



Teori Kuantum untuk Material

Bagian #03

-  Kombinasi Linear Orbital Atom (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:

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

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

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

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

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

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

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

Secular equation

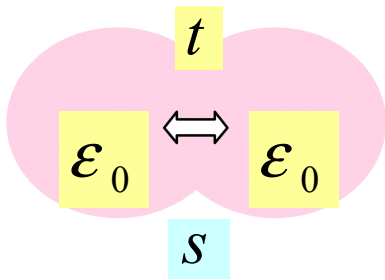
Langkah perhitungan

- Isi matriks H dan S
- Pecahkan determinan persamaan sekuler
- Dapatkan nilai eigen dan vektor eigen
- Susun keadaan elektron dari energi terendah

Fungsi eigen dibentuk dari koefisien vektor eigen

$$\Psi_k(x) = \sum_{i=1}^N C_{ik} \varphi(x - \mathbf{R}_i)$$

Contoh molekul hidrogen: 2 elektron 2 orbital 1s

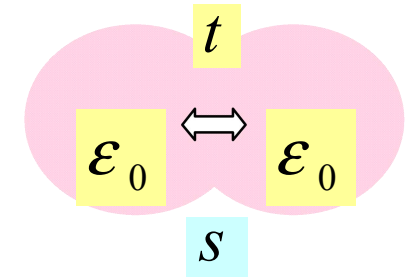


$$\Psi(x) = C_1 \varphi_1 + C_2 \varphi_2$$

$$H = \begin{pmatrix} \varepsilon_0 & t \\ t & \varepsilon_0 \end{pmatrix}, S = \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix}$$

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

Hasil u/ molekul hidrogen



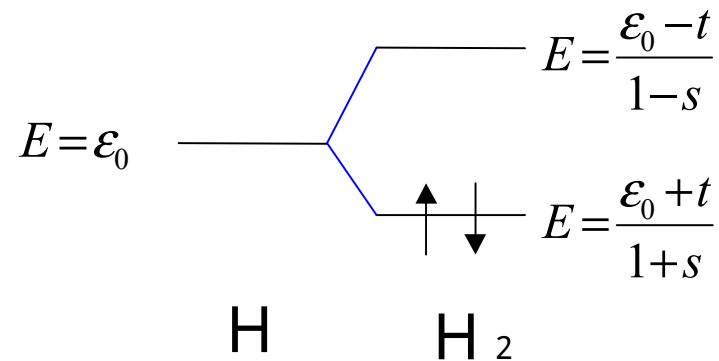
$$\det(H-ES) = \begin{vmatrix} \epsilon_0 - E & t - sE \\ t - sE & \epsilon_0 - E \end{vmatrix} = 0 \quad t < 0, \quad s > 0$$

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

Energi: $E = \frac{\epsilon_0 \pm t}{1 \pm s}$

Vektor eigen:

$$\begin{pmatrix} \epsilon_0 - E & t - sE \\ t - sE & \epsilon_0 - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$$



Masukkan nilai setiap energi ke persamaan matriks

$$E = \frac{\epsilon_0 + t}{1 + s} \Leftrightarrow C_1 : C_2 = 1 : 1$$

$$E = \frac{\epsilon_0 - t}{1 - s} \Leftrightarrow C_1 : C_2 = 1 : -1$$

Normalisasi

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


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

Bagaimana dengan molekul 3 atom?

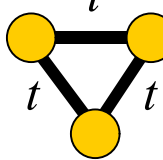
Contoh: Li_3 (basis 3 elektron 2s)

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

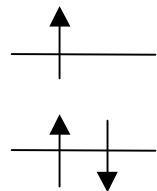
$$H = \begin{pmatrix} 0 & t & t \\ t & 0 & t \\ t & t & 0 \end{pmatrix}$$


$$E = 0, \pm\sqrt{2}t$$

$$\Leftarrow \det(H - EI) = 0 \Rightarrow$$

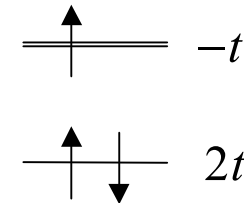
$$E = 2t, -t, -t$$

$$\text{————— } -\sqrt{2}t$$



Manakah struktur yang lebih stabil?

