原子と原子の結合

ベンゼン

一次元原子鎖の強結合模型

化学結合の基本的な考え方

- 二つの原子が接近しているとき、解を個々の原子軌道の線形結合で近似的に表わす

$$H\psi = E\psi$$

$$\psi = c_0\varphi_0 + c_1\varphi_1$$

$$H\psi = c_0 H\varphi_0 + c_1 H\varphi_1$$

$$c_0 H\varphi_0 + c_1 H\varphi_1 = E\left(c_0\varphi_0 + c_1\varphi_1\right)$$

$$c_0\langle\varphi_0|H|\varphi_0\rangle + c_1\langle\varphi_0|H|\varphi_1\rangle = Ec_0\langle\varphi_0|\varphi_0\rangle + Ec_1\langle\varphi_0|\varphi_1\rangle$$

$$c_0\langle\varphi_1|H|\varphi_0\rangle + c_1\langle\varphi_1|H|\varphi_1\rangle = Ec_0\langle\varphi_1|\varphi_0\rangle + Ec_1\langle\varphi_1|\varphi_1\rangle$$

化学結合の基本的な考え方

$$c_0\langle\varphi_0|H|\varphi_0\rangle + c_1\langle\varphi_0|H|\varphi_1\rangle = Ec_0\langle\varphi_0|\varphi_0\rangle + Ec_1\langle\varphi_0|\varphi_1\rangle$$

$$c_0\langle\varphi_1|H|\varphi_0\rangle + c_1\langle\varphi_1|H|\varphi_1\rangle = Ec_0\langle\varphi_1|\varphi_0\rangle + Ec_1\langle\varphi_1|\varphi_1\rangle$$

$\langle\varphi_0|H|\varphi_1\rangle = \langle\varphi_1|H|\varphi_0\rangle = -t$ 遷移積分

$$\boxed{\begin{aligned}&\langle\varphi_0|H|\varphi_0\rangle = \varepsilon\\ &\langle\varphi_1|H|\varphi_1\rangle = \varepsilon\\ &\langle\varphi_0|\varphi_0\rangle = 1\\ &\langle\varphi_1|\varphi_1\rangle = 1\\ &\langle\varphi_0|\varphi_1\rangle = 0\end{aligned}}$$

$$\varepsilon c_0 - tc_1 = Ec_0$$

$$-tc_0 + \varepsilon c_1 = Ec_1$$

$$(E-\varepsilon)c_0 + tc_1 = 0$$

$$tc_0 + (E-\varepsilon)c_1 = 0$$

化学結合の基本的な考え方

$$\begin{aligned}(E-\varepsilon)c_0 + tc_1 &= 0\\ tc_0 + (E-\varepsilon)c_1 &= 0\end{aligned} \quad \Rightarrow \begin{bmatrix} E-\varepsilon & t \\ t & E-\varepsilon \end{bmatrix}\begin{bmatrix} c_0 \\ c_1 \end{bmatrix} = 0$$

$$\begin{vmatrix} E-\varepsilon & t \\ t & E-\varepsilon \end{vmatrix} = 0$$

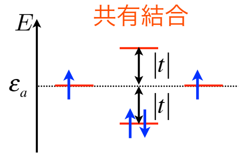
$$(E-\varepsilon)^2 - t^2 = 0$$

$$E = \varepsilon \pm t$$

化学結合の基本的な考え方

$$E = \varepsilon \pm t \quad (t>0)$$

$$\begin{bmatrix} E-\varepsilon & t \\ t & E-\varepsilon \end{bmatrix}\begin{bmatrix} c_0 \\ c_1 \end{bmatrix} = 0$$



$$\begin{bmatrix} -t & t \\ t & -t \end{bmatrix}\begin{bmatrix} 1 \\ 1 \end{bmatrix} = 0 \quad \Rightarrow \psi = \frac{1}{\sqrt{2}}\left(1\varphi_0 + 1\varphi_1\right)$$ 結合性軌道

$$\begin{bmatrix} t & t \\ t & t \end{bmatrix}\begin{bmatrix} 1 \\ -1 \end{bmatrix} = 0 \quad \Rightarrow \psi = \frac{1}{\sqrt{2}}\left(1\varphi_0 - 1\varphi_1\right)$$ 反結合性軌道

