Teori Kuantum untuk Material
Bagian #04

- Review Metode LCAO
- Metode Ikatan Terkuat (*tight-binding*)

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Aproksimasi Struktur Elektronik Molekul

Kombinasi linear orbital atom: $\Psi(x) = \sum_{i=1}^{N} C_i \varphi(x - \mathbf{R}_i)$

$\varphi(x - \mathbf{R}_i)$: Orbital atom pada $\mathbf{R} = \mathbf{R}_i$

Perhitungan energi:

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{i,j} C_i^* C_j H_{ij}}{\sum_{i,j} C_i^* C_j S_{ij}}$$

$S_{ij} = \langle \varphi_i | \varphi_j \rangle : \mathbf{S}$ (*Overlap matrix*)

$H_{ij} = \langle \varphi_i | H | \varphi_j \rangle : \mathbf{H}$ (*Hamiltonian matrix*)

$$\sum_j C_j H_{ij} - E \sum_j C_j S_{ij} = 0, (i = 1, \cdots, N)$$

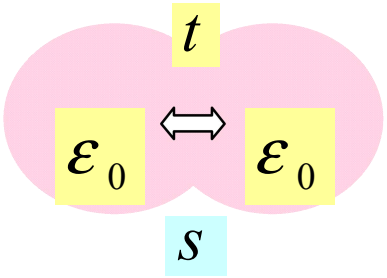
Overlap matrix $\mathbf{S} = \{S_{ij}\}$, $\mathbf{C} =^{\mathrm{t}} \{C_j\}$

$(\mathbf{H} - E\mathbf{S})\mathbf{C} = 0$ Hamiltonian matrix $\mathbf{H} = \{H_{ij}\}$

$$\mathbf{C} \neq 0 \Leftrightarrow \det(\mathbf{H} - E\mathbf{S}) = 0$$

Secular equation

Hasil u/ molekul hidrogen

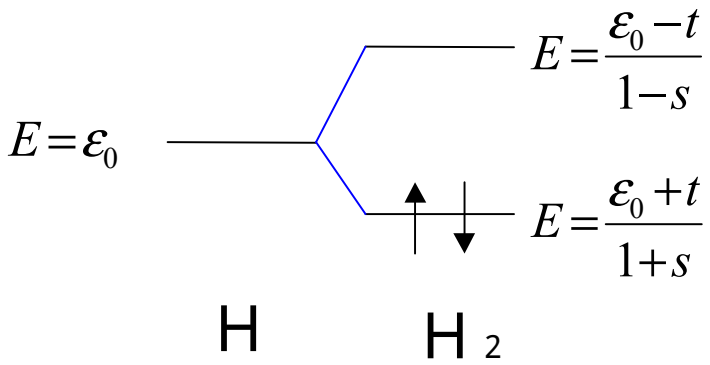


$$\det(H-ES)=\begin{vmatrix}\varepsilon_0-E & t-sE\\ t-sE & \varepsilon_0-E\end{vmatrix}=0$$

$$t<0,\ s>0$$

$$\Psi(x)=C_1\varphi_1+C_2\varphi_2$$

Energi: $E=\dfrac{\varepsilon_0\pm t}{1\pm s}$



Vektor eigen:

$$\begin{pmatrix}\varepsilon_0-E & t-sE\\ t-sE & \varepsilon_0-E\end{pmatrix}\begin{pmatrix}C_1\\ C_2\end{pmatrix}=0$$

Masukkan nilai setiap energi ke persamaan matriks

$$E=\frac{\varepsilon_0+t}{1+s}\ \Leftrightarrow\ C_1:C_2=1:1$$

$$E=\frac{\varepsilon_0-t}{1-s}\ \Leftrightarrow\ C_1:C_2=1:-1$$

Normalisasi

$$|\psi|^2=1\Leftrightarrow|C_1|^2+2|C_1||C_2|s+|C_2|^2=1$$

$$\begin{pmatrix}C_1\\ C_2\end{pmatrix}=\frac{1}{\sqrt{2(1+s)}}\begin{pmatrix}1\\ 1\end{pmatrix},\ \frac{1}{\sqrt{2(1-s)}}\begin{pmatrix}1\\ -1\end{pmatrix}$$

Bagaimana dengan molekul 3 atom?

