & -qe^{iqb} & -i|\kappa| e^{-ika} e^{-|\kappa|(a-b)} & i|\kappa| e^{-ika} e^{|\kappa|(a-b)} \end{pmatrix} \begin{pmatrix} A \\ C \\ B \\ D \end{pmatrix} = 0$$

The characteristic equation is

$$\begin{aligned} & -q(-2i|\kappa|e^{-i2ka}) + i|\kappa|(i|\kappa|e^{-ika}e^{iqb}e^{|\kappa|(a-b)} - qe^{-ika}e^{iqb}e^{|\kappa|(a-b)}) \\ & + i|\kappa|(-i|\kappa|e^{-ika}e^{iqb}e^{-|\kappa|(a-b)} - qe^{-ika}e^{iqb}e^{-|\kappa|(a-b)}) \\ & -q(-2i|\kappa|e^{-i2ka}) - i|\kappa|(i|\kappa|e^{-ika}e^{-iqb}e^{|\kappa|(a-b)} + qe^{-ika}e^{-iqb}e^{|\kappa|(a-b)}) \\ & -i|\kappa|(-i|\kappa|e^{-ika}e^{-iqb}e^{-|\kappa|(a-b)} + qe^{-ika}e^{-iqb}e^{-|\kappa|(a-b)}) \\ & -q(i|\kappa|e^{-ika}e^{iqb}e^{|\kappa|(a-b)} - qe^{-ika}e^{iqb}e^{|\kappa|(a-b)}) - q(i|\kappa|e^{-ika}e^{-iqb}e^{|\kappa|(a-b)} + qe^{-ika}e^{-iqb}e^{|\kappa|(a-b)}) \\ & -i|\kappa|(-2q) \\ & + q(-i|\kappa|e^{-ika}e^{iqb}e^{-|\kappa|(a-b)} - qe^{-ika}e^{iqb}e^{-|\kappa|(a-b)}) + q(-i|\kappa|e^{-ika}e^{-iqb}e^{-|\kappa|(a-b)} + qe^{-ika}e^{-iqb}e^{-|\kappa|(a-b)}) \\ & -i|\kappa|(-2q) = 0 \end{aligned}$$

Convert the qb terms to trig functions:

$$\begin{aligned} & 4i|\kappa|qe^{-i2ka} + 4i|\kappa|q \\ & + e^{-ika} \left\{ \begin{aligned} & -2i|\kappa|^2 e^{|\kappa|(a-b)} \sin qb + 2i|\kappa|^2 e^{-|\kappa|(a-b)} \sin qb \\ & + 2iq^2 e^{|\kappa|(a-b)} \sin qb - 2iq^2 e^{-|\kappa|(a-b)} \sin qb \\ & - 4qi|\kappa| e^{|\kappa|(a-b)} \cos qb - 4qi|\kappa| e^{-|\kappa|(a-b)} \cos qb \end{aligned} \right\} = 0 \end{aligned}$$

Then convert the κ terms to hyperbolic trig functions:

$$\begin{aligned} & ie^{-ika} (4|\kappa|qe^{-ika} + 4|\kappa|qe^{ika}) \\ & + ie^{-ika} \left\{ \begin{aligned} & -4|\kappa|^2 \sin qb \sin(|\kappa|(a-b)) + 4q^2 \sin qb \sin(|\kappa|(a-b)) \\ & - 8q|\kappa| \cos qb \cos(|\kappa|(a-b)) \end{aligned} \right\} = 0 \end{aligned}$$

Finally, convert the ka term to trig functions and divide out the ie^{-ika} term to get

$$8|\kappa|q \cos ka + 4(-|\kappa|^2 + q^2) \sin qb \sin(|\kappa|(a-b)) - 8q|\kappa| \cos qb \cos(|\kappa|(a-b)) = 0$$

