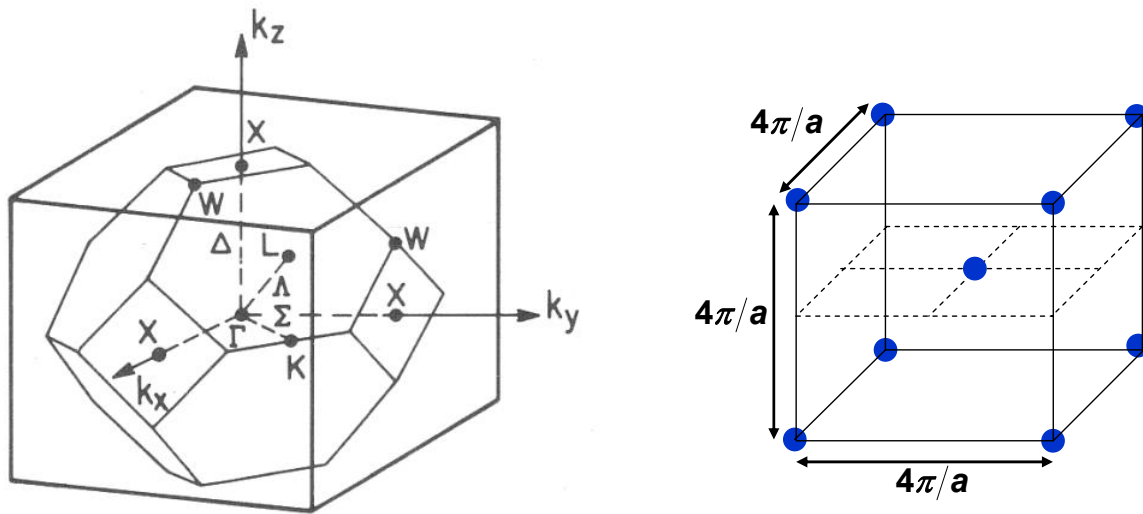
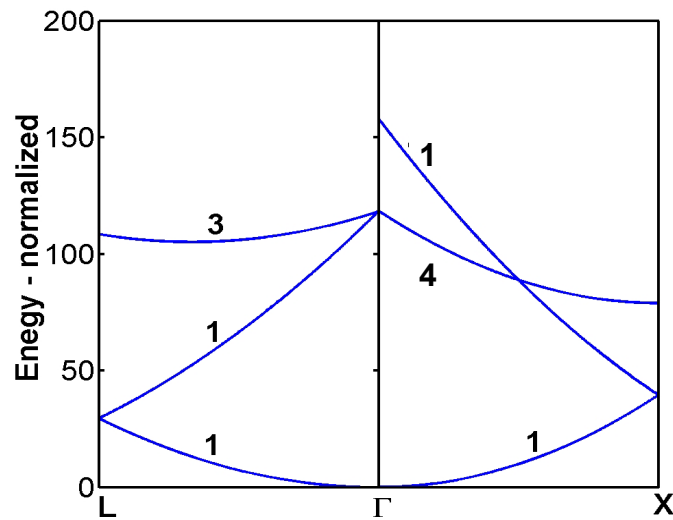


Homework 5 Solutions

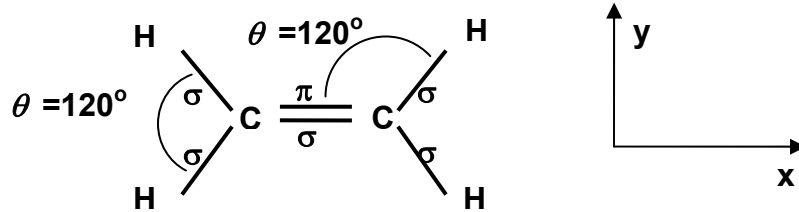
Problem 5.1 (Free electron energy bands for a FCC lattice in 3D)



a) and b)