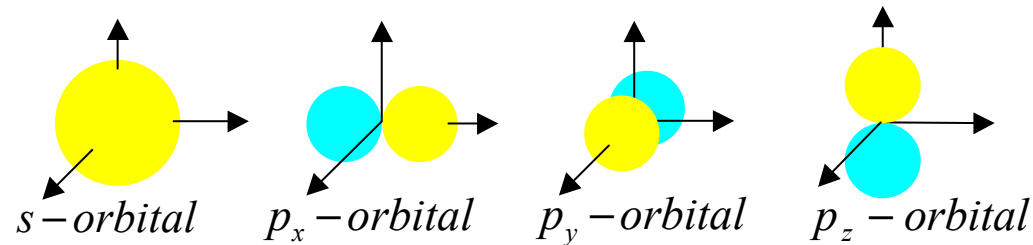
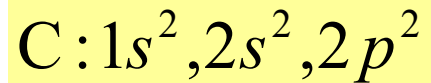
Cari energi total yang lebih rendah!



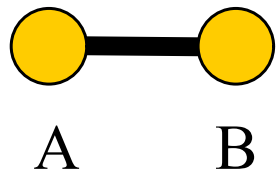
Kuis #8

- Asumsikan $t < 0$, konfigurasi paling stabil dari molekul Li_3 adalah:
 - (A) Rantai linear dengan energi total $2\sqrt{2}t$
 - (B) Segitiga dengan energi total 0
 - (C) Segitiga dengan energi total $3t$
 - (D) Rantai linear dengan energi total $-\sqrt{2}t$

Lebih banyak orbital atom?



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

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

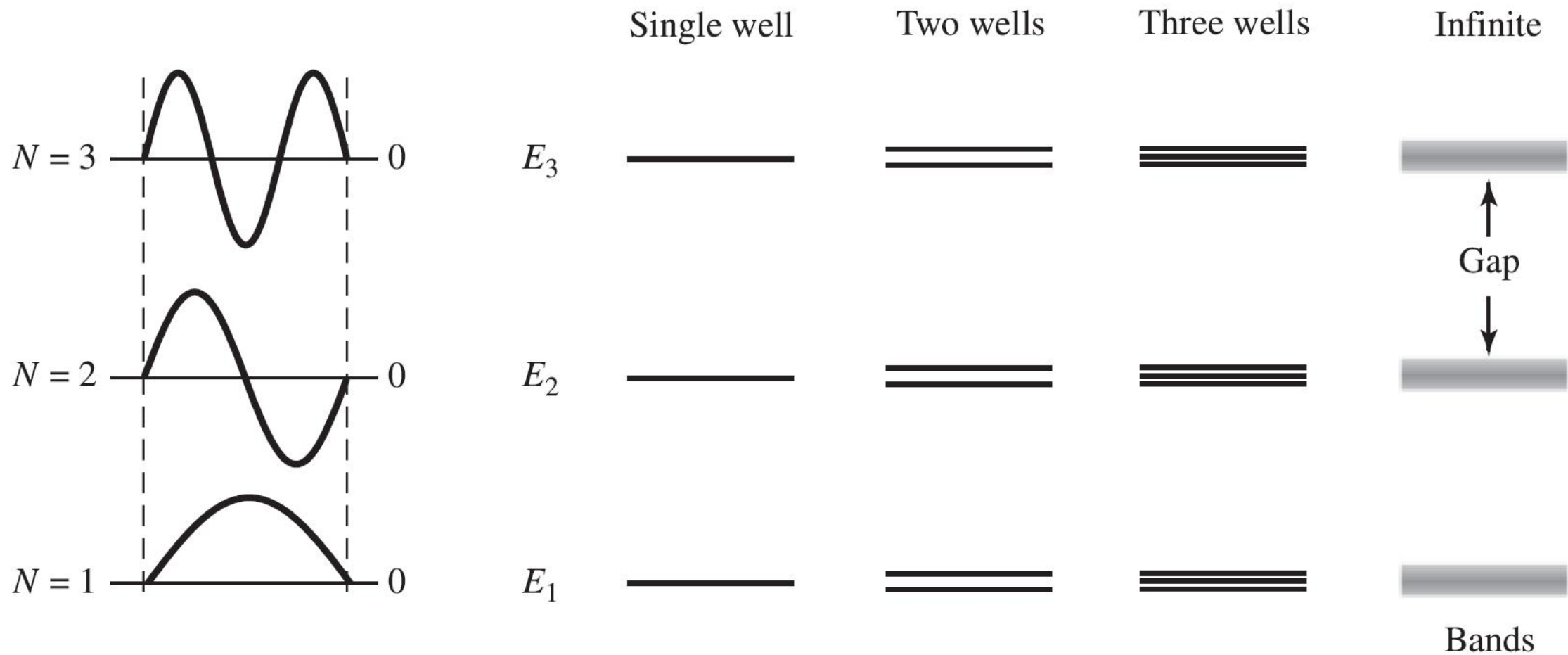
$$H_{AA} = H_{BB} = \begin{pmatrix} s & p_x & p_y & p_z \\ 0 & \epsilon & 0 & 0 \\ 0 & 0 & \epsilon & 0 \\ 0 & 0 & 0 & \epsilon \end{pmatrix} \begin{matrix} s \\ p_x \\ p_y \\ p_z \end{matrix}$$