Contoh: Li_3 (basis 3 elektron 2s)

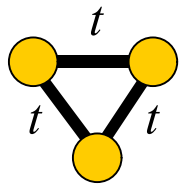
Aproksimasi $t < 0$ dan $s = 0$ **S** = **I** (matriks identitas)

- Rantai linear

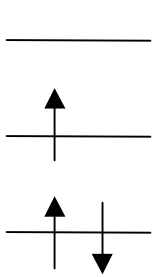
$$H = \begin{pmatrix} 0 & t & 0 \\ t & 0 & t \\ 0 & t & 0 \end{pmatrix}$$

- Segitiga

$$H = \begin{pmatrix} 0 & t & t \\ t & 0 & t \\ t & t & 0 \end{pmatrix}$$

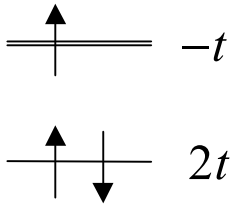


$E = 0, \pm\sqrt{2}\,t$ $\Leftarrow \det(H - EI) = 0 \Rightarrow$ $E = 2t, -t, -t$



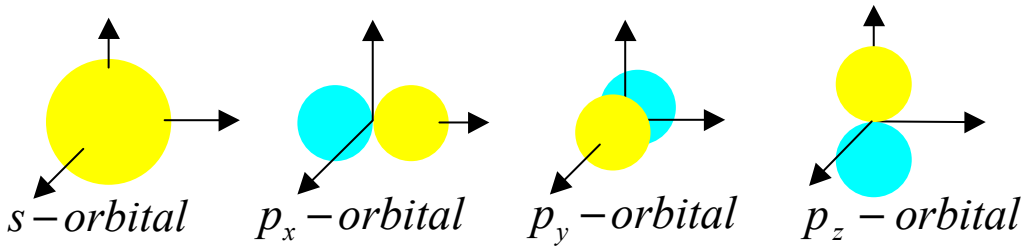
Manakah struktur yang lebih stabil?

Cari energi total yang lebih rendah!



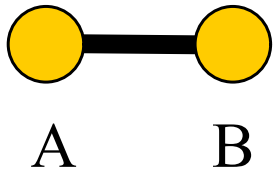
Lebih banyak orbital atom?

$$C: 1s^2, 2s^2, 2p^2$$



Contoh: C_2 Setiap atom menyumbang basis: 2 elektron 2s dan 2 elektron 2p

Total orbital basis = 8



Matriks 8x8 yang dapat dijadikan blok 2x2

$$H = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$

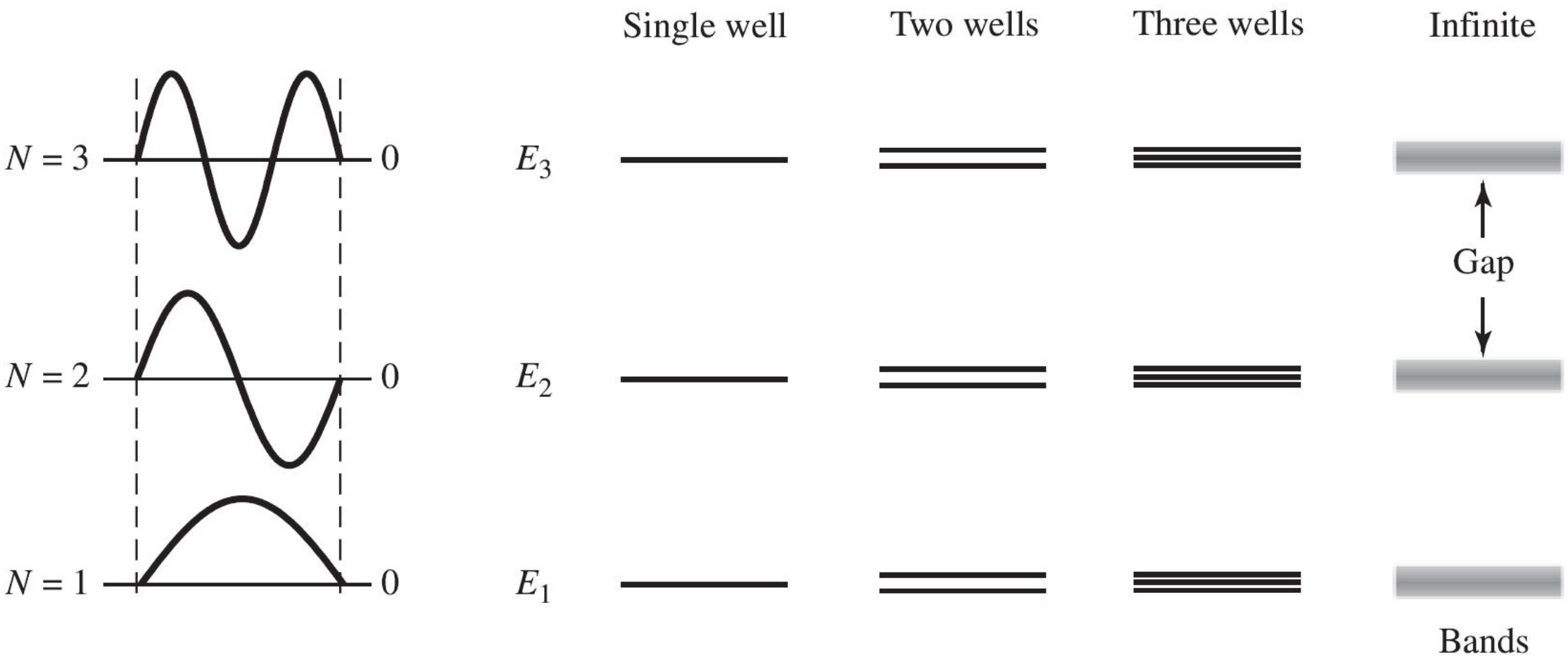
$$H_{AA} = H_{BB} = \begin{array}{c} \begin{matrix} s & p_x & p_y & p_z \end{matrix} \\ \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \varepsilon & 0 & 0 \\ 0 & 0 & \varepsilon & 0 \\ 0 & 0 & 0 & \varepsilon \end{pmatrix} \end{array} \begin{matrix} s \\ p_x \\ p_y \\ p_z \end{matrix}$$

