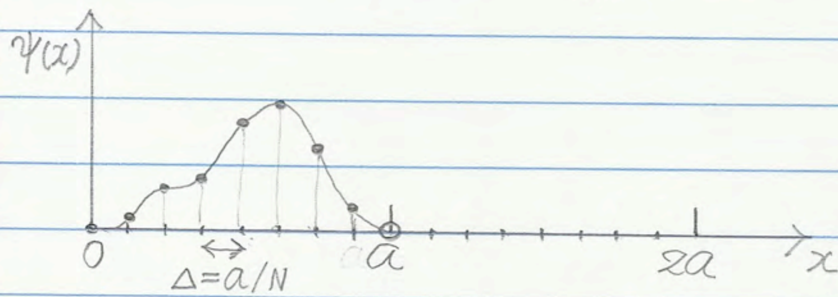
Super-cell Simulation and k-point Sampling

6/3/17

- 1D: 2 unit cells

Consider a plane-wave electronic-structure calculation a crystalline unit cell in the range, $x \in [0, a]$. The wave function $\psi(x)$ is assumed to be periodic,
$\psi(x+a) = \psi(x)$.
Let's discretize $\psi(x)$ on N mesh points, $x_j = j\Delta$ $(j = 0, \ldots, N-1)$ with uniform mesh spacing, $\Delta = a/N$.



Any wave function is then represented by a plane-wave basis,

$$\left\{ \frac{1}{\sqrt{N}} e^{ik_m x_j} \,\middle|\, k_m = 2\pi m/a;\ m = -\frac{N}{2}, \frac{N}{2}-1 \right\} \tag{1}$$

as

$$\psi_j = \psi(x_j) = \frac{1}{\sqrt{N}} \sum_{m=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_m e^{ik_m x_j} = \frac{1}{\sqrt{N}} \sum_{m=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_m e^{i\frac{2\pi m}{a} x_j} \tag{2}$$

where the Fourier component is

$$\tilde{\psi}_m = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \psi_j e^{-ik_m x_j} \tag{3}$$

Now, consider a 2-unit super-cell simulation in the range, $x \in [0, 2a]$, with the same mesh spacing Δ, thus with twice the grid points, $2N$.

Any wave function in the super-cell is represented as

$$\psi_j = \frac{1}{\sqrt{2N}} \sum_{m=-N}^{N-1} \tilde{\psi}_m e^{ik_m x_j} \qquad (4a)$$

$$= \frac{1}{\sqrt{2N}} \sum_{m=-N}^{N} \tilde{\psi}_m e^{i\frac{2\pi m}{2a} x_j} \qquad (4b)$$

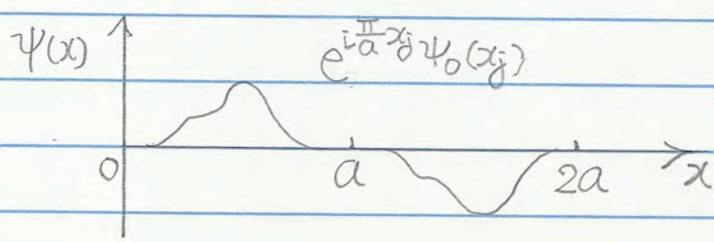
Let's split the sum (4b) into even and odd terms.

$$\psi_j = \underbrace{\frac{1}{\sqrt{2N}} \sum_{l=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_{2l} e^{i\frac{2\pi\cdot\cancel{2}l}{\cancel{2}a} x_j}}_{\text{even}} + \underbrace{\frac{1}{\sqrt{2N}} \sum_{l=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_{2l+1} e^{i\frac{2\pi(2l+1)}{2a} x_j}}_{\text{odd}}$$

