Problem Set 9

a) For a free electron $E(k) = \frac{k^2}{2m}$

$1^{st}$ BZ for a simple square lattice is:

\[
\begin{array}{c}
\vec{k}_x \\
\vec{k}_y
\end{array}
\]

The midpoints of the side faces are:

\[
\vec{k} = \pm \frac{\pi}{a} \hat{x}
\]

\[
\vec{k} = \pm \frac{\pi}{a} \hat{y}
\]

\[
E_{\text{midpoint}}(k) = \frac{k^2}{2m} \left(\frac{\pi}{a}\right)^2
\]

$E_{\text{corners}}$ are at $\vec{k} = \pm \frac{\pi}{a} \hat{x} \pm \frac{\pi}{a} \hat{y}$

\[
|\vec{k}| = \sqrt{2} \frac{\pi}{a}
\]

\[
E_{\text{corner}} = \frac{k^2}{2m} \left(\frac{\sqrt{2} \pi}{a}\right)^2 = 2 E_{\text{midpoint}}
\]

b) for a single cubic lattice

corners: $\vec{k} = \pm \frac{\pi}{a} \hat{x} \pm \frac{\pi}{a} \hat{y} = \frac{\pi}{a} \hat{z} \Rightarrow |\vec{k}| = \frac{\pi}{a}$

sides: $\vec{k} = \pm \frac{\pi}{a} \hat{x}$, etc $\Rightarrow |\vec{k}| = \frac{\pi}{a}$

Since $E(k) \sim k^2$, the energy at the corners will be 3 times larger than at midpoints.
c) A divalent crystal (2e⁻/atom) can be metal because of overlap of highest filled band and the next highest (partially filled) band.

In 3D the \( \tilde{G} = 0 \) and \( \tilde{G} = \frac{\pi}{a} \times \) overlap considerably in free e⁻ case since the highest energy in the \( \tilde{G} = 0 \) band is 3 times the lowest lying energy \( G = \frac{\pi}{a} \times \) energy.

i.e. the crystal potential has to be very strong to open an energy gap large enough to prevent overlapping and create an insulator.
\[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) = E \psi(x) \quad \text{Schrödinger's eqn} \]

\[ \Rightarrow \quad -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi = E \psi \quad \text{wells} \quad \text{let } \psi_1 = e^{\pm iax} \quad \text{wells} \]

\[ \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U_0 \right) \psi = E \psi \quad \text{barriers} \quad \psi_2 = e^{\pm \beta x} \quad \text{barriers} \]

\[ \Rightarrow \quad \frac{\hbar^2 \alpha^2}{2m} = E \psi \quad \text{wells} \quad \Rightarrow \quad \alpha = \sqrt{\frac{2mE}{\hbar^2}} \]

\[ \left( -\frac{\hbar^2 \beta^2}{2m} + U_0 \right) \psi = E \psi \quad \text{barriers} \quad \Rightarrow \quad \beta = \sqrt{\frac{2m}{\hbar^2} (U_0 - E)} \]

\[ \Rightarrow \quad \psi_1 = Ae^{i\alpha x} + Be^{-i\alpha x} \quad \text{wells} \]

\[ \psi_2 = Ce^{\beta x} + De^{-\beta x} \quad \text{barriers} \]

b) Bloch's theorem (periodicity \(a+b\))

\[ \psi_k (x+a+b) = e^{i\kappa(a+b)} \psi_k (x) \]

at \( x = -b \)

\[ \psi_k (a) = e^{i\kappa(a+b)} \psi_k (-b) \]
\[ \gamma \text{ and } \frac{\partial \gamma}{\partial x} \text{ are continuous at } 0=x \]

(b/c potential is finite ...)

a. \( \gamma_1(0) = \gamma_2(0) \Rightarrow A + B = C + D \)

b. \( \frac{\partial \gamma_1}{\partial x} \bigg|_0 = \frac{\partial \gamma_2}{\partial x} \bigg|_0 \Rightarrow i \langle A - B \rangle = \beta \langle C - D \rangle \)

c. \( \gamma_1(a) = e^{ik(atb)} \gamma_2(-b) \Rightarrow A e^{ia} + B e^{-ia} = e^{ik(atb)} \left[ C e^{-\beta b} + D e^{\beta b} \right] \)

d. \( \frac{\partial \gamma_2}{\partial x} = \frac{\partial \gamma_1}{\partial x} \cdot e^{ik(atb)} \Rightarrow ix \left[ A e^{ia} - B e^{-ia} \right] = e^{ik(atb)} \left[ C e^{-\beta b} - D e^{\beta b} \right] \)

\[
\begin{bmatrix}
1 & 1 & -1 & -1
\end{bmatrix}
\begin{bmatrix}
A \\
B \\
C \\
D
\end{bmatrix} = 0
\]
\[ \frac{P}{\alpha a} \sin \alpha a + \cos \alpha a = \cos k a \quad (\star) \]

\[ P = \frac{ma}{k} U_0 b \quad \alpha = \sqrt{\frac{2mE^2}{k^2}} \]