$$H_{AB} = {}^tH_{BA} = \begin{array}{c} \begin{matrix} s & p_x & p_y & p_z \end{matrix} \\ \begin{pmatrix} t_{2s} & t_{sp} & 0 & 0 \\ -t_{sp} & -t_{pp\sigma} & 0 & 0 \\ 0 & 0 & t_{pp\pi} & 0 \\ 0 & 0 & 0 & t_{pp\pi} \end{pmatrix} \end{array} \begin{matrix} s \\ p_x \\ p_y \\ p_z \end{matrix}$$

$$H = \begin{pmatrix} 0 & 0 & 0 & 0 & t_{2s} & t_{sp} & 0 & 0 \\ 0 & \varepsilon & 0 & 0 & -t_{sp} & -t_{pp\sigma} & 0 & 0 \\ 0 & 0 & \varepsilon & 0 & 0 & 0 & t_{pp\pi} & 0 \\ 0 & 0 & 0 & \varepsilon & 0 & 0 & 0 & t_{pp\pi} \\ t_{2s} & -t_{sp} & 0 & 0 & 0 & 0 & 0 & 0 \\ t_{sp} & -t_{pp\sigma} & 0 & 0 & 0 & \varepsilon & 0 & 0 \\ 0 & 0 & t_{pp\pi} & 0 & 0 & 0 & \varepsilon & 0 \\ 0 & 0 & 0 & t_{pp\pi} & 0 & 0 & 0 & \varepsilon \end{pmatrix}$$

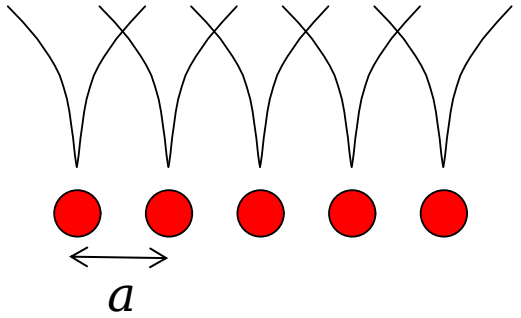
Komponen diagonal $E_{2p} - E_{2s} \equiv \varepsilon$