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

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

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

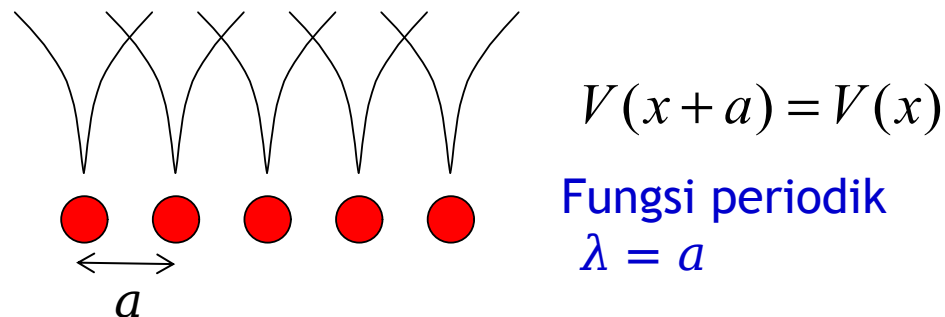
Atom vs. molekul vs. kristal



Kristal: Sistem Periodik dari Banyak Atom

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

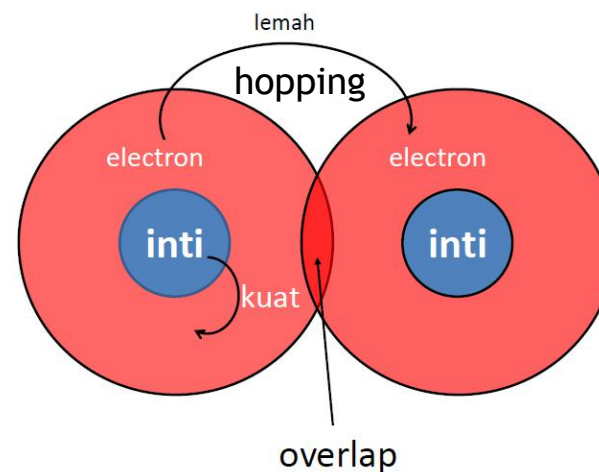
- Aproksimasi tight binding



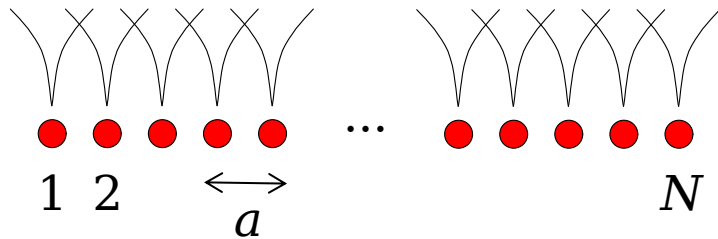
$\psi(x)$ adalah phase factor \times orbital atom