Problem 5.2 (Ethene (or Ethylene) molecule: LCAO)



a) As discussed in the lectures, the p_z -orbitals (the ones that stick out of the plane of the molecule) are anti-symmetric with respect to reflections about the x - y plane. On the other hand, p_x -orbitals, p_y -orbitals, and s -orbitals are all symmetric with respect to reflections about the x - y plane. Consequently, the energy matrix elements of p_z -orbitals with all other orbitals will be zero.

b) Each carbon atoms is sp^2 hybridized.

c) The trial solution could be:

$$|\psi(\vec{r})\rangle = \sum_{j=1}^4 c_j |\phi_{1s}^H(\vec{r} - \vec{r}_j)\rangle + \sum_{m=5}^6 c_m |\phi_{2s}^C(\vec{r} - \vec{r}_m)\rangle + c_{m+2} |\phi_{2p_x}^C(\vec{r} - \vec{r}_m)\rangle + c_{m+4} |\phi_{2p_y}^C(\vec{r} - \vec{r}_m)\rangle$$

or in terms of the carbon sp^2 orbitals:

$$|\psi(\vec{r})\rangle = \sum_{j=1}^4 c_j |\phi_{1s}^H(\vec{r} - \vec{r}_j)\rangle + \sum_{m=5}^6 c_m |\phi_1^C(\vec{r} - \vec{r}_m)\rangle + c_{m+2} |\phi_2^C(\vec{r} - \vec{r}_m)\rangle + c_{m+4} |\phi_3^C(\vec{r} - \vec{r}_m)\rangle$$

d) Let the energy of the s -orbital of the hydrogen atom be E_{1s} and let the energies of the $2s$ and $2p$ orbitals of the carbon atom be E_{2s} and E_{2p} , respectively. The average energy of the carbon sp^2 orbital is given by the expression:

$$E_{sp^2} = \left(\frac{E_{2s} + 2E_{2p}}{3} \right)$$

Each hydrogen atoms will make a sigma bond with the sp^2 -orbital of the carbon atom pointing towards it. This will result in a sigma bonding orbital and a sigma anti-bonding orbital with energies equal to:

$$E_{CH}(A) = \left(\frac{E_{1s} + E_{sp^2}}{2} \right) + \sqrt{\left(\frac{E_{1s} - E_{sp^2}}{2} \right)^2 + \eta^2} \quad \text{degeneracy} = 4$$

$$E_{CH}(B) = \left(\frac{E_{1s} + E_{sp^2}}{2} \right) - \sqrt{\left(\frac{E_{1s} - E_{sp^2}}{2} \right)^2 + \eta^2} \quad \text{degeneracy} = 4$$

where:

$$\eta = - \left(\frac{V_{sp\sigma} + \sqrt{2}V_{pp\sigma}}{\sqrt{3}} \right)$$

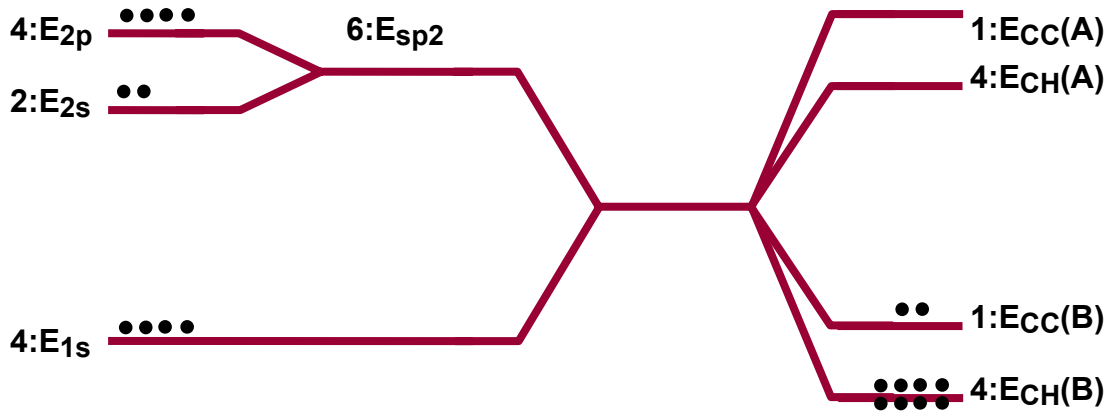
The sp^2 -orbitals of the two carbon atoms will make a sigma bond. This will result in a sigma bonding orbital and a sigma anti-bonding orbital with energies equal to:

$$E_{CC}(A) = E_{sp^2} + |\lambda| \quad \text{degeneracy} = 1$$

$$E_{CC}(B) = E_{sp^2} - |\lambda| \quad \text{degeneracy} = 1$$

where:

$$\lambda = - \left(\frac{V_{ss\sigma} + 2V_{pp\sigma} + 2\sqrt{2} V_{sp\sigma}}{3} \right)$$



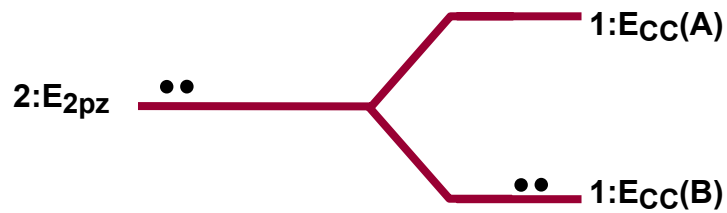
e) The solution is:

$$|\psi(\vec{r})\rangle = b_1 |\phi_{2pz}^C(\vec{r} - \vec{r}_5)\rangle + b_2 |\phi_{2pz}^C(\vec{r} - \vec{r}_6)\rangle$$

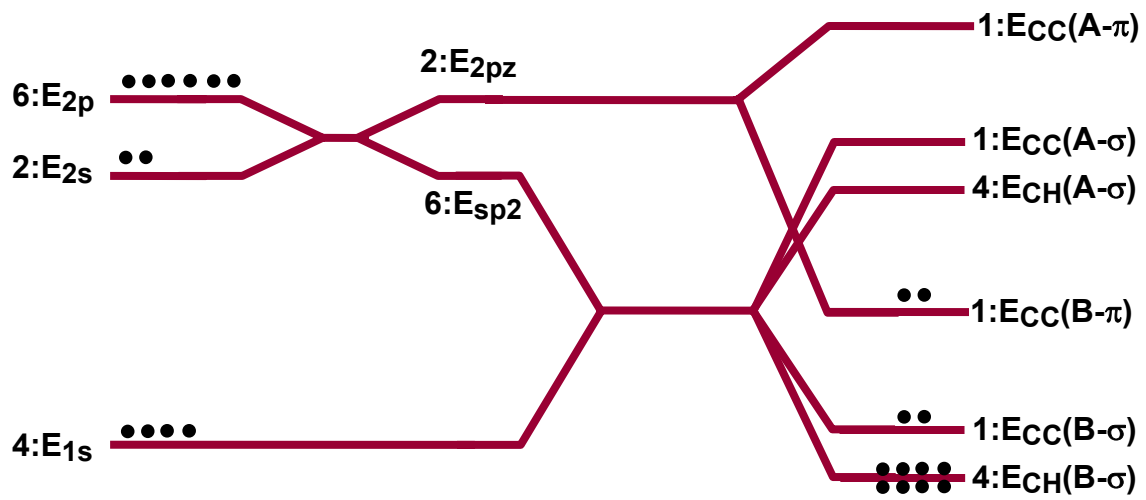
f) The pz-orbitals on carbon atoms make a π -bond with each other. The corresponding energies of the bonding and anti-bonding orbitals are:

$$E_{CC}(A) = E_{2p} + |V_{pp\pi}| \quad \text{degeneracy} = 1$$

$$E_{CC}(B) = E_{2p} - |V_{pp\pi}| \quad \text{degeneracy} = 1$$



g) The energy level diagram is shown below. The specific alignments are rough – my best guesses.