Atom vs. molekul vs. kristal



Kristal: Sistem Periodik dari Banyak Atom

$$\left[\frac{-\hbar^2\nabla^2}{2m}+V(r)\right]\psi(r)=E\ \psi(r)$$



$$V(x+a)=V(x)$$

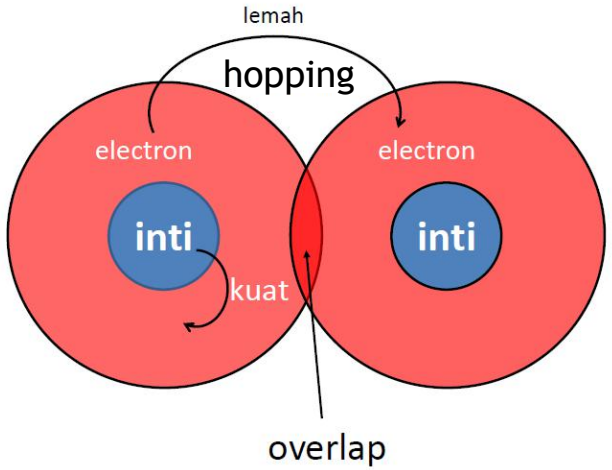
Fungsi periodik

$\lambda = a$

- Aproksimasi tight binding

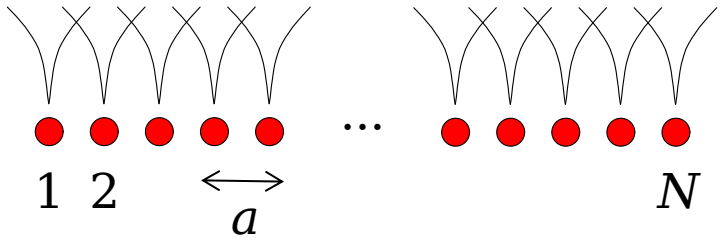
$\psi(x)$ adalah phase factor × orbital atom

$$\psi(x)=\frac{1}{\sqrt{N}}\sum_{n=1}^{N}e^{iknx}\phi(x-na)$$



$\phi(x-na)$ Orbital atom dengan posisi inti di $x=na$

Syarat batas periodik



$$\therefore \psi(x+Na) = \psi(x) \Leftrightarrow e^{ikNa} = 1$$

$$\psi(x+a) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikna}\, \varphi(x+a-na)$$

$$= e^{ika} \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ik(n-1)a}\, \varphi(x+(n-1)a)$$

$$= e^{ika}\psi(x)$$

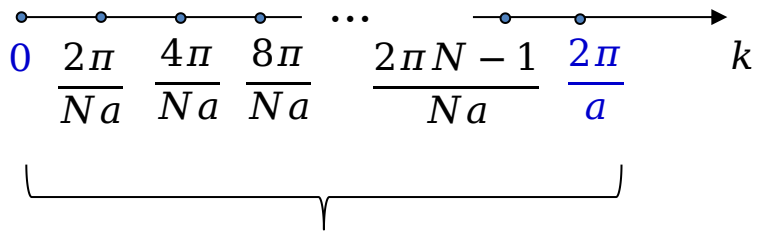
(Konsekuensi Teorema Bloch)

Teorema Bloch

$$H(x+a) = H(x) \quad \Rightarrow \quad \Psi(x+a) = e^{ika}\Psi(x)$$

$$\therefore k = \frac{2\pi m}{Na} (m = 0, \ldots, N-1)$$

Vektor kisi resiprok 1D: $\boldsymbol{b} = \frac{2\pi}{a}\,\hat{\boldsymbol{a}}$



Brillouin Zone: memuat kumpulan nilai $\boldsymbol{k}$

Kuis #9

- Manakah pernyataan berikut ini yang benar?

(A) Basis pada metode *tight-binding* untuk kristal dapat disusun dari kombinasi linear orbital atom untuk *N* sel satuan disertai faktor fase yang menyatakan fungsi gelombang yang periodik

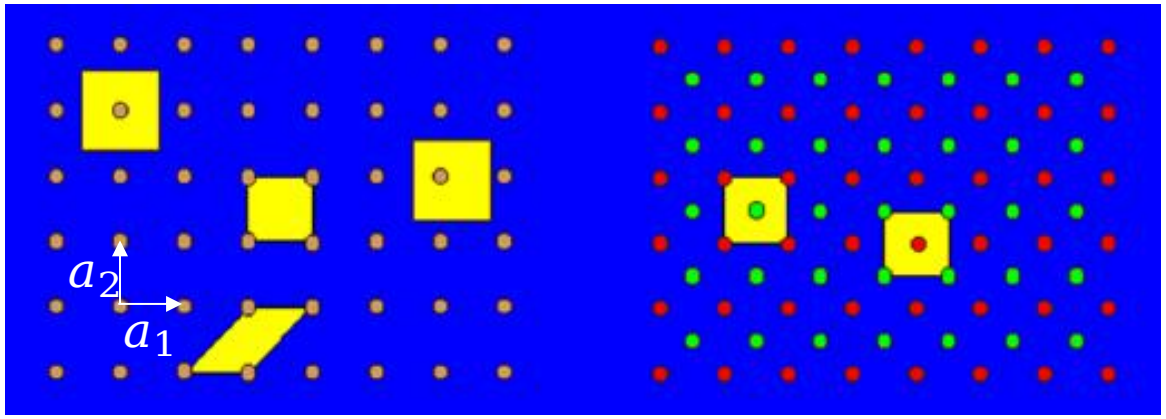
(B) Tak hingga banyaknya sumur potensial dapat membentuk celah energi antara pita-pita energi

