Teori Kuantum untuk Material
Bagian #03

- Struktur Elektronik Molekul
- Metode Kombinasi Linear Orbital Atom (LCAO)

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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

Langkah perhitungan

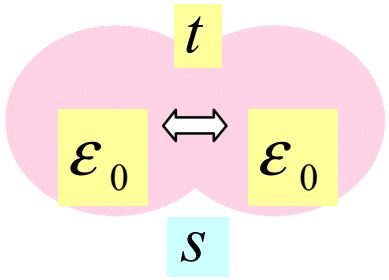
- Isi matriks H dan S
- Pecahkan determinan persamaan sekuler
- Dapatkan nilai eigen dan vektor eigen
- Susun keadaan elektron dari energi terendah

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

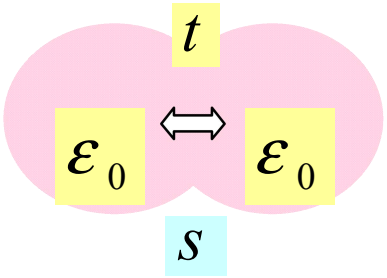


$$H = \begin{pmatrix} \varepsilon_0 & t \\ t & \varepsilon_0 \end{pmatrix}, \; S = \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix}$$

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

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

Hasil u/ molekul hidrogen

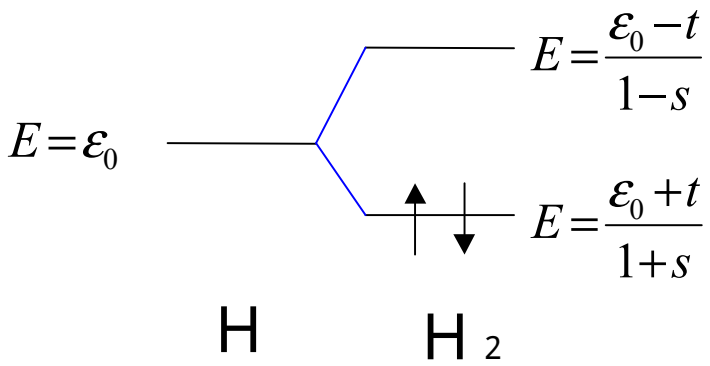


$$\det(H-ES)=\begin{vmatrix}\varepsilon_0-E & t-sE\\ t-sE & \varepsilon_0-E\end{vmatrix}=0$$

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

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

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)

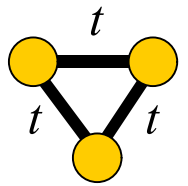
Aproksimasi $t < 0$ dan $s = 0$ **S** = **I** (matriks identitas)

- Rantai linear

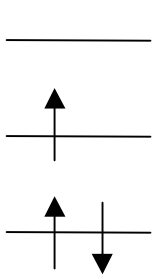
$$H = \begin{pmatrix} 0 & t & 0 \\ t & 0 & t \\ 0 & t & 0 \end{pmatrix}$$

- Segitiga

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

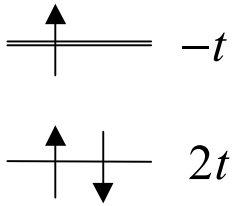


$E = 0, \pm\sqrt{2}\,t$ $\Leftarrow \det(H - EI) = 0 \Rightarrow$ $E = 2t, -t, -t$



Manakah struktur yang lebih stabil?

Cari energi total yang lebih rendah!



Kuis #8

- Asumsikan $t < 0$, konfigurasi paling stabil dari molekul Li_3 adalah:

  (A) Rantai linear dengan energi total $2\sqrt{2}t$

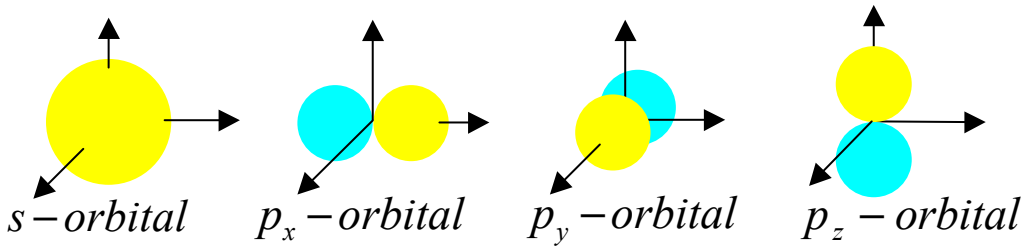
  (B) Segitiga dengan energi total 0

  (C) Segitiga dengan energi total $3t$

  (D) Rantai linear dengan energi total $-\sqrt{2}t$

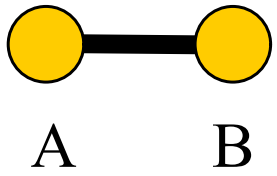
Lebih banyak orbital atom?

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



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