Problem 5.3

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

$$H_{14} = V_{ss\sigma} \left(-e^{i\vec{k} \cdot \vec{n}_1} - e^{i\vec{k} \cdot \vec{n}_2} - e^{i\vec{k} \cdot \vec{n}_3} \right) \quad H_{15} = V_{sp\sigma} \left(e^{i\vec{k} \cdot \vec{n}_1} - \frac{1}{2} e^{i\vec{k} \cdot \vec{n}_2} - \frac{1}{2} e^{i\vec{k} \cdot \vec{n}_3} \right)$$

b)
$$H_{16} = V_{sp\sigma} \left(\frac{\sqrt{3}}{2} e^{i\vec{k} \cdot \vec{n}_2} - \frac{\sqrt{3}}{2} e^{i\vec{k} \cdot \vec{n}_3} \right)$$

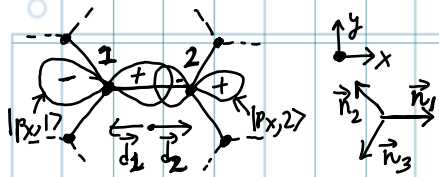
c)
$$H_{24} = V_{sp\sigma} \left(-e^{i\vec{k} \cdot \vec{n}_1} + \frac{1}{2} e^{i\vec{k} \cdot \vec{n}_2} + \frac{1}{2} e^{i\vec{k} \cdot \vec{n}_3} \right) \quad H_{34} = V_{sp\sigma} \left(-\frac{\sqrt{3}}{2} e^{i\vec{k} \cdot \vec{n}_2} + \frac{\sqrt{3}}{2} e^{i\vec{k} \cdot \vec{n}_3} \right)$$

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

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

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

The next page has all the matrix elements and pictorial representation of each of them.



$$\hat{H}|\psi\rangle = E|\psi\rangle \quad |\psi\rangle = \sum_m \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}_m} \left\{ e^{i\vec{k}\cdot\vec{d}_1} (c_1|s,1\rangle + c_2|p_x,1\rangle + c_3|p_y,1\rangle) + e^{i\vec{k}\cdot\vec{d}_2} (c_4|s,2\rangle + c_5|p_x,2\rangle + c_6|p_y,2\rangle) \right\}$$

Project on each of 6 orbitals:

$\langle \alpha | \hat{H} | \beta \rangle = E \langle \alpha | \beta \rangle \rightarrow$ solve eigenvalue $E_{\vec{k}}$ for the band structure.
6x6 matrix.

For signs: "H" is always -ve, so for example,

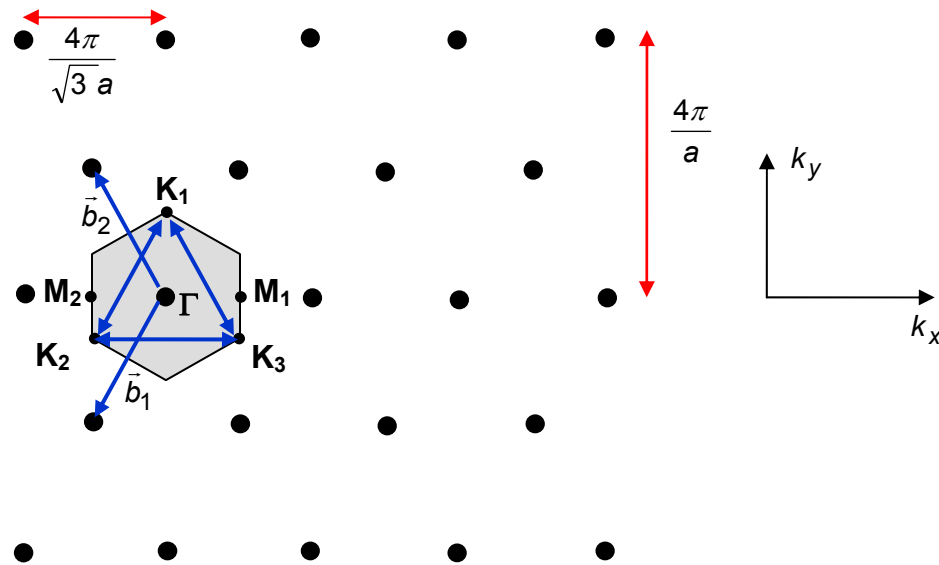
$$\langle s,1 | \hat{H} | s,2 \rangle = -V_{ss\sigma} \quad \text{the -ve the } \uparrow \text{ (-ve!)}$$