(C) Ukuran matriks Hamiltonian yang harus dipecahkan untuk sistem periodik (kristal) dapat tereduksi secara signifikan akibat peninjauan sel satuan sebagai representasi kristal keseluruhan

(D) Semua pernyataan di atas benar

“Unit cell” dan “Brillouin Zone”

- ***Unit cell***:
  unit perulangan terkecil
  dalam kristal



- Vektor satuan $\boldsymbol{a}_i$
  di dalam unit cell memiliki
  pasangan vektor resiprok $\boldsymbol{b}_i$ di dalam Brillouin zone

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij}$$

Contoh: $\boldsymbol{a_1} = a\hat{\boldsymbol{x}}$ dan $\boldsymbol{a_2} = c\hat{\boldsymbol{y}}$ maka $\boldsymbol{b_1} = \frac{2\pi}{a}\hat{\boldsymbol{x}}$ dan $\boldsymbol{b_2} = \frac{2\pi}{c}\hat{\boldsymbol{y}}$

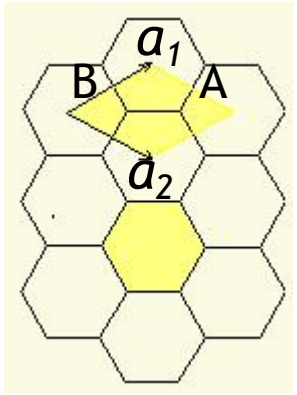
Formula langsung untuk menghitung vektor resiprok:

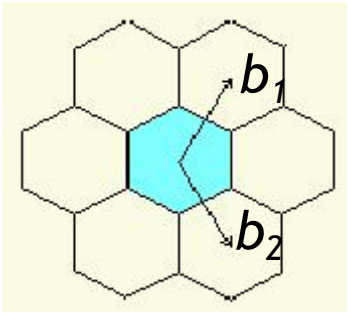
$$b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)} \qquad b_2 = 2\pi \frac{a_3 \times a_1}{a_2 \cdot (a_3 \times a_1)} \qquad b_3 = 2\pi \frac{a_1 \times a_2}{a_3 \cdot (a_1 \times a_2)}$$

Kuis #10

Definisikan:

$$\mathbf{a}_1 = (\frac{\sqrt{3}}{2}, \frac{1}{2})a, \mathbf{a}_2 = (\frac{\sqrt{3}}{2}, -\frac{1}{2})a$$





Manakah yang merupakan vektor-vektor kisi resiprok dari graphene?

(A) $\mathbf{b}_1 = \left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)\frac{4\pi}{\sqrt{3}a}$ $\mathbf{b}_2 = \left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)\frac{4\pi}{\sqrt{3}a}$

(B) $\mathbf{b}_1 = \left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)\frac{4\pi}{\sqrt{3}a}$ $\mathbf{b}_2 = \left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)\frac{4\pi}{\sqrt{3}a}$

(C) $\mathbf{b}_1 = \left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)\frac{4\pi}{\sqrt{3}a}$ $\mathbf{b}_2 = \left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)\frac{4\pi}{\sqrt{3}a}$

(D) $\mathbf{b}_1 = \left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)\frac{4\pi}{\sqrt{3}a}$ $\mathbf{b}_2 = \left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)\frac{4\pi}{\sqrt{3}a}$

Metode *tight-binding* pada metal 1D

$$\Psi_k(x) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikna} \varphi(x - na)$$

$$E_k = \frac{\langle \Psi_k(x) | H | \Psi_k(x) \rangle}{\langle \Psi_k(x) | \Psi_k(x) \rangle}$$

