First Principle 2017-Fall Homework 1 Solution

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1. The hcp structure is shown as following :

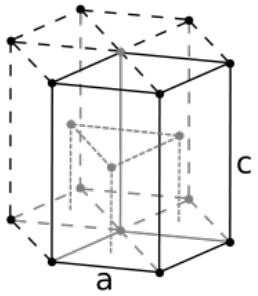

FIG. 1. hcp structure

we can calculate the c/a ratio as :

$$x \equiv \frac{c}{2}$$
$$x = \sqrt{a^2 - (\frac{a}{\sqrt{3}})^2} = a \cdot \sqrt{\frac{2}{3}}$$
$$c/a = 2\sqrt{\frac{2}{3}}_{\#}$$

2. (a) for all $n_i \in$ even with primitive vectors $(2\hat{x}, 2\hat{y}, 2\hat{z})$, the lattice is a simple cubic lattice with side length 2 origin at $(0\hat{x}, 0\hat{y}, 0\hat{z})$

   for all $n_i \in$ odd with primitive vectors $(2\hat{x}, 2\hat{y}, 2\hat{z})$, the lattice is also a simple cubic lattice with side length 2 include point $(0\hat{x}, 0\hat{y}, 0\hat{z})$

   (b) In the case where $\sum_i n_i$ is even, this is a simple cubic lattice with side length $\sqrt{3}$ (which can be thought as a $\sqrt{3}$ scaled + 45^o rotated version of sc.)

3. Let's defined the primitive reciprocal lattice is formed by $\langle G_1, G_2, G_3 \rangle$. Which defined as :

$$G_i \cdot b_j = 2\pi\delta_{ij} \tag{1}$$

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With the known relation:

$$\begin{aligned} b_i &\equiv \frac{2\pi(a_j \times a_k)}{|a_1 \cdot (a_2 \times a_3)|} \\ a_i \cdot b_j &= 2\pi\delta_{ij} \end{aligned} \tag{2}$$

we can see :

$$G_i = a_{i\#} \tag{3}$$

4. The honeycomb lattice is formed by primitive vectors as the same as parallelogram, with basis contain 2-sites. In which the reciprocal vectors also forms parallelogram. Since the Brillouin zone is just the Wigner-Seitz cell in reciprocal space. The Wigner-Seitz cell formed from parallelogram is hexagonal structure.

5. The first Brilluion zone is the Wigner-Seitz cell in k-space. Which we can represent the boundary point (H,N,P) in terms of reciprocal vector $\vec{b_i}$:

$$\vec{k} = \alpha\vec{b_1} + \beta\vec{b_2} + \gamma\vec{b_3} \tag{4}$$

For Brilluion zone in bcc lattice, the reciprocal lattice is fcc structure with reciprocal vectors:

$$\begin{aligned} \vec{b_1} &= \frac{2\pi}{a}(\hat{x} + \hat{z}) \\ \vec{b_2} &= \frac{2\pi}{a}(\hat{y} + \hat{z}) \\ \vec{b_3} &= \frac{2\pi}{a}(\hat{y} + \hat{z}) \end{aligned}$$

The boundary point (H,N,P) thus can be represent in basis of reciprocal vector$\langle\alpha, \beta, \gamma\rangle$:

$$\begin{aligned} H &: \langle -0.5, 0.5, 0.5\rangle \\ N &: \langle 0, 0.5, 0\rangle \\ P &: \langle 0.25, 0.25, 0.25\rangle \end{aligned}$$

For Brilluion zone in fcc lattice, the reciprocal lattice is bcc structure with reciprocal vectors:

$$\begin{aligned} \vec{b_1} &= \frac{2\pi}{a}(\hat{x} - \hat{y} + \hat{z}) \\ \vec{b_2} &= \frac{2\pi}{a}(\hat{x} + \hat{y} - \hat{z}) \\ \vec{b_3} &= \frac{2\pi}{a}(-\hat{x} + \hat{y} + \hat{z}) \end{aligned}$$