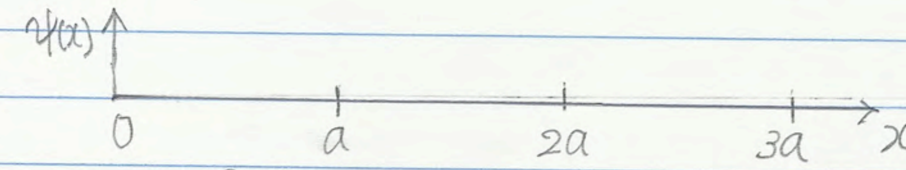
$$= \frac{1}{\sqrt{2N}} \sum_{l=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_{2l} e^{i\frac{2\pi l}{a} x_j} + e^{i\frac{\cancel{2}\pi}{\cancel{2}a} x_j} \frac{1}{\sqrt{2N}} \sum_{l=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_{2l+1} e^{i\frac{2\pi l}{a} x_j} \qquad (5)$$

$$\equiv \underbrace{\psi_e(x_j)}_{\Gamma\text{-point}} + \underbrace{e^{i\frac{\pi}{a} x_j} \psi_o(x_j)}_{k=\frac{\pi}{a}\text{ sample}} \qquad (6)$$

Note that both $\psi_e(x_j)$ and $\psi_o(x_j)$ is periodic with the period of a ($\because$ see Eq. (2)), and the second term is anti periodic w.r.t. $[0, a]$ and $[a, 2a]$ due to the $e^{i(\pi/a)x_j}$ factor. This is Bloch theorem, with 2 k-point samples.



1D: 3 unit cells



$$\psi_j = \frac{1}{\sqrt{3N}} \sum_{m=-\frac{3}{2}N}^{\frac{3}{2}N-1} \tilde{\psi}_m \, e^{i\frac{2\pi m}{3a} x_j}$$

$$= \frac{1}{\sqrt{3N}} \sum_{l=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_{3l} \, e^{\frac{i2\pi(3l)}{3a} x_j} + \frac{1}{\sqrt{3N}} \sum_{l=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_{3l+1} \, e^{\frac{i2\pi(3l+1)}{3a} x_j}$$

$$+ \frac{1}{\sqrt{3N}} \sum_{l=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_{3l+2} \, e^{\frac{i2\pi(3l+2)}{3a} x_j}$$

$$= \frac{1}{\sqrt{3N}} \sum_{l=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_{3l} \, e^{i\frac{2\pi}{a} x_j} + e^{i\frac{2\pi}{3a} x_j} \frac{1}{\sqrt{3N}} \sum_{l=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_{3l+1} \, e^{i\frac{2\pi \cdot 3l}{3a} x_j}$$

$$+ e^{i\frac{4\pi}{3a} x_j} \frac{1}{\sqrt{3N}} \sum_{l=-\frac{N}{2}}^{\frac{N}{2}-1} \tilde{\psi}_{3l+1} \, e^{i\frac{2\pi \cdot 3l}{3a} x_j}$$

$$= \psi_0(x_j) + e^{i\frac{2\pi}{3a} x_j} \psi_1(x_j) + e^{i\frac{4\pi}{3a} x_j} \psi_2(x_j) \qquad (7)$$

This is the Bloch theorem with 3 k-point sampling, $0, \frac{2\pi}{3a}, \frac{4\pi}{3a}$. Note that $k \pm 2\pi/a$ has the same periodicity with k w.r.t. the unit cell, a. We fold back $\frac{4\pi}{3a}$ to $\frac{4\pi}{3a} - \frac{2\pi}{a} = -\frac{2\pi}{3a}$.

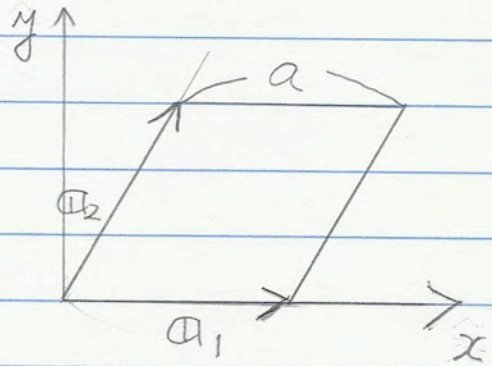
$$\therefore \psi_j = \psi_0(x_j) + e^{i\frac{2\pi}{3a} x_j} \psi_1(x_j) + e^{-i\frac{2\pi}{3a} x_j} \psi_2(x_j) \qquad (8)$$