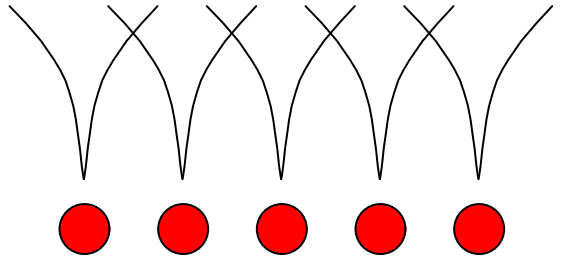
$$E_k = \frac{\langle \Psi_k(x) | H | \Psi_k(x) \rangle}{\langle \Psi_k(x) | \Psi_k(x) \rangle}$$ nilai harap energi

$$= \frac{\frac{1}{N} \sum_{n,m=1}^{N} e^{ik(n-m)a} \int \varphi^*(x - ma) H \varphi(x - na) dx}{\frac{1}{N} \sum_{n,m=1}^{N} e^{ik(n-m)a} \int \varphi^*(x - ma) \varphi(x - na) dx}$$

$$= \frac{\sum_{n,m=1}^{N} e^{ik(n-m)a} H_{n-m}}{\sum_{n,m=1}^{N} e^{ik(n-m)a} S_{n-m}}$$

$$H = -\frac{\hbar^2}{2m} \Delta + V(r)$$

$$V(x + a) = V(x)$$



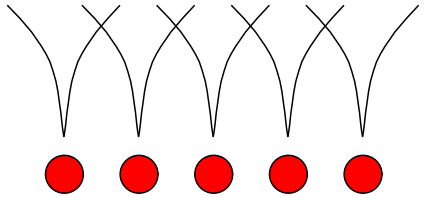
H : Hamiltonian matrix *S*: Overlap matrix

$$H_{nm} = H_{n-m,0} \equiv H_{n-m} = \int \varphi^*(x - ma) H \varphi(x - na) dx$$

$$S_{nm} = S_{n-m,0} \equiv S_{n-m} = \int \varphi^*(x - ma) \varphi(x - na) dx$$

Metode *tight-binding* pada metal 1D

- Aproksimasi tetangga terdekat



$$E_k = \frac{\sum_{n,m=1}^{N} e^{ik(n-m)a} H_{n-m}}{\sum_{n,m=1}^{N} e^{ik(n-m)a} S_{n-m}}$$

pembilang : $n = m, m \pm 1 \Rightarrow H_0, H_1$

penyebut : $n = m \Rightarrow S_0$

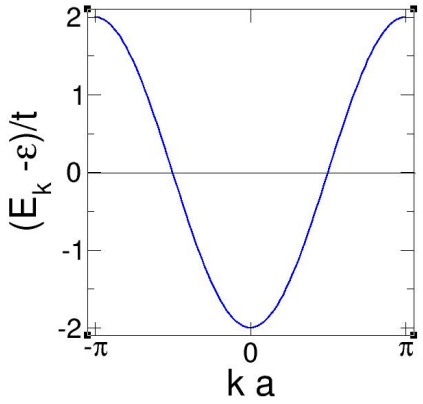
$$= \frac{H_0 + e^{ika} H_1 + e^{-ika} H_1}{S_0}$$

$$= \varepsilon - 2t \cos ka$$

dengan

$$\varepsilon = \frac{H_0}{S_0}, -t = \frac{H_1}{S_0}$$

$-t < 0$



$E(k)$: energy dispersion
$|4t|$: energy band width

$(-\pi \le ka \le \pi)$

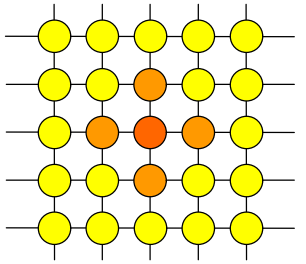
$$k = \frac{2\pi m}{Na}$$

$(m = 0, \ldots, N-1)$

Terdapat 2 elektron dalam 1 pita energi

Kali ini kita definisikan *t* positif, tetapi secara keseluruhan *hopping parameter* bernilai negatif

Metode tight-binding 1 orbital 1 atom



- 1 atom per unit cell dan 1 orbital :
  - vector to nearest neighbor atom : $\Delta\mathbf{R}_j = \mathbf{R}_j - \mathbf{R}_0$
  - transfer parameter : $\varepsilon = 0, -t = \frac{H_1}{S_0}$
  - energy dispersion relation :

