First Principle 2017-Fall Homework 1 Solution

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1. The hcp structure is shown as following :

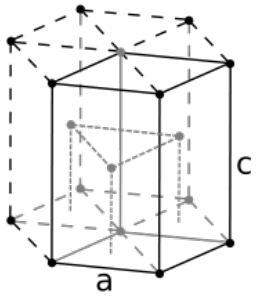

FIG. 1. hcp structure

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 $(1\hat{x}, 1\hat{y}, 1\hat{z})$

   (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 basis vectors $\vec{G_1}, \vec{G_2}, \vec{G_3}$. Which defined as :

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

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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) $GaAs$

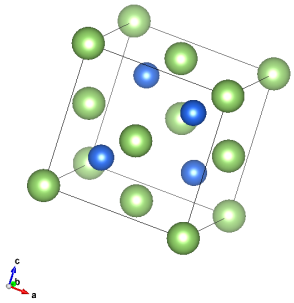

FIG. 2. GaAs zinc-blende structure

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) $NaCl$

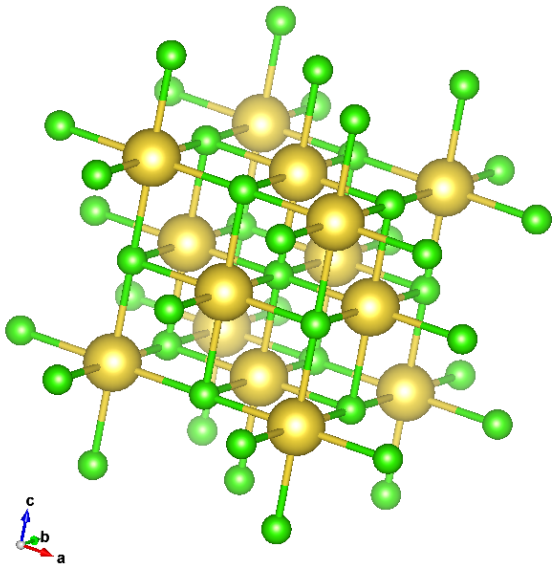

FIG. 3. NaCl fcc structure

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) $SrTiO_3$

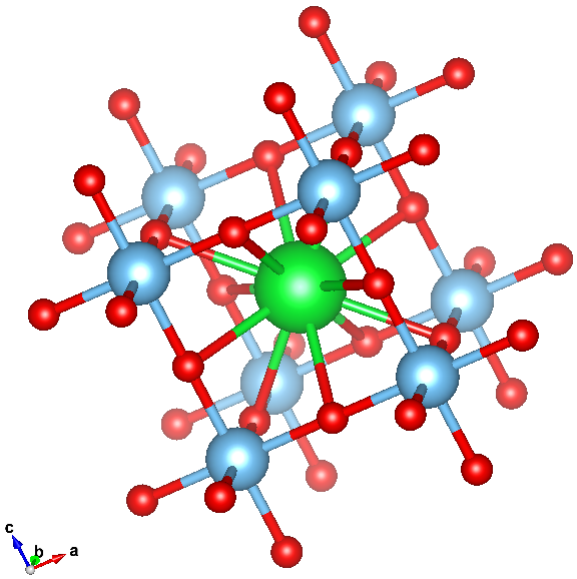

FIG. 4. SrTiO3 sc structure

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) $2HMoS_2$

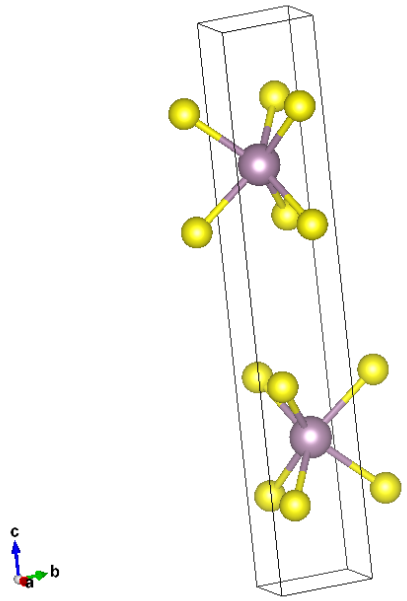

FIG. 5. MoS2-2H

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 $\epsilon^0_{\gamma}(\vec{k})$.