$$\langle p_x,1 | \hat{H} | p_x,2 \rangle = +V_{pp\sigma} \quad \text{the -ve -ve } \uparrow \text{ (+ve!)}$$

$$\begin{cases} \cos 60^\circ = \frac{1}{2} \\ \cos 30^\circ = \frac{\sqrt{3}}{2} \end{cases}$$

	$ s,1\rangle$	$ p_x,1\rangle$	$ p_y,1\rangle$	$ s,2\rangle$	$ p_x,2\rangle$	$ p_y,2\rangle$
$\langle s,1 $	E_s	E_p	E_p	$-V_{ss\sigma} (e^{i\vec{k}\cdot\vec{n}_1} + e^{i\vec{k}\cdot\vec{n}_2} + e^{i\vec{k}\cdot\vec{n}_3})$	$V_{sp\sigma} (e^{i\vec{k}\cdot\vec{n}_1} \cos 60^\circ e^{i\vec{k}\cdot\vec{n}_2} - \cos 60^\circ e^{i\vec{k}\cdot\vec{n}_3})$	$-V_{sp\sigma} \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_3} + V_{sp\sigma} \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_2}$
$\langle p_x,1 $	/	E_p	E_p	$-V_{sp\sigma} e^{i\vec{k}\cdot\vec{n}_1} + V_{sp} \cos 60^\circ e^{i\vec{k}\cdot\vec{n}_2} + V_{sp} \cos 60^\circ e^{i\vec{k}\cdot\vec{n}_3}$	$+V_{pp\sigma} e^{i\vec{k}\cdot\vec{n}_1} + V_{pp\sigma} \cos 60^\circ e^{i\vec{k}\cdot\vec{n}_2} + V_{pp\sigma} \cos 60^\circ e^{i\vec{k}\cdot\vec{n}_3}$ $-V_{pp\pi} \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_2}$ $-V_{pp\pi} \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_3}$	$+V_{pp\sigma} (\cos 60^\circ) e^{i\vec{k}\cdot\vec{n}_3} + V_{pp\sigma} (\cos 30^\circ) e^{i\vec{k}\cdot\vec{n}_2} - V_{pp\sigma} \cos 60^\circ (\cos 30^\circ) e^{i\vec{k}\cdot\vec{n}_1}$ $+V_{pp\pi} \cos 60^\circ \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_3}$ $-V_{pp\pi} \cos 60^\circ \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_2}$
$\langle p_y,1 $	HERMITIAN CONJUGATES.		E_p	$+V_{sp\sigma} \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_3} - V_{sp\sigma} \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_2}$	$+V_{pp\sigma} \cos 60^\circ \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_1} - V_{pp\sigma} \cos 60^\circ \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_2}$ $+V_{pp\pi} \cos 30^\circ \cos 60^\circ e^{i\vec{k}\cdot\vec{n}_3}$ $-V_{pp\pi} \cos 30^\circ \cos 60^\circ e^{i\vec{k}\cdot\vec{n}_2}$	$-V_{pp\pi} e^{i\vec{k}\cdot\vec{n}_1} - V_{pp\pi} \cos 60^\circ e^{i\vec{k}\cdot\vec{n}_3} - V_{pp\pi} \cos 60^\circ e^{i\vec{k}\cdot\vec{n}_2}$ $+V_{pp\sigma} (\cos 30^\circ) e^{i\vec{k}\cdot\vec{n}_2} + \cos 30^\circ e^{i\vec{k}\cdot\vec{n}_3}$
$\langle s,2 $	/	e.g. $H_{42} = H_{24}^*$	/	E_s	E_p	E_p
$\langle p_x,2 $	/	/	/	/	E_p	E_p
$\langle p_y,2 $	/	/	/	/	/	E_p