化学結合の基本的な考え方

- 3つの原子が正三角形状に配置しているとする。

$$H\psi = E\psi$$

$$\psi = c_0\varphi_0 + c_1\varphi_1 + c_2\varphi_2$$

$$c_0 H\varphi_0 + c_1 H\varphi_1 + c_2 H\varphi_2 = E\left(c_0\varphi_0 + c_1\varphi_1 + c_2\varphi_2\right)$$

$$c_0\langle\varphi_0|H|\varphi_0\rangle + c_1\langle\varphi_0|H|\varphi_1\rangle + c_2\langle\varphi_0|H|\varphi_2\rangle = Ec_0\langle\varphi_0|\varphi_0\rangle + Ec_1\langle\varphi_0|\varphi_1\rangle + Ec_2\langle\varphi_0|\varphi_2\rangle$$

$$c_0\langle\varphi_1|H|\varphi_0\rangle + c_1\langle\varphi_1|H|\varphi_1\rangle + c_2\langle\varphi_1|H|\varphi_2\rangle = Ec_0\langle\varphi_1|\varphi_0\rangle + Ec_1\langle\varphi_1|\varphi_1\rangle + Ec_2\langle\varphi_1|\varphi_2\rangle$$

$$c_0\langle\varphi_2|H|\varphi_0\rangle + c_1\langle\varphi_2|H|\varphi_1\rangle + c_2\langle\varphi_2|H|\varphi_2\rangle = Ec_0\langle\varphi_2|\varphi_0\rangle + Ec_1\langle\varphi_2|\varphi_1\rangle + Ec_2\langle\varphi_2|\varphi_2\rangle$$

化学結合の基本的な考え方

$$c_0\langle\varphi_0|H|\varphi_0\rangle+c_1\langle\varphi_0|H|\varphi_1\rangle+c_2\langle\varphi_0|H|\varphi_2\rangle$$
$$=Ec_0\langle\varphi_0|\varphi_0\rangle+Ec_1\langle\varphi_0|\varphi_1\rangle+Ec_2\langle\varphi_0|\varphi_2\rangle$$

$$\boxed{\begin{aligned}&\langle\varphi_0|H|\varphi_1\rangle=\langle\varphi_1|H|\varphi_2\rangle=\langle\varphi_2|H|\varphi_0\rangle=-t\\&\langle\varphi_0|H|\varphi_0\rangle=\langle\varphi_1|H|\varphi_1\rangle=\langle\varphi_2|H|\varphi_2\rangle=\varepsilon\\&\langle\varphi_0|\varphi_0\rangle=\langle\varphi_1|\varphi_1\rangle=\langle\varphi_2|\varphi_2\rangle=1\\&\langle\varphi_0|\varphi_1\rangle=\langle\varphi_1|\varphi_2\rangle=\langle\varphi_2|\varphi_0\rangle=0\end{aligned}}$$

$$\varepsilon c_0-tc_1-tc_2=Ec_0$$

化学結合の基本的な考え方

$$\begin{aligned}\varepsilon c_0-tc_1-tc_2&=Ec_0\\-tc_0+\varepsilon c_1-tc_2&=Ec_1\\-tc_0-tc_1+\varepsilon c_2&=Ec_2\end{aligned}\Rightarrow\begin{bmatrix}E-\varepsilon&t&t\\t&E-\varepsilon&t\\t&t&E-\varepsilon\end{bmatrix}\begin{bmatrix}c_0\\c_1\\c_2\end{bmatrix}=0$$

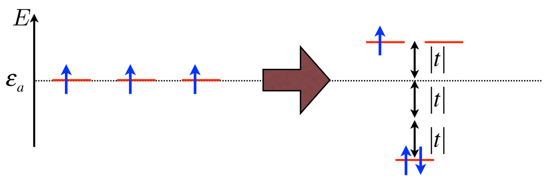
$$\Rightarrow\begin{vmatrix}E-\varepsilon&t&t\\t&E-\varepsilon&t\\t&t&E-\varepsilon\end{vmatrix}=0$$

$$(E-\varepsilon)\left[(E-\varepsilon)^2-t^2\right]-2t^2\left[(E-\varepsilon)-t\right]=\left[(E-\varepsilon)-t\right]^2\left[(E-\varepsilon)+2t\right]$$
$$=0$$

$$E=\varepsilon-2t,\varepsilon+t,\varepsilon+t$$

化学結合の基本的な考え方

$$E=\varepsilon-2t,\varepsilon+t,\varepsilon+t\quad(t>0)$$

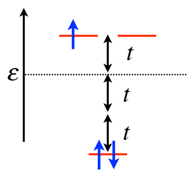


$$E_{total}=2(\varepsilon-2t)+\varepsilon+t=3(\varepsilon-t)$$

化学結合の基本的な考え方

$$E=\varepsilon-2t$$

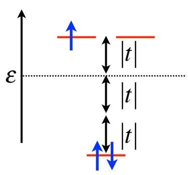
$$\begin{bmatrix}-2t&t&t\\t&-2t&t\\t&t&-2t\end{bmatrix}\begin{bmatrix}1\\1\\1\end{bmatrix}=0\quad\Rightarrow\psi=\frac{1}{\sqrt{3}}\left(1\varphi_0+1\varphi_1+1\varphi_2\right)$$