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

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



Syarat batas periodik



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

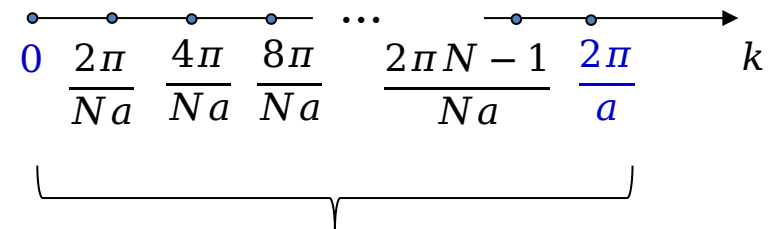
$$\begin{aligned} \psi(x + a) &= \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ikna} \varphi(x + a - na) \\ &= e^{ika} \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ik(n-1)a} \varphi(x + (n-1)a) \\ &= e^{ika} \psi(x) \end{aligned} \quad \text{(Konsekuensi Teorema Bloch)}$$

Teorema Bloch

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

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

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



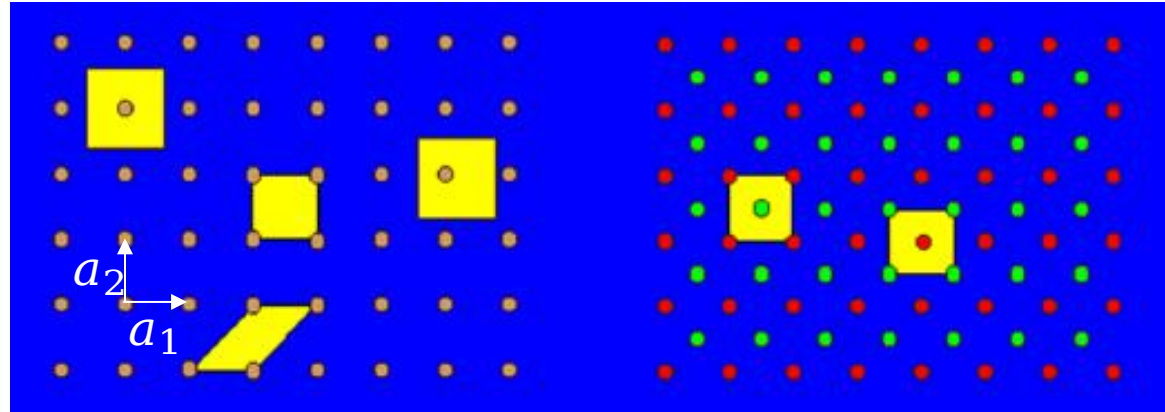
Brillouin Zone: memuat kumpulan nilai \mathbf{k}

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 \mathbf{a}_i di dalam **unit cell** memiliki pasangan vektor resiprok \mathbf{b}_i di dalam **Brillouin zone**



$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad \text{Contoh: } \mathbf{a}_1 = a\hat{\mathbf{x}} \text{ dan } \mathbf{a}_2 = c\hat{\mathbf{y}} \text{ maka } \mathbf{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}} \text{ dan } \mathbf{b}_2 = \frac{2\pi}{c}\hat{\mathbf{y}}$$

Formula langsung untuk menghitung vektor resiprok:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

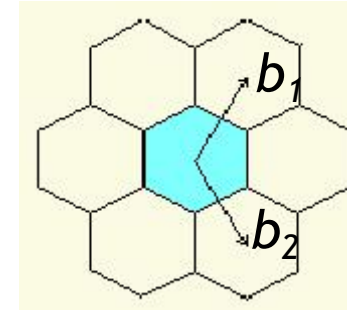
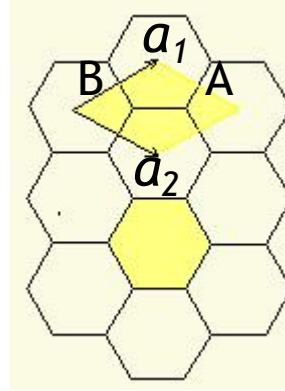
$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}$$

Kuis #10

Definisikan:

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



Manakah yang merupakan vektor-vektor kisi resiprok dari graphene?

