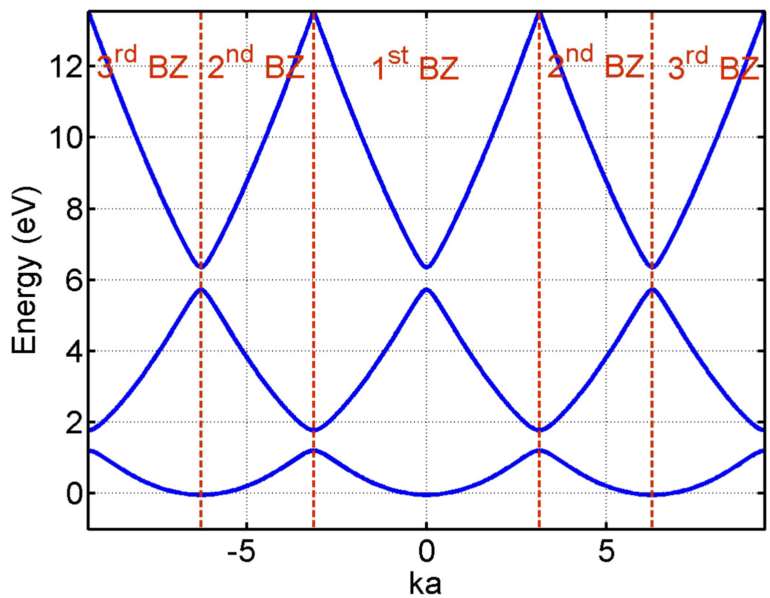
Problem 5.1



a) **Lesson:** The lesson is that if one chooses a value of the wavevector outside the FBZ for numerical solution then one does not obtain any new energy eigenvalues or wavefunctions that are not already in the FBZ. The reason for that, as discussed in the class, is that a solution found for a wavevector in the FBZ already contains superposition of plane waves, different from the starting wavevector value, by reciprocal lattice vectors. If one obtains a solution for a wavevector value, say k, outside the FBZ then it is identical to the solution obtained for a wavevector value, say k', that lies in the FBZ and is related to k via a relation of the form: $k'=k+G$, where G is that (unique) reciprocal lattice vector for which k' is in the FBZ. This was also the motivation for zone-folding in which free-electron bands outside the FBZ were translated by appropriate reciprocal lattice vectors and placed in the FBZ.

Also notice that if one were to solve for and plot energy bands outside the FBZ, as we did in this problem, then the bands will be periodic in k-space with the periodicity of the reciprocal lattice, in the sense that: $E(\vec{k}+\vec{G})=E(\vec{k})$ where $\vec{G}$ is any reciprocal lattice vector. This property, of course, holds in all dimensions, and even for the tight binding solutions (check!).

Problem 5.2

a) $H_{11} = E_s, H_{22} = E_p\ , H_{33} = E_p\ , H_{44} = E_s, H_{55} = E_p, H_{66} = E_p$

b)
$$H_{14} = V_{ss\sigma}\left(-e^{i\vec{k}.\vec{n}_1} - e^{i\vec{k}.\vec{n}_2} - e^{i\vec{k}.\vec{n}_3}\right) \qquad H_{15} = V_{sp\sigma}\left(e^{i\vec{k}.\vec{n}_1} - \frac{1}{2}e^{i\vec{k}.\vec{n}_2} - \frac{1}{2}e^{i\vec{k}.\vec{n}_3}\right)$$
$$H_{16} = V_{sp\sigma}\left(\frac{\sqrt{3}}{2}e^{i\vec{k}.\vec{n}_2} - \frac{\sqrt{3}}{2}e^{i\vec{k}.\vec{n}_3}\right)$$

c) $H_{24} = V_{sp\sigma}\left(-e^{i\vec{k}.\vec{n}_1} + \frac{1}{2}e^{i\vec{k}.\vec{n}_2} + \frac{1}{2}e^{i\vec{k}.\vec{n}_3}\right) \qquad H_{34} = V_{sp\sigma}\left(-\frac{\sqrt{3}}{2}e^{i\vec{k}.\vec{n}_2} + \frac{\sqrt{3}}{2}e^{i\vec{k}.\vec{n}_3}\right)$