The boundary point (X,W,K,U) thus can be represent in basis of reciprocal vector$\langle\alpha,\beta,\gamma\rangle$:

$$X : \langle 0, 0.5, 0.5\rangle$$
$$W : \langle 0.25, 0.75, 0.5\rangle$$
$$K : \langle 0.25, 0.25, 0.25\rangle$$
$$U : \langle 0.375, 0.75, 0.375\rangle$$

6. (a) $GaAs$

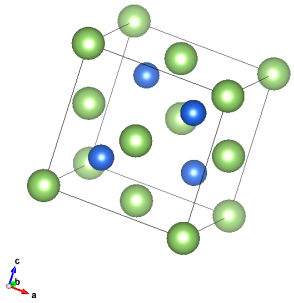

FIG. 2. GaAs zinc-blende structure

POSCAR :

```
GaAs
5.653
1.000000000   0.000000000   0.000000000
0.000000000   1.000000000   0.000000000
0.000000000   0.000000000   1.000000000
Ga     As
4      4
Direct
0.000000000   0.000000000   0.000000000
0.000000000   0.500000000   0.500000000
0.500000000   0.500000000   0.000000000
0.500000000   0.000000000   0.500000000
0.750000000   0.250000000   0.750000000
0.250000000   0.250000000   0.250000000
0.250000000   0.750000000   0.750000000
0.750000000   0.750000000   0.250000000
```

(b) $NaCl$

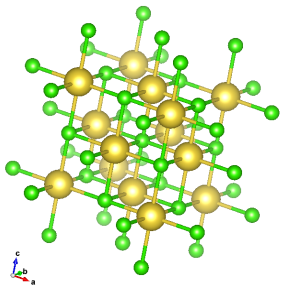

FIG. 3. NaCl fcc structure

POSCAR :

```
NaCl
5.64
1.000000000   0.000000000   0.000000000
0.000000000   1.000000000   0.000000000
0.000000000   0.000000000   1.000000000
Na    Cl
4     4
Direct
0.000000000   0.000000000   0.000000000
0.000000000   0.500000000   0.500000000
0.500000000   0.000000000   0.500000000
0.500000000   0.500000000   0.000000000
0.500000000   0.500000000   0.500000000
0.500000000   0.000000000   0.000000000
0.000000000   0.500000000   0.000000000
0.000000000   0.000000000   0.500000000
```

(c) $SrTiO_3$

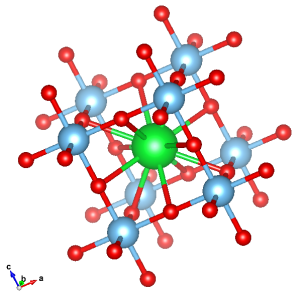

FIG. 4. SrTiO3 sc structure

POSCAR :

```
SrTiO3
3.98805
1.000000000   0.000000000   0.000000000
0.000000000   1.000000000   0.000000000
0.000000000   0.000000000   1.000000000
Sr    Ti    O
1     1     3
Direct
0.500000000   0.500000000   0.500000000
0.000000000   0.000000000   0.000000000
0.500000000   0.000000000   0.000000000
0.000000000   0.500000000   0.000000000
0.000000000   0.000000000   0.500000000
```

(d) $2HMoS_2$

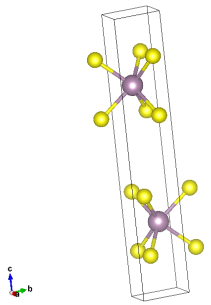

FIG. 5. MoS2-2H

POSCAR :

```
2H–MoS2
3.19
  1.000000000   0.000000000   0.000000000
 −0.500000000   0.866025403   0.000000000
  0.000000000   0.000000000   4.664263323
Mo  S
2  4
Direct
0.3333333333   0.666666667   0.250000000
0.6666666666   0.333333333   0.750000000
0.3333333333   0.666666667   0.855174000
0.3333333333   0.666666667   0.644826000
0.6666666666   0.333333333   0.355174000
0.6666666666   0.333333333   0.144826000
```