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

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

Metode *tight-binding* pada metal 1D

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

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

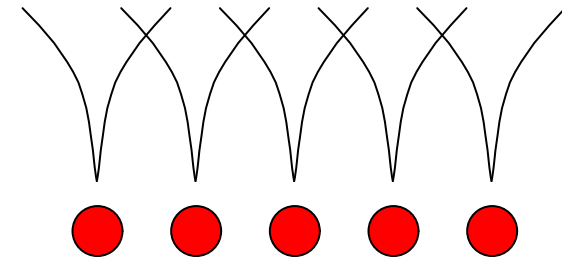
$$= \frac{\frac{1}{N} \sum_{n,m=1}^N e^{ik(n-m)a} \int \varphi^*(x-ma) H \varphi(x-na) dx}{\frac{1}{N} \sum_{n,m=1}^N e^{ik(n-m)a} \int \varphi^*(x-ma) \varphi(x-na) dx}$$

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

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

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

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



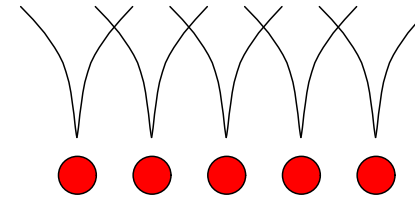
H : Hamiltonian matrix S : Overlap matrix

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

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

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 : $n = m \Rightarrow S_0$

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

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

$$(-\pi \leq ka \leq \pi)$$

Terdapat 2 elektron dalam 1 pita energi

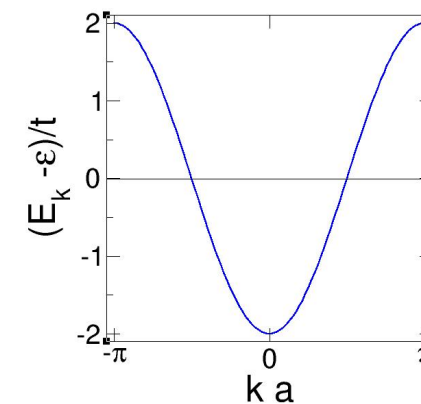
dengan

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

$$-t < 0$$

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

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



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

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

Metode tight-binding 1 orbital 1 atom

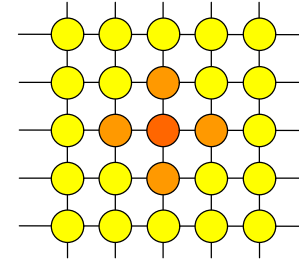
- 1 atom per unit cell dan 1 orbital :

– 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 :

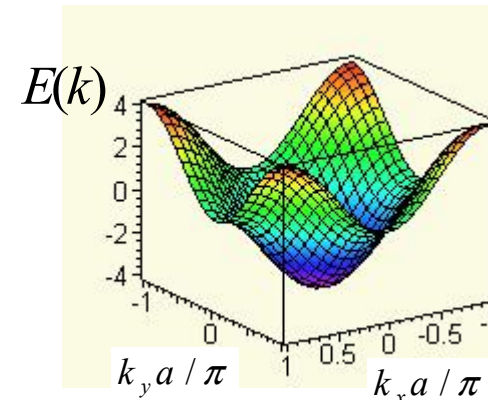
$$E(k) = -t \sum_j e^{-i\mathbf{k} \cdot \mathbf{R}_j}$$



- Contoh kisi persegi 2D

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

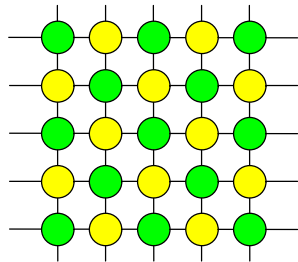
$$\begin{aligned} E(k) &= -t \left(e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a} \right) \\ &= -2t (\cos k_x a + \cos k_y a) \end{aligned}$$



Beberapa atom dalam *unit cell*

- m atom dalam unit cell \rightarrow m fungsi Bloch : Φ_i^k ($i = 1, \dots, m$)

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



$$E_k = \frac{\langle \Psi_k | H | \Psi_k \rangle}{\langle \Psi_k | \Psi_k \rangle} = \frac{\sum_{i,j} C_i^* C_j H_{ij}}{\sum_{i,j} C_i^* C_j S_{ij}} \quad (C_i, C_i^* : \text{Complex numbers} \Leftrightarrow \text{differentiate separately } \bar{C}_i)$$