At \( k = 0 \), (\star) becomes

\[ \frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = 1 \quad (\star \star) \]

If \( P < 1 \), (\star \star) has only solutions for \( \alpha a \ll 1 \)

I can then expand \( \sin + \cos \)

\[ \frac{\sin x}{x} = 1 - \frac{x^2}{6} + \ldots \quad \cos x = 1 - \frac{x^2}{2} + \ldots \]

\[ P \left( 1 - \frac{(\alpha a)^2}{6} \right) + 1 - \frac{\alpha a^2}{2} = x^2 \]

\[ P = \frac{(\alpha a)^2}{2} + O(\alpha a)^4 \rightarrow \alpha^2 = \frac{2P}{a^2} \]

\[ E(k=0) = \frac{k^2 P}{ma^2} = \frac{U_0 b}{\alpha} \]

d) At \( k = \frac{\pi}{a} \), (\star) becomes:

\[ \frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = -1 \]

For \( P < 1 \) this equation has solution

\[ \alpha a = \pi + \delta \quad \text{with} \quad \delta \ll 1 \]

\[ \cos (\pi + \delta) = -\cos \delta \approx -1 + \frac{\delta^2}{2} + \ldots \]

\[ \frac{8 \sin (\pi + \delta)}{\pi + \delta} = -\frac{\sin \delta}{\delta + \pi} = -\frac{1}{\pi} \left( 1 - \frac{\delta}{\pi} + O(\delta^2) \right) \]

\[ (\delta - \frac{\delta^3}{3\pi} + \ldots) \]
\[ \cos \theta = - \frac{5}{\pi} \left( 1 - \frac{5}{\pi} \right) + O(\delta^2) \]

\[ - P \left[ \frac{5}{\pi} \left( 1 - \frac{5}{\pi} \right) \right] - 1 + \frac{\delta^2}{2} = -1 \]

2 solutions: \( \delta = 0 \)
\[ \delta = \frac{2P}{\pi} \]

The two values of the energy at \( k = \frac{\pi}{a} \) are
\[ \delta = 0 \Rightarrow E_1 \left( \frac{\pi}{a} \right) = \frac{k^2 \pi^2}{2ma^2} \]
\[ \delta = \frac{2P}{\pi} \Rightarrow E_2 \left( \frac{\pi}{a} \right) = \frac{k^2}{2ma^2} \left( \pi + \delta \right)^2 \]
\[ = \frac{k^2 \pi^2}{2ma^2} + \frac{k^2}{ma^2} \frac{2P}{\pi} \]

\[ \Rightarrow \text{gap is} \ E_2 - E_1 = \frac{k^2}{ma^2} \frac{2P}{\pi} = 2U_0 \frac{k}{a} \checkmark \]

3. Square Lattice \( U(x, y) = -4U \cos \left( \frac{2\pi x}{a} \right) \cos \left( \frac{2\pi y}{a} \right) \)

Let \( U(x, y) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i \mathbf{G} \cdot \mathbf{r}} \)

The potential energy contains Fourier components at the following reciprocal lattice vectors:

\[ \mathbf{G} = \left( \frac{2\pi}{a}, \frac{2\pi}{a} \right) \]
\[ \mathbf{G}' = \left( \frac{2\pi}{a}, -\frac{2\pi}{a} \right) \]
\[ \mathbf{G}'' = \left( -\frac{2\pi}{a}, \frac{2\pi}{a} \right) \]
\[ \mathbf{G}''' = \left( -\frac{2\pi}{a}, -\frac{2\pi}{a} \right) \]
4a cont'd:

with Fourier components $U \tilde{a} = -U$

(to see this, note for example that

$$U_{x1} = \int_0^{1/a} dy \int_0^{1/a} U(x,y) \cos (G_x x) \cos (G_y y)$$

and $\int_0^a \cos (G_x x) \cos (k x) = \frac{1}{2} \delta(G_x - k)$

at the zone corner $\tilde{k}_1 = \left( \frac{\pi}{a}, \frac{\pi}{a} \right) = \frac{1}{2} \bar{G} (11)$

for $\tilde{k}$ near the zone corner, to lowest order in $U$:

$$\left( \lambda_{k_1} - E \right) C(\tilde{k}_1) + \frac{1}{G_x} U_{x1} C(k_1 - \tilde{G}) = 0$$

so the only things that $\tilde{k} = \left( \frac{\pi}{a}, \frac{\pi}{a} \right)$ are connected to are

$\tilde{k} + 11, \tilde{k} + \bar{11}, \tilde{k} + 1\bar{1}, \tilde{k} + 1\bar{1}$ (see figure)

only this one is still in 1st BZ. call this one $\tilde{k}_2$.