7. Considering the general periodic potential with same periodicity of lattice, we can express the potential $U(r)$ as block form :

$$U(r) = \sum_{\alpha} U_{\vec{\alpha}} e^{-i\vec{\alpha}\cdot\vec{r}}$$

And block wave function :

$$\psi_{\vec{k}}(r) = \sum_{\gamma} C_{\vec{k}-\vec{\gamma}} e^{-i(\vec{k}-\vec{\gamma})\cdot\vec{r}}$$

where $\vec{\alpha}$ and $\vec{\gamma}$ is reciprocal lattice point.

By inserting the block wave function into the Schrdinger equation, we have :

$$\left(\frac{\hbar^2}{2m}|\vec{k}-\vec{\gamma}|^2-\epsilon\right)C_{\vec{k}-\vec{\gamma}}+\sum_{\alpha}C_{\vec{k}-\vec{\alpha}}U_{\vec{\alpha}-\vec{\gamma}}=0$$
$$\left(\epsilon^0_{\vec{\gamma}}-\epsilon\right)C_{\vec{k}-\vec{\gamma}}+\sum_{\alpha}C_{\vec{k}-\vec{\alpha}}U_{\vec{\alpha}-\vec{\gamma}}=0$$

Where we express the free electron energy at different reciprocal point $\vec{\gamma}$ as $\epsilon^0_{\gamma}(\vec{k})$.

Thus for the first order approximation with 4 fold degeneracy of free electron energy at $\vec{k}_w$ with given as ϵ^0_1, ϵ^0_2, ϵ^0_3, ϵ^0_4, we have following equation sets:

$$\begin{aligned}
\left(\epsilon-\epsilon^0_1\right)C_{\vec{k}-\vec{\gamma_1}}&=C_{\vec{k}-\vec{\gamma_2}}U_{\vec{\gamma_2}-\vec{\gamma_1}}+C_{\vec{k}-\vec{\gamma_3}}U_{\vec{\gamma_3}-\vec{\gamma_1}}+C_{\vec{k}-\vec{\gamma_4}}U_{\vec{\gamma_4}-\vec{\gamma_1}}\\
\left(\epsilon-\epsilon^0_2\right)C_{\vec{k}-\vec{\gamma_2}}&=C_{\vec{k}-\vec{\gamma_1}}U_{\vec{\gamma_1}-\vec{\gamma_2}}+C_{\vec{k}-\vec{\gamma_3}}U_{\vec{\gamma_3}-\vec{\gamma_2}}+C_{\vec{k}-\vec{\gamma_4}}U_{\vec{\gamma_4}-\vec{\gamma_2}}\\
\left(\epsilon-\epsilon^0_3\right)C_{\vec{k}-\vec{\gamma_3}}&=C_{\vec{k}-\vec{\gamma_1}}U_{\vec{\gamma_1}-\vec{\gamma_3}}+C_{\vec{k}-\vec{\gamma_2}}U_{\vec{\gamma_2}-\vec{\gamma_3}}+C_{\vec{k}-\vec{\gamma_4}}U_{\vec{\gamma_4}-\vec{\gamma_3}}\\
\left(\epsilon-\epsilon^0_4\right)C_{\vec{k}-\vec{\gamma_4}}&=C_{\vec{k}-\vec{\gamma_1}}U_{\vec{\gamma_1}-\vec{\gamma_4}}+C_{\vec{k}-\vec{\gamma_2}}U_{\vec{\gamma_2}-\vec{\gamma_4}}+C_{\vec{k}-\vec{\gamma_3}}U_{\vec{\gamma_3}-\vec{\gamma_4}}
\end{aligned}$$