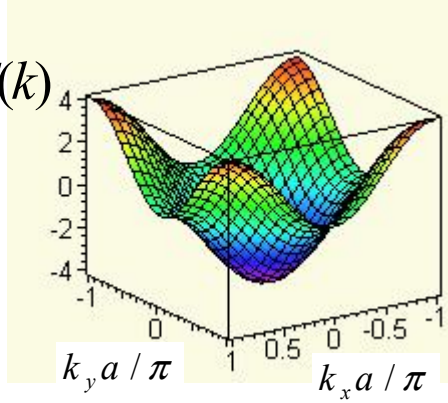
$$E(k) = -t\sum_j e^{-i\mathbf{k}\cdot\mathbf{R}_j}$$

- Contoh kisi persegi 2D

$$\Delta\mathbf{R}_j = (\pm a, 0), (0, \pm a)$$

$$E(k) = -t\left(e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a}\right)$$

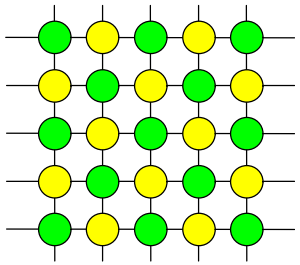
$$= -2t(\cos\ k_x a + \cos\ k_y a)$$



Beberapa atom dalam *unit cell*

- m atom dalam unit cell→ m fungsi Bloch $:\Phi_i^{\boldsymbol{k}} \quad (i = 1, \ldots, m)$

$$\Psi_k = \sum_i C_i \Phi_i^k \qquad C_i \quad \text{:variational parameter} \qquad \Phi_i^k = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_i} e^{i\mathbf{k}\cdot\Delta\mathbf{R}_i} \varphi_i(\mathbf{r} - \mathbf{R}_i)$$



$$E_k = \frac{\langle \Psi_k | H | \Psi_k \rangle}{\langle \Psi_k | \Psi_k \rangle} = \frac{\sum_{i,j} C_i^* C_j H_{ij}}{\sum_{i,j} C_i^* C_j S_{ij}}$$

$$S_{ij} = \left\langle \Phi_i^k \middle| \Phi_i^k \right\rangle \mathbf{S} \quad \text{: overlap matrix}$$

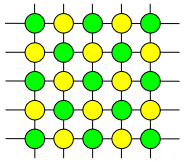
$$H_{ij} = \left\langle \Phi_i^k \middle| H \middle| \Phi_j^k \right\rangle \mathbf{H} \quad \text{: Hamiltonian matrix}$$

$(C_i, C_i^*$: Complex numbers $\Leftrightarrow$ differentiate separately $\bar{\mathrm{I}}$

Variational principles

$$\frac{\partial E_k}{\partial C_i^*} = \frac{\sum_j C_j H_{ij}}{\sum_{i,j} C_i^* C_j S_{ij}} - \frac{\sum_{i,j} C_i^* C_j H_{ij}}{\left(\sum_{i,j} C_i^* C_j S_{ij} \right)^2} \times \sum_j C_j S_{ij} = 0, (i = 1, \cdots, N)$$

Persamaan Sekuler



$$\Psi_k = \sum_i C_i \Phi_i^k,$$

$$E_k = \frac{\sum_{i,j} C_i^* C_j H_{ij}}{\sum_{i,j} C_i^* C_j S_{ij}}$$

- Kondisi variasional → *m* buah pers. simultan

Variation condition

$$\frac{\partial E_k}{\partial C_i^*} = \frac{\sum_j C_j H_{ij}}{\sum_{i,j} C_i^* C_j S_{ij}} - \frac{\sum_{i,j} C_i^* C_j H_{ij}}{\left(\sum_{i,j} C_i^* C_j S_{ij}\right)^2} \times \sum_j C_j S_{ij} = 0, \quad (i = 1, \ldots, m)$$

$$E_k = \frac{\sum_{i,j} C_i^* C_j H_{ij}}{\sum_{i,j} C_i^* C_j S_{ij}}$$

$$\sum_j C_j H_{ij} - E_k \sum_j C_j S_{ij} = 0, \quad (i = 1, \ldots, m)$$

$$(\mathbf{H} - E_k \mathbf{S})\mathbf{C} = 0$$

Overlap matrix $\mathbf{S} = \{S_{ij}\}$, $\mathbf{C} = {}^{\mathrm{t}}\{C_j\}$

Hamiltonian matrix $\mathbf{H} = \{H_{ij}\}$

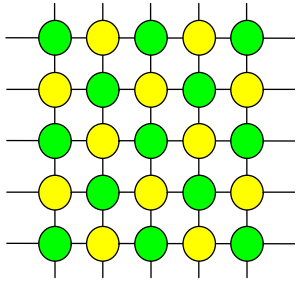
$$\mathbf{C} \neq 0 \Leftrightarrow \det(\mathbf{H} - E_k \mathbf{S}) = 0$$