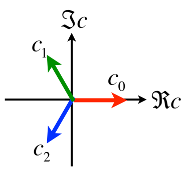


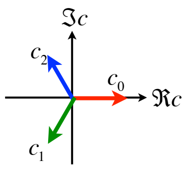
化学結合の基本的な考え方

$$E=\varepsilon+t$$

$$\begin{bmatrix}t&t&t\\t&t&t\\t&t&t\end{bmatrix}\begin{bmatrix}c_0\\c_1\\c_2\end{bmatrix}=0\quad\Rightarrow c_0+c_1+c_2=0$$







化学結合の基本的な考え方

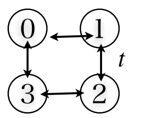
- 4つの原子が正方形の頂点に配置しているとする。

$$\psi=c_0\varphi_0+c_1\varphi_1+c_2\varphi_2$$

$$\begin{aligned}\varepsilon c_0-tc_1-tc_2&=Ec_0\\-tc_0+\varepsilon c_1-tc_2&=Ec_1\\-tc_0-tc_1+\varepsilon c_2&=Ec_2\end{aligned}$$

$$\psi=c_0\varphi_0+c_1\varphi_1+c_2\varphi_2+c_3\varphi_3$$

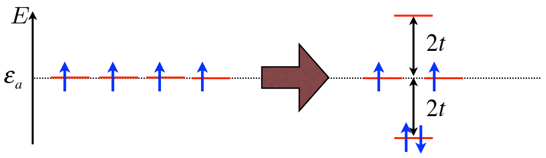
$$\begin{aligned}\varepsilon c_0-tc_1-tc_3&=Ec_0\\-tc_0+\varepsilon c_1-tc_2&=Ec_1\\-tc_3-tc_1+\varepsilon c_2&=Ec_2\\-tc_0-tc_2+\varepsilon c_3&=Ec_2\end{aligned}$$



化学結合の基本的な考え方

$$\begin{vmatrix} E-\varepsilon & t & 0 & t \\ t & E-\varepsilon & t & 0 \\ 0 & t & E-\varepsilon & t \\ t & 0 & t & E-\varepsilon \end{vmatrix} = 0$$

$$(E-\varepsilon)^2(E-\varepsilon-2t)(E-\varepsilon+2t)=0 \qquad E=\varepsilon-2t,\varepsilon,\varepsilon,\varepsilon+2t$$

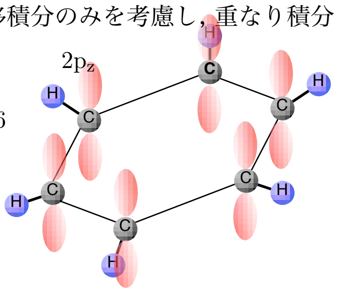


例題（ベンゼン）

- ベンゼン分子の6個の炭素の2pz軌道の一次結合で波動関数を近似する.
- ただし、隣接原子間の遷移積分のみを考慮し，重なり積分などは無視する.

$$|\varphi\rangle = \sum_{n=0}^{N-1} c_n|\varphi_n\rangle \qquad N=6$$

$$\langle\varphi_n|\mathcal{H}|\varphi_n\rangle = \alpha$$
$$\langle\varphi_n|\mathcal{H}|\varphi_{n+1}\rangle = -\beta$$
$$\langle\varphi_m|\varphi_n\rangle = \delta_{n,m}$$



例題（ベンゼン）

$$|\varphi\rangle = \sum_{n=0}^{N-1} c_n|\varphi_n\rangle \qquad \langle\varphi_m|\varphi_n\rangle = \delta_{n,m} \qquad \langle\varphi_n|\mathcal{H}|\varphi_n\rangle = \alpha$$
$$\langle\varphi_n|\mathcal{H}|\varphi_{n+1}\rangle = -\beta$$
$$\mathcal{H}|\varphi\rangle = E|\varphi\rangle$$
$$\langle\varphi_m|\mathcal{H}|\varphi\rangle = \sum_{n=0}^{N-1} c_n\langle\varphi_m|\mathcal{H}|\varphi_n\rangle = E\sum_{n=0}^{N-1} c_n\langle\varphi_m|\varphi_n\rangle$$
$$c_{m-1}\langle\varphi_m|\mathcal{H}|\varphi_{m-1}\rangle + c_m\langle\varphi_m|\mathcal{H}|\varphi_m\rangle + c_{m+1}\langle\varphi_m|\mathcal{H}|\varphi_{m+1}\rangle = Ec_m$$
$$(E-\alpha)c_m + \beta(c_{m+1}+c_{m-1}) = 0$$
$$c_m^{(k)} = e^{2\pi i\frac{km}{N}} \qquad c_m^{(k+N)} = e^{2\pi i\frac{(k+N)m}{N}} = e^{2\pi i\frac{km}{N}} = c_m^{(k)}$$
$$c_{m+N}^{(k)} = c_m^{(k)} \qquad m,k = 0,1,2,\cdots,N-1$$
$$N=6$$

