Periodic Systems

- Crystalline solid system (crystal)

$$\mathbb{L} = \{ \vec{R} \mid \vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3,\ n_1, n_2, n_3 \in \mathbb{Z} \}$$

$\mathbb{L}$: Bravais lattice

$\vec{a}_\alpha$: basis vector.

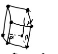
$V(\vec{r})$: periodic : $V(\vec{r}) = V(\vec{r} + \vec{R})$

- unit cell Ω

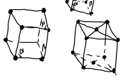
$$\Omega = \{ \vec{r} = c_1\vec{a}_1 + c_2\vec{a}_2 + c_3\vec{a}_3,\ 0 < c_1, c_2, c_3 \in 1 \}$$

- All lattices in $\mathbb{R}^3$ categorized in 7 types of crystal systems and 14 types of Bravais lattices.

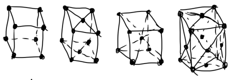
1. Triclinic: $\alpha, \beta, \gamma \neq 90^\circ$



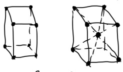
2. Monoclinic: $\alpha \neq 90^\circ$, $\beta, \gamma = 90^\circ$



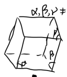
3. Orthorhombic $a \neq b \neq c$



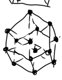
4. Tetragonal $a \neq c$



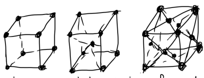
5. Rhombohedral. $\alpha, \beta, \gamma \neq 90^\circ$



6. Hexagonal.



7. Cubic



simple cubic   body-centered cubic   face-centered cubic

- Hamiltonian H in this case,

$$H|\psi\rangle = E|\psi\rangle$$

H has a periodic potential.

$|\psi\rangle$ is not square integrable!

(Therefore is called generalized wavefunction)

- Even if H is periodic, ψ is not necessarily periodic
  - $V=0$, periodic for any arbitrary number.
    The solution, plane wave. are not necessarily periodic for any arbitrary number.

- Bloch decomposition.
  - Translation operator $L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$,

$$T_R: \quad (T_R f)(r) = f(r+R), \quad \vec{R} \in \mathbb{L}, \text{fixed}.$$

  - $[T_R, H] = 0$, They could be diagonalized simultaneously.

$$H\psi = E\psi \Rightarrow \exists C_R,\ T_R\psi = C_R\psi,$$

$$\Rightarrow \psi(\vec{r}+\vec{R}) = C_R\psi(\vec{r}), \text{ for any } \vec{R} \in L$$

and

$$\psi(\vec{r}+\vec{R}+\vec{R}') = C_R\psi(\vec{r}+\vec{R}') = C_{R+R'}\psi(\vec{r}), \quad \forall \vec{R}, \vec{R}' \in \mathbb{L}$$

$$\Rightarrow C_{\vec{R}+\vec{R}'} = C_{\vec{R}}C_{\vec{R}'}, \quad \forall \vec{R}, \vec{R}' \in L.$$

The solution must be

$$C_R = e^{i\vec{R}\cdot\vec{k}} \quad \text{for some } \vec{k} \in \mathbb{R}^3.$$

$$\Rightarrow \quad \psi(\vec{r}+\vec{R}) = \psi(\vec{r})\, e^{i\vec{k}\cdot\vec{R}}.$$

<u>Twisted Boundary Condition</u>

- Let $\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u(\vec{r})$

then $e^{i\vec{k}\cdot(\vec{r}+\vec{R})}u(\vec{r}+\vec{R}) = \psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{R}}e^{i\vec{k}\cdot\vec{r}}u(r)$

$\Rightarrow u(\vec{r}) = u(\vec{r}+\vec{R})$, i.e. u is periodic w.r.t $\vec{R}$.

V, u both periodic. one can solve only in unit cell Ω.

- Reciporal lattice

$$L^* = \{ \vec{G} \mid \vec{G} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3,\ n_1, n_2, n_3 \in \mathbb{Z} \}$$

Here $\quad \vec{a}_\alpha \cdot \vec{b}_\beta = 2\pi\delta_{\alpha\beta}, \quad \alpha, \beta = 1, 2, 3.$

  - The unit cell of reciporal lattice, Ω^* is,

$$\Omega^* = \{ \vec{k} = c_1\vec{b}_1 + c_2\vec{b}_2 + c_3\vec{b}_3,\ -\tfrac{1}{2} < c_1, c_2, c_3 < 1 \}$$

Ω^* is called the First Brillouin zone.

- For a given $\vec{k} \in \mathbb{R}^3$, we want to find:

$$H\psi_{n,k}(\vec{r}) = E_{n,k}\psi_{n,k}(\vec{r}), \quad n = 0, 1, 2, \cdots$$

$$\psi_{n,k}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n,\vec{k}}(\vec{r}), \quad u_{n,\vec{k}} \text{ is periodic}$$

$$\begin{aligned}
&\left(-\tfrac{1}{2}\Delta + V(\vec{r})\right)\left(e^{i\vec{k}\cdot\vec{r}}u_{n,k}(\vec{r})\right) \\
&= -\tfrac{1}{2}\Delta\left(e^{i\vec{k}\cdot\vec{r}}u_{n,k}(\vec{r})\right) + V(r)e^{i\vec{k}\cdot\vec{r}}u_{n,k}(\vec{r}) \\
&= -\tfrac{1}{2}\nabla\cdot\left(i\vec{k}e^{i\vec{k}\cdot\vec{r}}u_{n,k}(\vec{r}) + e^{i\vec{k}\cdot\vec{r}}\nabla_{\vec{r}}u_{n,k}(\vec{r})\right) + V(\vec{r})e^{i\vec{k}\cdot\vec{r}}u_{n,k}(\vec{r}) \\
&= -\tfrac{1}{2}\Big((i\vec{k})^2e^{i\vec{k}\cdot\vec{r}}u_{n,k}(\vec{r}) + ik\,e^{i\vec{k}\cdot\vec{r}}\nabla u_{n,k}(\vec{r}) + i\vec{k}\cdot e^{i\vec{k}\cdot\vec{r}}\nabla u_{n,k}(\vec{r}) \\
&\qquad + e^{i\vec{k}\cdot\vec{r}}\Delta u_{n,k}(\vec{r})\Big) + V(r)e^{i\vec{k}\cdot\vec{r}}u_{n,k} \\
&= \left(-\tfrac{1}{2}(\nabla + i\vec{k})^2 + V(\vec{r})\right)u_{n,k}(\vec{r})e^{i\vec{k}\cdot\vec{r}} = E_{n,k}e^{i\vec{k}\cdot\vec{r}}u_{n,k}(\vec{r})
\end{aligned}$$

$$\Rightarrow \mathcal{H}_k = -\tfrac{1}{2}(\nabla + i\vec{k})^2 + V(\vec{r}), \quad \text{self-adjoint}.$$

$$\mathcal{H}_{\vec{k}}u_{n,\vec{k}}(\vec{r}) = E_{n,\vec{k}}u_{n,\vec{k}}(\vec{r}) \qquad \langle u_{n,\vec{k}}, u_{m,\vec{k}}\rangle = \delta_{n,m}.$$

$$\int_\Omega u^*_{n,k}(r)\,u_{m,k}(r)\,dr = \delta_{nm},$$

$E_{n,\vec{k}}$ is a function of $\vec{k}$. for fixed n?

This is called a Bloch band.

$\{E_{n,k}\}$ is called the band structure.