The above equation can re-align into matrix form :

$$\begin{bmatrix}
\left(\epsilon^0_1-\epsilon\right) & U_{\vec{\gamma_2}-\vec{\gamma_1}} & U_{\vec{\gamma_3}-\vec{\gamma_1}} & U_{\vec{\gamma_4}-\vec{\gamma_1}}\\
U_{\vec{\gamma_1}-\vec{\gamma_2}} & \left(\epsilon^0_2-\epsilon\right) & U_{\vec{\gamma_3}-\vec{\gamma_2}} & U_{\vec{\gamma_4}-\vec{\gamma_2}}\\
U_{\vec{\gamma_1}-\vec{\gamma_3}} & U_{\vec{\gamma_2}-\vec{\gamma_3}} & \left(\epsilon^0_3-\epsilon\right) & U_{\vec{\gamma_4}-\vec{\gamma_3}}\\
U_{\vec{\gamma_1}-\vec{\gamma_4}} & U_{\vec{\gamma_2}-\vec{\gamma_4}} & U_{\vec{\gamma_3}-\vec{\gamma_4}} & \left(\epsilon^0_4-\epsilon\right)
\end{bmatrix}
\begin{bmatrix}
C_{\vec{k}-\vec{\gamma_1}}\\
C_{\vec{k}-\vec{\gamma_2}}\\
C_{\vec{k}-\vec{\gamma_3}}\\
C_{\vec{k}-\vec{\gamma_4}}
\end{bmatrix}=0 \tag{5}$$

which the solution is when the determinant = 0. and for fcc :

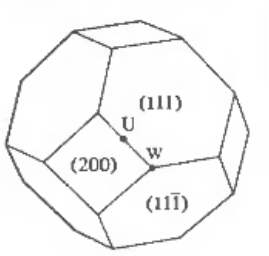

FIG. 6. fcc brilluion zone

Consider also the symmetry within Brillouin zone, we can easily see :

$$\begin{aligned}
U_{\vec{\gamma_4}-\vec{\gamma_1}}&=U_{200}\\
U_{\vec{\gamma_2}-\vec{\gamma_3}}&=U_{002}\\
U_2&=U_{200}=U_{002}
\end{aligned}$$

$$
\begin{aligned}
&U_{\gamma_2-\vec{\gamma_1}} = U_{111} \\
&U_{\gamma_3-\vec{\gamma_1}} = U_{11-1} \\
&U_{\gamma_4-\vec{\gamma_2}} = U_{1-1-1} \\
&U_1 = U_{111} = U_{11-1} = U_{1-1-1}
\end{aligned}
$$

thus the solution is:

$$
\begin{vmatrix}
(\epsilon_1^0 - \epsilon) & U_1 & U_1 & U_2 \\
U_1 & (\epsilon_2^0 - \epsilon) & U_2 & U_1 \\
U_1 & U_2 & (\epsilon_3^0 - \epsilon) & U_1 \\
U_2 & U_1 & U_1 & (\epsilon_4^0 - \epsilon)
\end{vmatrix} = 0 \tag{6}
$$

8. Considering the block wave function $\psi_{n,\vec{k}}(r)$ with band index n, and wave vector$\vec{k}$. The Wannier functions center at lattice position $\vec{R}$ can be written in terms of inverse Fourier transform with constant κ :

$$
\phi_n(\vec{r} - \vec{R}) = \kappa \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}} \psi_{n,\vec{k}}(\vec{r}) \tag{7}
$$

Thus :

$$
\begin{aligned}
&\int \phi_n(\vec{r} - \vec{R}) \phi_{n'}(\vec{r} - \vec{R}') d^D\vec{r} \\
&= \kappa^2 \sum_{\vec{k},\vec{h}} e^{i\vec{k}\cdot\vec{R}} e^{-i\vec{h}\cdot\vec{R}'} \int \psi^*_{n,\vec{k}}(\vec{r}) \psi_{n',\vec{h}}(\vec{r}) d^D\vec{r} \\
&= \kappa^2 \sum_{\vec{k},\vec{h}} e^{i\vec{k}\cdot\vec{R}} e^{-i\vec{h}\cdot\vec{R}'} \delta_{n,n'} \delta_{\vec{k},\vec{h}'} \\
&= \kappa^2 \delta_{n,n'} \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \\
&= \kappa^2 N \delta_{n,n'} \delta_{\vec{R},\vec{R}'} \\
&\propto \delta_{n,n'} \delta_{\vec{R},\vec{R}'} \#
\end{aligned} \tag{8}
$$