secular equation

Esensi tight-binding:
Peroleh H dan S pada tiap *k*
dan pecahkan pers. sekuler

Contoh kisi persegi 2D

$$\det(\mathbf{H} - E_k\mathbf{S}) = 0$$ Persamaan sekuler



- Dua atom, A and B, dalam kisi persegi

overlap matrix $\mathbf{S} = \delta_{ij}$, (unit matrix)

Hamiltonian matrix $\mathbf{H} = \{H_{ij}\}$

$$H_{AA} = +\Delta/2,\ H_{BB} = -\Delta/2$$

$$H_{AB} = -t\left(e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a}\right)$$

$$H_{BA} = H_{AB}^{*}$$

$$\Psi_k = \sum_i C_i \Phi_i^k,\ (i = A, B)$$

$$\therefore E_k = \pm\sqrt{(\Delta/2)^2 + |H_{AB}|^2}$$

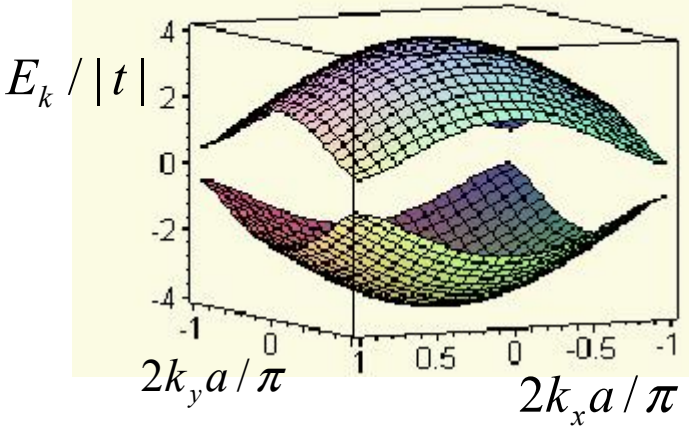
$$|H_{AB}|^2 = 4t^2(\cos k_x a + \cos k_y a)^2$$

$$-\frac{\pi}{2a} \le k_x, k_y \le \frac{\pi}{2a}$$ (sel satuan memiliki batas $2a$)

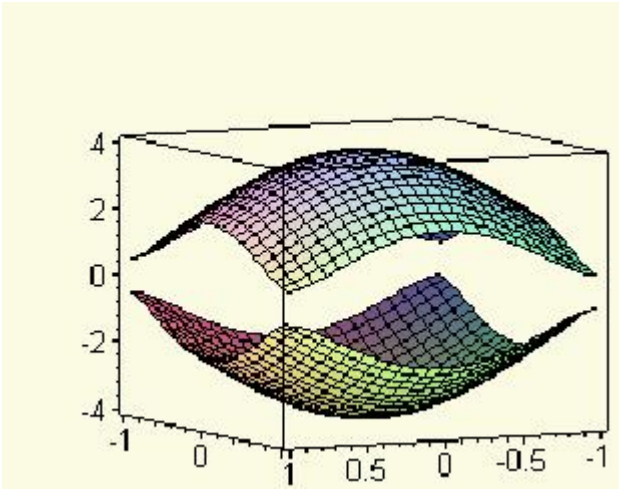
$$\det(\mathbf{H} - E_k\mathbf{S}) = \begin{vmatrix} +\Delta/2 - E_k & H_{AB} \\ H_{BA} & -\Delta/2 - E_k \end{vmatrix}$$

$$= E_k^2 - (\Delta/2)^2 - |H_{AB}|^2$$

$$= 0$$



Kuis #11



- Diketahui:

$$E_k = \pm\sqrt{(\Delta/2)^2 + |H_{AB}|^2}$$

$$|H_{AB}|^2 = 4t^2(\cos k_x a + \cos k_y a)^2$$

$$-\frac{\pi}{2a} \le k_x, k_y \le \frac{\pi}{2a}$$

Berapakah nilai celah energi (*band gap*) dari sistem tersebut?

(A) $|\Delta|/2$ (B) $|\Delta|$

(C) $2|\Delta|$ (D) $4|\Delta|$