So $\left( \lambda_{\tilde{k}_1} - E \right) C(\tilde{k}_1) - U C(\tilde{k}_2) = 0$ \quad $\lambda_{k_1} = \frac{h^2}{2m} \cdot 2 \left( \frac{\pi}{a} \right)^2$

and similarly for $\tilde{k}_2$ (only connected to $\tilde{k}_1$ via $G_{11}$)

$$\left( \lambda_{\tilde{k}_2} - E \right) C(\tilde{k}_2) - U C(\tilde{k}_1) = 0$$ \quad $\lambda_{k_2} = \frac{k^2}{2m} \cdot 2 \left( \frac{\pi}{a} \right)^2$

Solving these equations we have

$$(\lambda - E)^2 - U^2 = 0 \quad \Rightarrow \quad E = \lambda \pm U$$

$\Rightarrow$ gap is $E_g = E_+ - E_- = 2U$. \checkmark
Extra credit

\( E(\mathbf{k}) \) for free electrons in reduced zone.

(Recall the "reduced zone" is where all the bands are drawn in the 1st BZ.) So, any wave vector \( \mathbf{\bar{q}} \) can be written as \( \mathbf{\bar{q}} = \mathbf{\bar{k}} + \mathbf{\bar{G}}_1 \) where \( \mathbf{\bar{k}} \) is \( \mathbf{\bar{k}} \) in 1st BZ and \( \mathbf{\bar{G}}_1 \) is a reciprocal lattice vector.

\[
E(\mathbf{k}) = \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G}_1)^2
\]

Recall that for an fcc lattice we can write the reciprocal lattice as: \( \mathbf{\bar{G}}_1 = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \):

\[
\mathbf{\bar{G}}_1 = \frac{2\pi}{a} \left[ (h-k+l)\hat{x} + (h+k-l)\hat{y} + (-h+k+l)\hat{z} \right]
\]

fcc (real space) \hspace{4cm} bcc (reciprocal)

\[
\mathbf{b}_1 = \frac{2\pi}{a}(\hat{x} + \hat{y} - \hat{z})
\]
\[
\mathbf{b}_2 = \frac{2\pi}{a}(\hat{y} + \hat{z} - \hat{x})
\]
\[
\mathbf{b}_3 = \frac{2\pi}{a}(\hat{z} + \hat{x} - \hat{y})
\]
and \( \mathbf{k} \) is in 1st BZ somewhere; i.e.,

\[
\hat{\mathbf{k}} = \frac{2\pi}{a} (\hat{x} + \hat{y} + \hat{z}) \text{ with } -1 \leq u \leq 1
\]

So energy is

\[
E(k') = \frac{k'}{2m} \left( \frac{\pi^2}{a^2} \right) \left\{ (u + 2(h - k + l))^2 + (u + 2(h + k - l))^2 + (u + 2(-h + k + l))^2 \right\}^{\frac{1}{2}}
\]

So the lowest energy at zone boundary \((u = \pm 1)\) is at \( \hat{\mathbf{u}} = 0 \) and

\[
E_0 = \frac{\hbar^2 \pi^2}{2ma^2} \cdot 3
\]

Now, we want to plot in the \([1, 1, 1]\) direction the energies of all the bands s.t. the energy at the zone boundary is \( \leq 6E_0 = \frac{\hbar^2 \pi^2}{2ma^2} \cdot 18 \)

So, let's look at various \( h, k, l \) values:

Let \( \varepsilon(k') = \frac{2ma^2}{\pi^2 m^2} E(k') \), and we'll parameterize curves by \( u \):

\[
\Rightarrow 1) \ n = k = l = 0 \Rightarrow E_{000} (u) = 3u^2
\]
2) \( h = 1, \ k = l = 0 \)
\[ \varepsilon_{100} (u) = 2(u+2)^2 + (u-2)^2 \]
\[ \varepsilon_{100} (0) = 12 \]
\[ \varepsilon_{100} (1) = 19 > 18 \ (\text{too high?}) \]

3) \( h = -1, \ k = l = 0 \)
\[ \varepsilon_{100} (u) = 2(u-2)^2 + (u+2)^2 \]
\[ \text{also} \ (010), (001) \]
\[ \varepsilon_{100} (0) = 12 \quad \varepsilon_{100} (1) = 11 \]
\( \) (good, on plot)

4) \( h = k = l = 1 \)
\[ \varepsilon_{110} (u) = 2u^2 + (u+4)^2 \]
\[ \varepsilon_{110} (1) = 27 > 18 \ (\text{too high!}) \]

5) \( h = k = -1, \ l = 0 \)
\[ \varepsilon_{110} (u) = 2u^2 + (u-4)^2 \]
\[ \varepsilon_{110} (0) = 16 \quad \varepsilon_{110} (1) = 11 \]
\( \) (good, on plot)

6) \( h = k = 1, \ l = 1 \)
\[ \varepsilon_{111} (u) = 3(u+2)^2 \]
\[ \varepsilon_{111} (0) = 27 \ (\text{too high!}) \]

7) \( h = k = l = -1 \)
\[ \varepsilon_{111} (u) = 3(u-2)^2 \]
\[ \varepsilon_{111} (0) = 12 \quad \varepsilon_{111} (1) = 3 \]
\( \) (good, on plot.)