(a) 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:

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

The above equation can be 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 :

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

$$U_{\vec{\gamma_4-\gamma_1}} = U_{200}$$
$$U_{\vec{\gamma_2-\gamma_3}} = U_{002}$$
$$U_2 = U_{200} = U_{002}$$

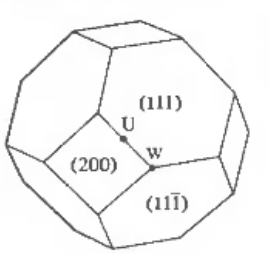

FIG. 6. fcc brilluion zone

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

thus the solution is:

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

Which by row elimination process and reductive algorithm we can derive the root as $\vec{k_w}$

$$(\epsilon_w - \epsilon - U_2)^2 \left[(\epsilon_w - \epsilon + U_2)^2 - (2A)^2 \right] \tag{7}$$
$$= (\epsilon_w - \epsilon - U_2)^2 (\epsilon_w - \epsilon + U_2 + 2U_1)(\epsilon_w - \epsilon + U_2 - 2U_1) \tag{8}$$
$$\epsilon = \epsilon_w - U_2(d.root) \tag{9}$$
$$\epsilon = \epsilon_w + U_2 \pm 2U_{1\#} \tag{10}$$

(b) For point U, which plane((200),(111)) meets. we have solutions :

$$\begin{vmatrix} (\epsilon_1^0 - \epsilon) & U_1 & U_2 \\ U_1 & (\epsilon_2^0 - \epsilon) & U_1 \\ U_2 & U_1 & (\epsilon_4^0 - \epsilon) \end{vmatrix} = 0 \tag{11}$$

Which the solution is :

$$(\epsilon_U - \epsilon - U_2) \left[(\epsilon_U - \epsilon + U_2) - (2U_1)^2 \right] \tag{12}$$
$$= (\epsilon_U - \epsilon - U_2) \left[(\epsilon_U - \epsilon)^2 + U_2(\epsilon_U - \epsilon) - 2{U_1}^2 \right] \tag{13}$$
$$\epsilon = \epsilon_U - U_2 \tag{14}$$
$$\epsilon = \epsilon_U + \frac{U_2 \pm \sqrt{U_2^2 + 8U_1^2}}{2}{}_{\#} \tag{15}$$

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 :

$$\phi_n(\vec{r}-\vec{R}) = \kappa \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}} \psi_{n,\vec{k}}(\vec{r}) \tag{16}$$

Thus :

$$\begin{aligned}
&\int \phi_n(\vec{r}-\vec{R})\phi_{n'}(\vec{r}-\vec{R}')d^D\vec{r} \\
&= \kappa^2 \sum_{\vec{k},\vec{h}} e^{i\vec{k}\cdot\vec{R}} e^{-i\vec{h}\cdot\vec{R}'} \int \psi^*_{n,\vec{k}}(\vec{r})\psi_{n',\vec{h}}(\vec{r})d^D\vec{r} \\
&= \kappa^2 \sum_{\vec{k},\vec{h}} e^{i\vec{k}\cdot\vec{R}} e^{-i\vec{h}\cdot\vec{R}'} \delta_{n,n'}\delta_{\vec{k},\vec{h}'} \\
&= \kappa^2 \delta_{n,n'} \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \\
&= \kappa^2 N \delta_{n,n'}\delta_{\vec{R},\vec{R}'} \\
&\propto \delta_{n,n'}\delta_{\vec{R},\vec{R}'} \#
\end{aligned} \tag{17}$$

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 :

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

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:

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

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) :

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

(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 :

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

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

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

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 :

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

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