– 2D hexagonal lattice

cf. https://lampx.tugraz.at/~hadley/ss1/bzones/hexagonal.php

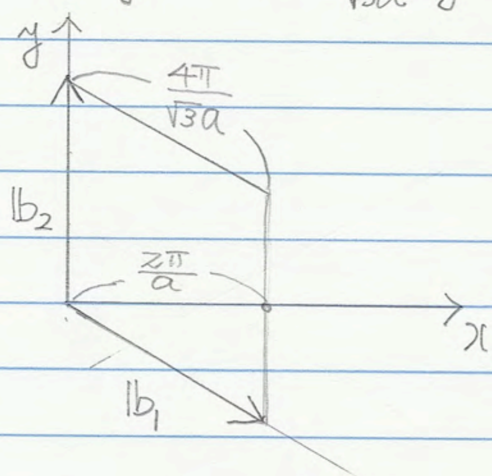
Real-space primitive vectors:

$$\mathbf{a}_1 = a\hat{x}, \quad \mathbf{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}a}{2}\hat{y} \tag{9}$$



Reciprocal-space primitize vectors

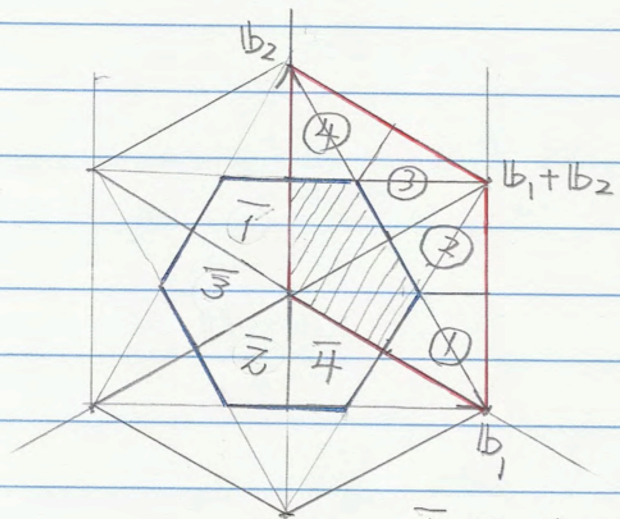
$$\mathbf{b}_1 = \frac{2\pi}{\sqrt{3}a}(\sqrt{3}\,\hat{k}_x - \hat{k}_y), \quad \mathbf{b}_2 = \frac{4\pi}{\sqrt{3}a}\hat{k}_y \tag{10}$$



Note

$$\begin{cases} \mathbf{a}_1 \cdot \mathbf{b}_1 = \cancel{a} \cdot \dfrac{2\pi}{\cancel{a}} = 2\pi & (11) \\ \mathbf{a}_2 \cdot \mathbf{b}_2 = \dfrac{\cancel{\sqrt{3}a}}{\cancel{2}} \cdot \dfrac{\overset{2}{\cancel{4}}\pi}{\cancel{\sqrt{3}a}} = 2\pi & (12) \\ \mathbf{a}_1 \cdot \mathbf{b}_2 = 0 & (13) \\ \mathbf{a}_2 \cdot \mathbf{b}_1 = \dfrac{\cancel{a}}{\cancel{2}} \cdot \dfrac{\cancel{2}\pi\cancel{\sqrt{3}}}{\cancel{\sqrt{3}a}} - \dfrac{\cancel{\sqrt{3}a}}{\cancel{2}} \cdot \dfrac{\cancel{2}\pi}{\cancel{\sqrt{3}a}} = 0 & \end{cases}$$

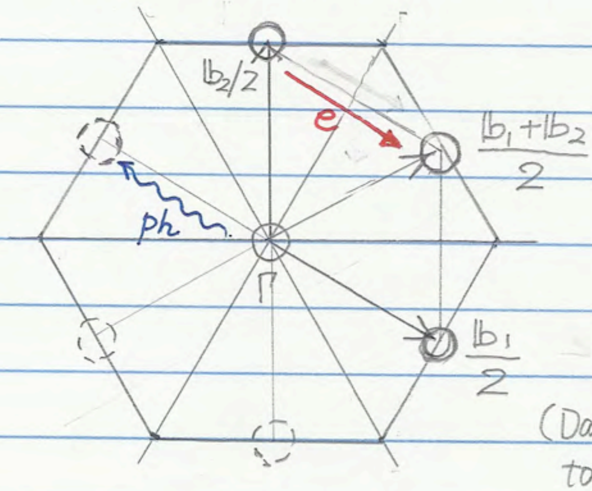
First Brillouin zone ~ fold back outer halves.
Note any shifts $\pm \mathbb{b}_1$, $\pm \mathbb{b}_2$, $\pm(\mathbb{b}_1+\mathbb{b}_2)$ are allowed in Voronoi-like centralization.