The constant κ can be derived by the normalization:

$$
\begin{aligned}
&\int \phi_n(\vec{r} - \vec{R}) \phi_{n'}(\vec{r} - \vec{R}') d^D\vec{r} = \delta_{n,n'} \delta_{\vec{R},\vec{R}'} \\
&\kappa^2 N = 1 \\
&\kappa = \frac{1}{\sqrt{N}} \#
\end{aligned}
$$

9. The free electron energy is related to the wave vector $\vec{k}$ with a general form :

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

For a free end, we can consider a small region with length L in each dimension and impose the periodic boundary condition.

(a) In case of a channel, where the wave function subject to the constrain $\Psi(x, y, z) = 0$ for $|x| > a, |y| > b$,we impose periodic BC in z direction. the possible value of k is constrained as :

$$k_x = \frac{n\pi}{2a}$$
$$k_y = \frac{m\pi}{2b}$$
$$k_z = \frac{l2\pi}{Lz}$$

where n, m and l are integer. To express the density of state, we see that in k to $k + dk$, $D_v(k)$ is:

$$D_v(k)dk = g\frac{1}{8}4\pi k^2/(\frac{\pi^3}{2abL_z})dk$$
$$= \frac{gabL_zk^2}{\pi^2}dk$$

where g is the degeneracy. With the relation:

$$dk = \frac{\sqrt{m}}{\hbar\sqrt{2}}E^{-1/2}dE$$

we have the states $D_v(E)$:

$$D_v(E)dE = \frac{\sqrt{2}gabL_z(m)^{3/2}}{\pi^2\hbar^3}E^{1/2}dE$$

Finally divided by the total volumn $4abL_z$, and insert $g = 2$ we get DOS (per volumn) :

$$D(E)dE = \frac{\sqrt{2}m^{3/2}g}{4\pi^2\hbar^3}E^{1/2}dE$$
$$D(E) = \frac{(2m)^{3/2}}{2\pi^2\hbar^3}E^{1/2}{}_{\#}$$

(b) In case of a slab, where the wave function subject to the constrain $\Psi(x, y, z) = 0$ for $|x| > a$,we

impose periodic BC in y,z direction. The possible value of k is constrained as :

$$k_x = \frac{n\pi}{2a}$$
$$k_y = \frac{2m\pi}{Ly}$$
$$k_z = \frac{2l\pi}{Lz}$$

where n, m, l as integer. To express the density of state, we see that in k to $k + dk$, $D_v(k)$ is:

$$D_v(k)dk = g\frac{1}{8}4\pi k^2/(\frac{2\pi^3}{aL_yL_z})dk$$
$$= g\frac{ak^2L_yL_z}{4\pi^2}dk$$

where g is the degeneracy. With the relation:

$$dk = \frac{\sqrt{m}}{\hbar\sqrt{2}}E^{-1/2}dE$$

we have the states $D_v(E)$:

$$D_v(E)dE = \frac{gaL_zL_ym^{3/2}E^{1/2}}{2\sqrt{2}\hbar^3\pi^2}dE$$

Finally divided by the total volumn $2aL_yL_z$, and insert $g = 2$ we get DOS :

$$D(E)dE = \frac{m^{3/2}g}{4\sqrt{2}\hbar^3\pi^2}E^{1/2}dE$$
$$D(E) = \frac{m^{3/2}}{2\sqrt{2}\hbar^3\pi^2}E^{1/2}{}_{\#}$$