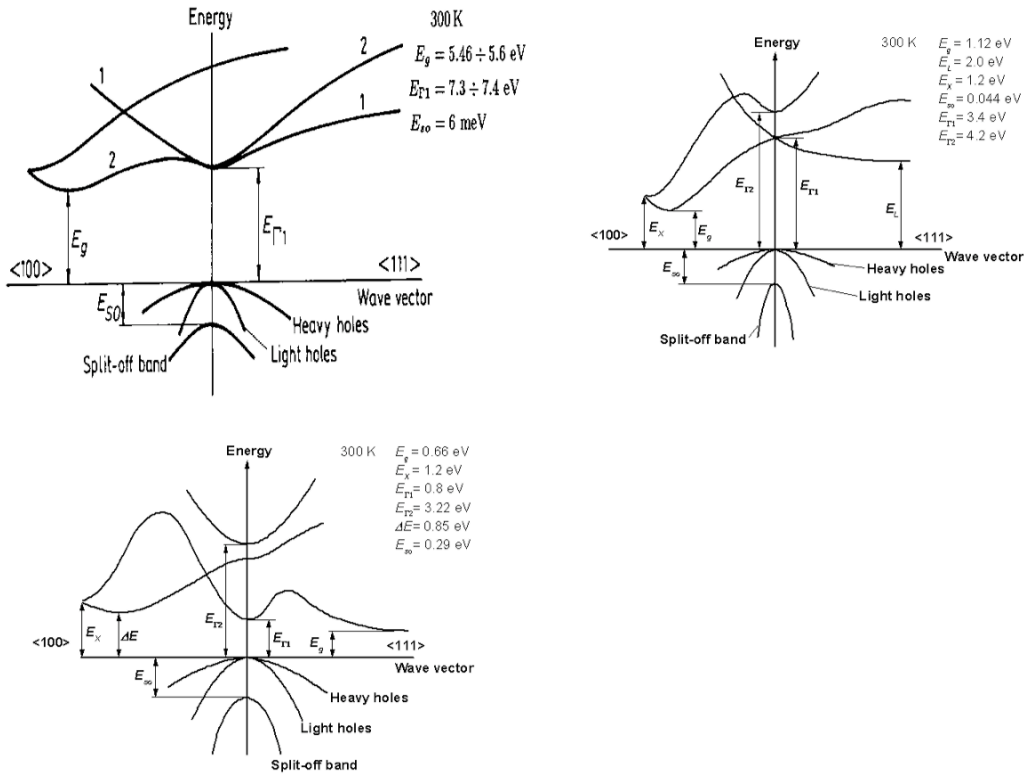
The dispersion relation is thus

$$\cos qb \cos(|\kappa|(a-b)) - \frac{(q^2 - |\kappa|^2)}{2|\kappa|q} \sin qb \sin(|\kappa|(a-b)) = \cos ka$$

15.10 (a) There's a good compilation of IV and III-V semiconductor properties at <http://www.ioffe.ru/SVA/NSM/Semicond/index.html>. Pictures here are taken from that site.

The group IV elements C, Si, Ge, alpha-Sn all crystallize into the same diamond structure. The band structures of the four forms are all therefore very similar. All four have a "gap" in the density of states above the highest occupied state at $T = 0$. The band gap is 5 eV in C, which is an insulator, falling to 1.1 eV in Si to 0.7 eV in Ge, and to effectively 0 eV in Sn, so Sn could be called a weak metal, or semimetal.

The true semiconductors have indirect band gaps, which means that the CB minimum and the VB maximum are not at the same value of k . The VB maximum is at Γ for all, but the CB minimum is different. See below for $E(k)$ for C (top left), Si (top right), Ge (bottom left).



(b) Lower-lying bands are a result of overlap of low-lying ("core") states. The overlap between such states is much weaker than the overlap between higher-energy, or valence, states. Lower bands are therefore narrower than higher bands, and, with similar widths of the Brillouin zones, have less curvature.

15.11 If bands in solids were derived exclusively from the overlap of like atomic orbitals, the highest occupied band in solid Mg would be a $3s$ band with capacity for $2N$ electrons, and it would be full because there are two electrons in the $3s$ atomic orbital of Mg. The next band, capacity $6N$, but empty, would be a $3p$ band. Mg would be classified a semiconductor or insulator. Within the LCAO model, we recognize that such " $3s$ " and " $3p$ " bands would be sufficiently broad as to overlap, or that the s and p atomic orbitals contribute to the same band with capacity $8N$. Such a band would be $\frac{1}{4}$ full, and Mg is metallic in this scenario.

15.12 a) Visible photons have wavelengths in the range 400 – 700 nm. Using the relation

$$E = \frac{hc}{\lambda} = \frac{1240 \text{ eV nm}}{\lambda}$$

yields an energy range for visible photons of 3.1 eV – 1.7 eV. The band gaps of important semiconductors are Si: 1.1 eV, Ge: 0.7 eV, GaAs: 1.4 eV. Visible photons thus have sufficient energy to excite electrons above the band gaps of all these materials.

b) The momentum of a photon is $p = h/\lambda$. An indirect transition has a wave vector change of order $\Delta k = \pi/a$, as shown in Fig. 15.21. The momentum change is thus $\Delta p = \hbar \Delta k = \pi \hbar / a$. Comparing the photon momentum with the required electron momentum change, we get

$$\frac{p}{\Delta p} = \frac{h/\lambda}{\pi \hbar / a} = \frac{2a}{\lambda}$$

The typical lattice parameter a is 0.3-0.5 nm, which is much smaller than the typical visible photon wavelength. So the small momentum of a photon is insufficient to change the electron k value significantly.

c) The phonon momentum is $p = h/\lambda$ and since $\lambda \sim a$, the phonon has sufficient momentum for an indirect transition. However, the phonon energy is

$$E = h\nu = (4.135 \times 10^{-15} \text{ eVs}) 10^{13} \text{ Hz} = 4.135 \times 10^{-2} \text{ eV}$$

which is much less than the required electron-volt-scale energy.