$$\bar{1} = 1 - \mathbb{b}_1$$
$$\bar{2} = 2 - (\mathbb{b}_1+\mathbb{b}_2)$$
$$\bar{3} = 3 - (\mathbb{b}_1+\mathbb{b}_2)$$
$$\bar{4} = 4 - \mathbb{b}_2$$

- 2D hexagonal 2×2 super-cell

In analogy with the 1D example, doubling the unit cell in both $\mathbf{a}_1$ & $\mathbf{a}_2$ direction amounts to k-point sampling at 0, $\mathbf{b}_1/2$, $\mathbf{b}_2/2$, $(\mathbf{b}_1+\mathbf{b}_2)/2$.



(Dashed circles are equivalent to solid ones.)

This is thus M-point sampling of the first Brillouin zone. Note that band-structure calculations show that conduction-band minima are $K \lesssim \Sigma = \frac{\Gamma+K}{2} < M$, and valence-band maxima are $K \geq \Gamma \geq M$. Consequently, electrons reside at M, while holes reside at Γ.

$\downarrow$

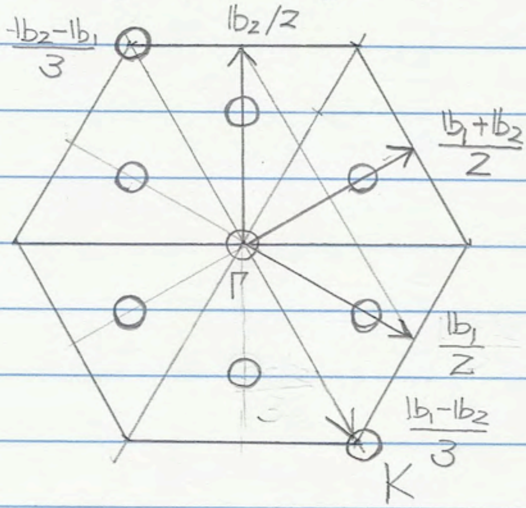
Electrons can scatter by emitting M phonons, if energy-matching bands exist, but holes cannot emit phonons.

- 3D hexagonal 3×3 super-cell

Sampled k-points are

$$\left(0 \vee \frac{\mathbb{b}_1}{3} \vee -\frac{\mathbb{b}_1}{3}\right) \wedge \left(0 \vee \frac{\mathbb{b}_2}{3} \vee -\frac{\mathbb{b}_2}{3}\right)$$

$$= 0, \pm\frac{\mathbb{b}_1}{3}, \pm\frac{\mathbb{b}_2}{3}, \pm\frac{\mathbb{b}_1+\mathbb{b}_2}{3}, \pm\frac{\mathbb{b}_1-\mathbb{b}_2}{3} \qquad (14)$$



Now K points are sampled (what happened the other 4 K points?) along with $\frac{2}{3}$ way from $\Gamma \to M$.

↓

Electrons reside at $\underbrace{K \lesssim \frac{2}{3}M}$, holes $\underbrace{K \gtrsim \Gamma}$.

$K \to$ (missing) K : K phonon $K \to \Gamma$: K-phonon

$\frac{2}{3}M \to \frac{2}{3}M$: K-phonon

$\frac{2}{3}M, \frac{4M}{3}$ phonon

From: **Aiichiro Nakano** anakano@usc.edu
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Dear Lindsay,

Since each of the 6 K valleys in the first Brillouin zone is shared by 3 neighboring zones, there are a total of 6/3 = 2 K valleys, which we already have. Also, the other 4 are equivalent to the +-(b1-b2)/3 valleys we have (see the arrows in the attached image). After all, a 3x3 supercell simulation contains full K valleys.

Let's start finalizing your MoSe2 paper. Please share you charge-density images once you make them. When you plot them in the reciprocal space, you might fold them into the first Brillouin zone.

Best wishes,
Aiichiro