Problem 5.4 (Energy bands for a hexagonal lattice in 2D)



a) The K-point $(0, 4\pi/3a)$ is strongly coupled to two other equivalent K-points in the FBZ, as shown in the picture above (all three K-points have been labeled with subscripts 1,2, and 3 for convenience). The equivalent three K-points are related to each other by a reciprocal lattice vector, and the free-electron states with these wavevectors have the same energy. The wavevectors of the other two K-points (2 and 3) are $(2\pi/\sqrt{3}a, -2\pi/3a)$ and $(-2\pi/\sqrt{3}a, -2\pi/3a)$.

$$b) |\psi_{K_1}\rangle = c_1 |\phi_{K_1}\rangle + c_2 |\phi_{K_2}\rangle + c_3 |\phi_{K_3}\rangle$$

After plugging into the solution into the Schrodinger equation and multiplying by the bras corresponding to the three plane wave states one by one we obtain three equations which in the matrix form are:

$$\begin{bmatrix} e(K) & V_1/2 & V_1/2 \\ V_1/2 & e(K) & V_1/2 \\ V_1/2 & V_1/2 & e(K) \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = E(\vec{K}_1) \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix}$$

Where $e(K)$ equals the free electron energy at (all the equivalent) K-points. Also note that the vector $(\vec{b}_1 + \vec{b}_2)$ points from K_3 to K_2 and so in the expression for the potential the term with the wavevector equal to this vector couples points K_3 and K_2 .

The energies of the 3 bands at the K_1 -point are found to be:

$$E_1(K_1) = E_2(K_1) = e(K) - V_1/2$$

$$E_3(K_1) = e(K) + V_1$$

Note that two bands are still degenerate and one has a higher energy.

The corresponding wavefunctions are:

$$E_1(K_1) \Rightarrow |\psi_{K_1}\rangle = \frac{|\phi_{K_1}\rangle - |\phi_{K_2}\rangle}{\sqrt{2}}$$

$$E_2(K_1) \Rightarrow |\psi_{K_1}\rangle = \frac{|\phi_{K_1}\rangle - |\phi_{K_3}\rangle}{\sqrt{2}}$$

$$E_3(K_1) \Rightarrow |\psi_{K_1}\rangle = \frac{|\phi_{K_1}\rangle + |\phi_{K_2}\rangle + |\phi_{K_3}\rangle}{\sqrt{3}}$$

c) The M_1 -point ($2\pi/\sqrt{3} \mathbf{a}, 0$) is coupled to the equivalent M_2 -point ($-2\pi/\sqrt{3} \mathbf{a}, 0$). The subscripts 1 and 2 have been added for clarity.

$$d) |\psi_{M_1}\rangle = c_1 |\phi_{M_1}\rangle + c_2 |\phi_{M_2}\rangle$$

After plugging into the solution into the Schrodinger equation and multiplying by the bras corresponding to the two plane wave states one by one we obtain two equations which in the matrix form are:

$$\begin{bmatrix} e(M) & V_1/2 \\ V_1/2 & e(M) \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E(M_1) \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