d)
$$H_{25} = V_{pp\sigma}\left(e^{i\vec{k}.\vec{n}_1} + \frac{1}{4}e^{i\vec{k}.\vec{n}_2} + \frac{1}{4}e^{i\vec{k}.\vec{n}_3}\right) + V_{pp\pi}\left(-\frac{3}{4}e^{i\vec{k}.\vec{n}_2} - \frac{3}{4}e^{i\vec{k}.\vec{n}_3}\right)$$
$$H_{36} = V_{pp\pi}\left(-e^{i\vec{k}.\vec{n}_1} - \frac{1}{4}e^{i\vec{k}.\vec{n}_2} - \frac{1}{4}e^{i\vec{k}.\vec{n}_3}\right) + V_{pp\sigma}\left(\frac{3}{4}e^{i\vec{k}.\vec{n}_2} + \frac{3}{4}e^{i\vec{k}.\vec{n}_3}\right)$$

e) There will be 6 bands; 3 will be completely filled and 3 completely empty at zero temperature.

Problem 5.3

a)

I will do a few of the more difficult ones ($\hat{H}_{26}$ and $\hat{H}_{27}$)

H_{26}

This corresponds to the energy matrix element between the p_x orbital of Ga and p_x orbitals of 4 neighboring As atoms located at $\vec{d}_1, \vec{d}_2, \vec{d}_3$ and $\vec{d}_4$. First take the σ-overlaps between $|\phi_{p_x G}(\vec{r})\rangle$ and $|\phi_{p_x A}(\vec{r}-\vec{d}_1)\rangle$. The projection of each p_x orbital along the $\frac{1}{\sqrt{3}}(1,1,1)$ direction gives a factor of $\left(\frac{1}{\sqrt{3}}\right)^2 = \frac{1}{3}$ and so the matrix element will be $+\frac{V_{pp\sigma}}{3} e^{i\vec{k}\cdot\vec{d}_1}$. Adding up contributions from the other 3 p_x-orbitals one gets:

$$\frac{V_{pp\sigma}}{3}\left[e^{i\vec{k}\cdot\vec{d}_1} + e^{i\vec{k}\cdot\vec{d}_2} + e^{i\vec{k}\cdot\vec{d}_3} + e^{i\vec{k}\cdot\vec{d}_4}\right]$$

Now we look at the π-overlap between $|\phi_{p_x G}(\vec{r})\rangle$ and $|\phi_{p_x A}(\vec{r}-\vec{d}_1)\rangle$. We project each p_x-orbital in direction perpendicular to $\frac{1}{\sqrt{3}}(1,1,1)$. This perpendicular direction is $\hat{n}_1$.

$$\hat{n}_1 = \frac{\frac{2}{3}\hat{x} - \frac{1}{3}\hat{y} - \frac{1}{3}\hat{z}}{\sqrt{\frac{2}{3}}}$$

. There can be many directions perpendicular to $\frac{1}{\sqrt{3}}(1,1,1)$ but the one that we are looking for is such that the three vectors: $\frac{1}{\sqrt{3}}(1,1,1)$ and $\hat{n}_1$ and $\hat{x}$ all lie in the same plane. $\hat{n}_1$ can be found by the relation:

$$\hat{n}_1 = \left\{\hat{x} - \frac{(\hat{x}\cdot\vec{d}_1)\,\vec{d}_1}{|\vec{d}_1|^2}\right\}_{\text{normalized to unity}}$$

One we have projected both p_x-orbitals along the $\hat{n}_1$ direction they will be parallel but we will get a factor of $\left(\sqrt{\frac{2}{3}}\right)^2 = \frac{2}{3}$. So the matrix element becomes

$$- \frac{2}{3} V_{pp\pi} \; e^{i\vec{k}\cdot\vec{d_1}}$$

Adding up contributions from the other 3 p_x orbitals gives the total matrix element:

$$- \frac{2}{3} V_{pp\pi} \left(e^{i\vec{k}\cdot\vec{d_1}} + e^{i\vec{k}\cdot\vec{d_2}} + e^{i\vec{k}\cdot\vec{d_3}} + e^{i\vec{k}\cdot\vec{d_4}} \right)$$