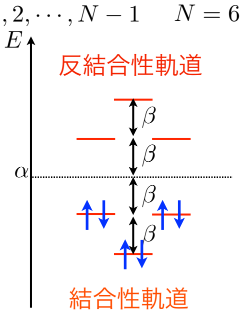
例題（ベンゼン）

$$(E-\alpha)c_m + \beta(c_{m+1}+c_{m-1}) = 0$$
$$c_m^{(k)} = e^{2\pi i\frac{km}{N}}$$
$$(E-\alpha)e^{2\pi i\frac{km}{N}} + \beta(e^{2\pi i\frac{k(m+1)}{N}} + e^{2\pi i\frac{k(m-1)}{N}}) = 0$$
$$(E-\alpha+\beta e^{2\pi i\frac{k}{N}} + \beta e^{-2\pi i\frac{k}{N}})e^{2\pi i\frac{km}{N}} = 0$$
$$E = \alpha - 2\beta\cos\frac{2\pi k}{N} \equiv E_k \qquad k=0,1,2,\cdots,N-1$$
$$N=6$$

例題（ベンゼン）

$$E = \alpha - 2\beta\cos\frac{2\pi k}{N} \equiv E_k \qquad k=0,1,2,\cdots,N-1 \qquad N=6$$

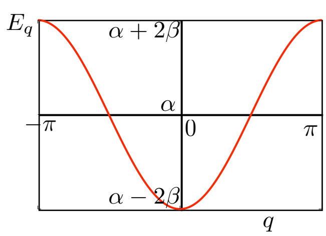
$$E_0 = \alpha - 2\beta\cos 0 = \alpha - 2\beta$$
$$E_1 = \alpha - 2\beta\cos\frac{\pi}{3} = \alpha - \beta$$
$$E_2 = \alpha - 2\beta\cos\frac{2\pi}{3} = \alpha + \beta$$
$$E_3 = \alpha - 2\beta\cos\pi = \alpha + 2\beta$$
$$E_4 = \alpha - 2\beta\cos\frac{4\pi}{3} = \alpha + \beta$$
$$E_5 = \alpha - 2\beta\cos\frac{5\pi}{3} = \alpha - \beta$$



電子のエネルギーバンド

$$E_k = \alpha - 2\beta\cos\frac{2\pi k}{N} \qquad k=0,1,2,\cdots,N-1$$

$$N \approx 10^{23} \approx \infty$$
$$0 \le \frac{2\pi k}{N} < 2\pi$$
$$-\pi \le \frac{2\pi k}{N} < \pi$$
$$q = \frac{2\pi k}{N}$$
$$E(q) = \alpha - 2\beta\cos q \qquad -\pi \le q < \pi$$



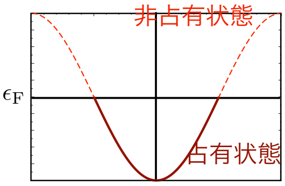
電子のエネルギーバンド

$q = \frac{2\pi k}{N}$　　$k = 0, 1, 2, \cdots, N-1$　であったので、

グラフの線の上の点の数と原子の数は等しい

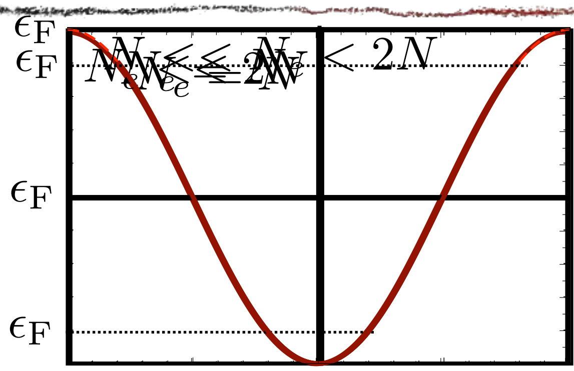
今考えている状態の電子数を N_e とすると

$N_e = N$ のとき



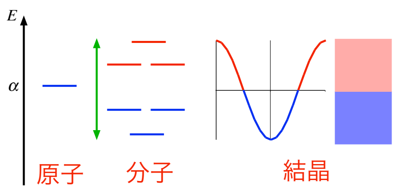
スピンの多重度「2」に注意

電子のエネルギーバンド



電子のエネルギーバンド

- 電子のバンド構造
  - 主に遷移積分によるエネルギーの分散による



電子のエネルギーバンド