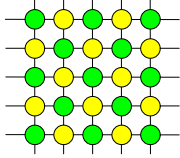
$$S_{ij} = \langle \Phi_i^k | \Phi_j^k \rangle \mathbf{S} : \text{overlap matrix}$$

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

Variational principles

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

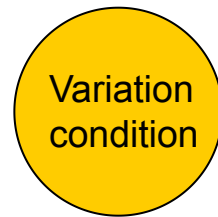
Persamaan Sekuler



- Kondisi variasional $\rightarrow m$ buah pers. simultan

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

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



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

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

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

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

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

- Dua atom, A and B, dalam kisi persegi

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

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

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

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

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

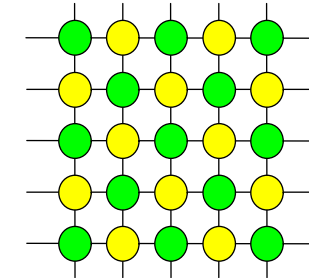
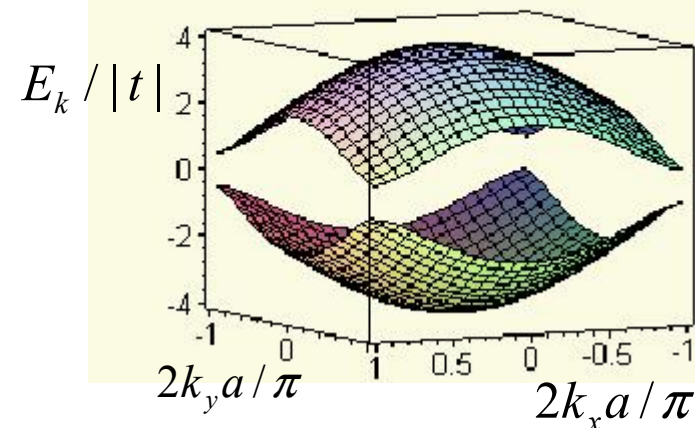
$$\begin{aligned} \det(\mathbf{H} - E_k \mathbf{S}) &= \begin{vmatrix} +\Delta/2 - E_k & H_{AB} \\ H_{BA} & -\Delta/2 - E_k \end{vmatrix} \\ &= E_k^2 - (\Delta/2)^2 - |H_{AB}|^2 \\ &= 0 \end{aligned}$$

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

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

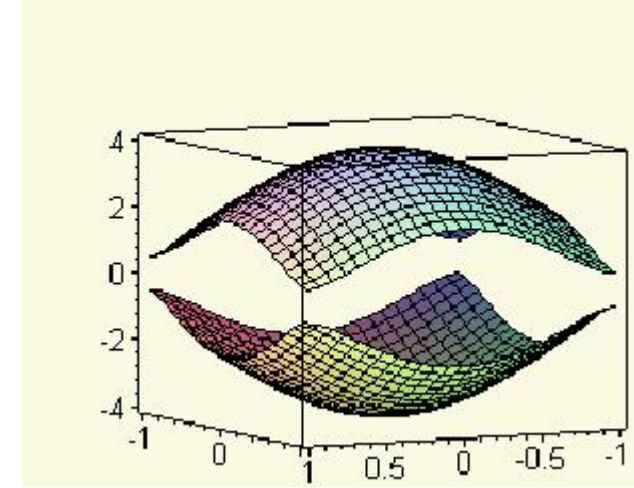
$$|H_{AB}|^2 = 4t^2 (\cos k_x a + \cos k_y a)^2$$

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



Kuis #11

- Diketahui: $E_k = \pm \sqrt{(\Delta/2)^2 + |H_{AB}|^2}$
 $|H_{AB}|^2 = 4t^2(\cos k_x a + \cos k_y a)^2$
 $-\frac{\pi}{2a} \leq k_x, k_y \leq \frac{\pi}{2a}$



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

- | | |
|------------------|-----------------|
| (A) $ \Delta /2$ | (B) $ \Delta $ |
| (C) $2 \Delta $ | (D) $4 \Delta $ |