Finally, adding up contributions from σ-overlaps and π-overlaps we get the end result:

$$\left(\frac{V_{pp\sigma}}{3} - \frac{2}{3} V_{pp\pi} \right) \left(e^{i\vec{k}\cdot\vec{d_1}} + e^{i\vec{k}\cdot\vec{d_2}} + e^{i\vec{k}\cdot\vec{d_3}} + e^{i\vec{k}\cdot\vec{d_3}} \right)$$

$$= V_1 \, g_0(\vec{k})$$

$\underline{H_{27}}$.

This corresponds to the energy matrix element between the P_x orbital of Ga and the P_y orbitals of neighboring As atoms. First take the σ-overlaps between $|\phi_{px\,G}(\vec{r})\rangle$ and $|\phi_{py\,A}(\vec{r}-\vec{d_1})\rangle$. Take the projection of each along $\frac{1}{\sqrt{3}}(1,1,1)$ to get a factor of $\left(\frac{1}{\sqrt{3}}\right)^2 = \frac{1}{3}$ and the matrix element is: $\frac{V_{pp\sigma}}{3} \, e^{i\vec{k}\cdot\vec{d_1}}$

The matrix elements with ~~As~~ atoms at $\vec{d_3}$ and $\vec{d_4}$ will give a negative sign. So we get:

$$\frac{V_{pp\sigma}}{3}\left(e^{i\vec{k}\cdot\vec{d_1}}+e^{i\vec{k}\cdot\vec{d_2}}-e^{i\vec{k}\cdot\vec{d_3}}-e^{i\vec{k}\cdot\vec{d_4}}\right).$$

Now we look at the π-overlap between $|\phi_{pxG}(\vec{r})\rangle$ and $|\phi_{pyA}(\vec{r}-\vec{d_1})\rangle$. We need to choose a direction perpendicular to $\frac{1}{\sqrt{3}}(1,1,1)$. Now we have two choices:

$$\hat{n}_1 = \frac{\frac{2}{3}\hat{x}-\frac{1}{3}\hat{y}-\frac{1}{3}\hat{z}}{\sqrt{\frac{2}{3}}} \quad \text{or} \quad \hat{n}_2 = \frac{-\frac{1}{3}\hat{x}+\frac{2}{3}\hat{y}-\frac{1}{3}\hat{z}}{\sqrt{\frac{2}{3}}}$$

$$\hat{n}_1 = \left\{\hat{x}-\frac{(\vec{d_1}\cdot\hat{x})\vec{d_1}}{|\vec{d_1}|^2}\right\}_{\text{normalized}} \qquad \hat{n}_2 = \left\{\hat{y}-\frac{(\vec{d_1}\cdot\hat{y})\vec{d_1}}{|\vec{d_1}|^2}\right\}_{\text{normalized}}.$$

Either choice will work. Choosing $\hat{n}_1$ gives a factor of

$$\left(\sqrt{\frac{2}{3}}\right)\left(-\frac{1}{\sqrt{2\cdot3}}\right) = -\frac{1}{3}.$$

So the matrix element becomes: $+\frac{V_{pp\pi}}{3}e^{i\vec{k}\cdot\vec{d_1}}$

The matrix elements with As atoms at $\vec{d_3}$ and $\vec{d_4}$ will give opposite signs. So we get:

$$\frac{V_{pp\pi}}{3}\left(e^{i\vec{k}\cdot\vec{d_1}}+e^{i\vec{k}\cdot\vec{d_2}}-e^{i\vec{k}\cdot\vec{d_3}}-e^{i\vec{k}\cdot\vec{d_4}}\right)$$

Finally, the total matrix element becomes:

$$\left(\frac{V_{pp\sigma}}{3}+\frac{1}{3}V_{pp\pi}\right)\left(e^{i\vec{k}\cdot\vec{d_1}}+e^{i\vec{k}\cdot\vec{d_2}}-e^{i\vec{k}\cdot\vec{d_3}}-e^{i\vec{k}\cdot\vec{d_4}}\right) = V_2\, g_3(\vec{k})$$

b)