The energies of the 2 bands at the M_1 -point are found to be:

$$E_1(M_1) = e(M) - V_1/2$$

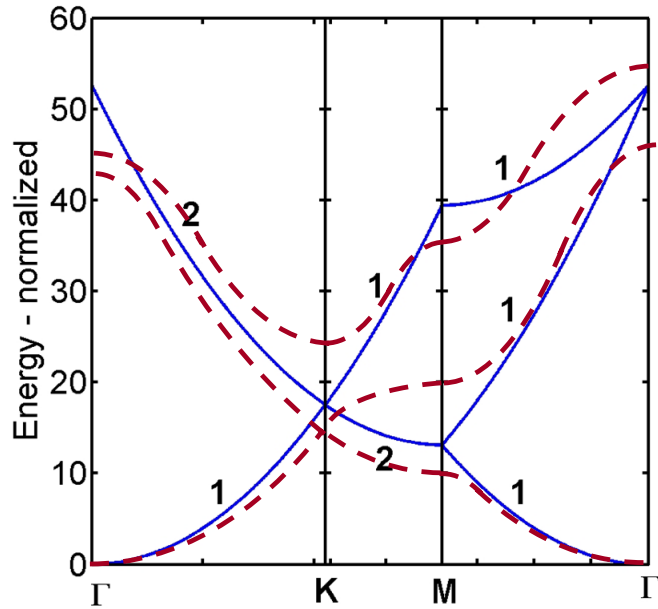
$$E_2(M_1) = e(M) + V_1/2$$

The corresponding wavefunctions are:

$$E_1(M_1) \Rightarrow |\psi_{M_1}\rangle = \frac{|\phi_{M_1}\rangle - |\phi_{M_2}\rangle}{\sqrt{2}}$$

$$E_2(M_1) \Rightarrow |\psi_{M_1}\rangle = \frac{|\phi_{M_1}\rangle + |\phi_{M_2}\rangle}{\sqrt{2}}$$

e) Notice the points where the bandgaps open up (M-point) and where they don't (K-point) between the first and the second energy bands. Note also that the exact shape of the bands comes from my imagination – so don't pay too much to it except to note where the bandgaps open up and where they don't.



f) and g) and h) Solution is obvious if you take the expression for the potential and write the vectors \vec{b}_1, \vec{b}_2 in terms of their x- and y-components.

$$i) |\psi_{K_1}\rangle = c_1 |\phi_{K_1}\rangle + c_2 |\phi_{K_2}\rangle + c_3 |\phi_{K_3}\rangle$$

After plugging into the solution into the Schrodinger equation and multiplying by the bras corresponding to the three plane wave states one by one we obtain three equations which in the matrix form are:

$$\begin{bmatrix} e(K) & V_1/2 & V_1/2 \\ V_1/2 & e(K) & i V_1/2 \\ V_1/2 & -i V_1/2 & e(K) \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = E(\vec{K}_1) \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix}$$

Notice how the entries (2,3) and (3,2) of the matrix have changed. The energies of the 3 bands at the K_1 -point are found to be:

$$E_1(K_1) = e(K) - \sqrt{3} V_1/2$$

$$E_2(K_1) = e(K)$$

$$E_3(K_1) = e(K) + \sqrt{3} V_1/2$$

Note that all bands are now non-degenerate at the K-point.

The corresponding wavefunctions are:

$$E_1(K_1) \Rightarrow |\psi_{K_1}\rangle = \frac{-e^{-i\pi/6}|\phi_{K_1}\rangle + e^{-i\pi/3}|\phi_{K_2}\rangle + |\phi_{K_3}\rangle}{\sqrt{3}}$$

$$E_2(K_1) \Rightarrow |\psi_{K_1}\rangle = \frac{|\phi_{K_1}\rangle + |\phi_{K_2}\rangle - |\phi_{K_3}\rangle}{\sqrt{3}}$$

$$E_3(K_1) \Rightarrow |\psi_{K_1}\rangle = \frac{e^{i\pi/6}|\phi_{K_1}\rangle + e^{i\pi/3}|\phi_{K_2}\rangle + |\phi_{K_3}\rangle}{\sqrt{3}}$$