

2準位原子A, B このペアがN個 (原子数2N) 原子間距離d 全長2Nd 周期2d(格子定数)

1 2 3 N N+1=1

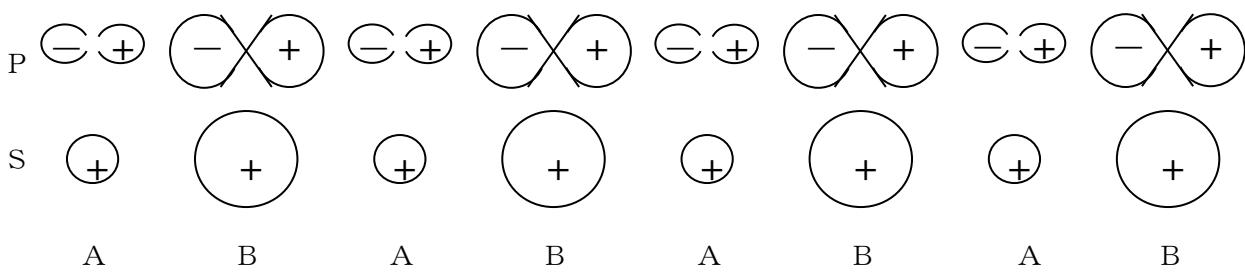
A B A B A B A B 周期的境界条件

d 2d 3d 4d 5d 6d (2N-1)d 2Nd

j-1

j

j+1



ある j について

$$\langle S_A^{jd} | H | S_B^{(j+1)d} \rangle = V_S < 0 \quad \langle P_A^{jd} | H | P_B^{(j+1)d} \rangle = V_P > 0 \quad \langle S_A^{jd} | H | P_B^{(j+1)d} \rangle = V > 0 \quad \langle P_A^{jd} | H | S_B^{(j+1)d} \rangle = -V' < 0$$

$$\langle S_A^{jd} | H | P_B^{(j-1)d} \rangle = -V < 0 \quad \langle P_A^{jd} | H | S_B^{(j-1)d} \rangle = V' > 0$$

ハミルトニアン H ($N=4$ の例)

	S_A^d	P_A^d	S_B^{2d}	P_B^{2d}	S_A^{3d}	P_A^{3d}						$S_A^{(2N-1)d}$	$P_A^{(2N-1)d}$	S_B^{2Nd}	P_B^{2Nd}	
S_A^d	E_S^A		V_S	V											V_S	$-V$
P_A^d		E_P^A	$-V'$	V_P											V'	V_P
S_B^{2d}	V_S	$-V'$	E_S^B		V_S	V'										
P_B^{2d}	V	V_P		E_P^B	$-V$	V_P										
S_A^{3d}			V_S	$-V$	E_S^A		V_S	V								
P_A^{3d}				V'	V_P		E_P^A	$-V'$	V_P							
					V_S	$-V'$	E_S^B		V_S	V'						
					V	V_P		E_P^B	$-V$	V_P						
							V_S	$-V$	E_S^A		V_S	V				
							V'	V_P		E_P^A	$-V'$	V_P				
									V_S	$-V'$	E_S^B		V_S	V'		
									V	V_P		E_P^B	$-V$	V_P		
$S_A^{(2N-1)d}$											V_S	$-V$	E_S^A		V_S	V
$P_A^{(2N-1)d}$											V'	V_P		E_P^A	$-V'$	V_P
S_B^{2Nd}	V_S	V'											V_S	$-V'$	E_S^B	
P_B^{2Nd}	$-V$	V_P											V	V_P		E_P^B

以下の4つの関数を新しい基底にとる (Bloch 関数)

$$X_j = d, 3d, 5d, \dots, (2N-1)d \text{ for } j=1, 2, 3, \dots, N$$

$$\Phi_S^A(k) = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{ikX_j} S_A^{X_j} \quad X_j = (2j-1)d$$

$$\Phi_P^A(k) = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{ikX_j} P_A^{X_j} \quad X_j = (2j-1)d$$

$$X_j = 2d, 4d, 6d, \dots, 2Nd \text{ for } j=1, 2, 3, \dots, N$$

$$\Phi_S^B(k) = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{ikX_j} S_B^{X_j} \quad X_j = 2jd$$

$$\Phi_P^B(k) = \frac{1}{\sqrt{N}} \sum_{j=1}^N e^{ikX_j} P_B^{X_j} \quad X_j = 2jd$$

$$k = \frac{2\pi n}{N \cdot 2d} = \frac{\pi}{Nd} n \quad \text{for } n = 0, \pm 1, \pm 2, \dots, \pm(N/2-1), N/2 \quad 2d : \text{周期} \quad n : \text{固有状態を指定}$$

$$-\frac{\pi}{2d} < k \leq \frac{\pi}{2d}$$

4N 次元のベクトル

$$\Phi_S^A(k) = \frac{1}{\sqrt{N}} \begin{pmatrix} e^{ikd} \\ 0 \\ 0 \\ 0 \\ e^{ik3d} \\ 0 \\ 0 \\ 0 \\ e^{ik5d} \\ 0 \\ 0 \\ 0 \\ \vdots \\ \vdots \\ \vdots \\ e^{ik(2N-1)d} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \Phi_P^A(k) = \frac{1}{\sqrt{N}} \begin{pmatrix} 0 \\ e^{ikd} \\ 0 \\ 0 \\ 0 \\ e^{ik3d} \\ 0 \\ 0 \\ 0 \\ e^{ik5d} \\ 0 \\ 0 \\ 0 \\ \vdots \\ \vdots \\ \vdots \\ e^{ik(2N-1)d} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \Phi_S^B(k) = \frac{1}{\sqrt{N}} \begin{pmatrix} 0 \\ 0 \\ e^{ik2d} \\ 0 \\ 0 \\ 0 \\ e^{ik4d} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \vdots \\ \vdots \\ \vdots \\ 0 \\ e^{ik6d} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \Phi_P^B(k) = \frac{1}{\sqrt{N}} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ e^{ik2d} \\ 0 \\ 0 \\ e^{ik4d} \\ 0 \\ 0 \\ 0 \\ 0 \\ \vdots \\ \vdots \\ \vdots \\ 0 \\ 0 \\ 0 \\ 0 \\ e^{ik6d} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \begin{array}{c} S_A^d \\ P_A^d \\ S_B^{2d} \\ P_B^{2d} \\ S_A^{3d} \\ P_A^{3d} \\ S_B^{4d} \\ P_B^{4d} \\ S_A^{5d} \\ P_A^{5d} \\ S_B^{6d} \\ P_B^{6d} \\ \vdots \\ \vdots \\ \vdots \\ S_A^{(2N-1)d} \\ P_A^{(2N-1)d} \\ S_B^{2Nd} \\ P_B^{2Nd} \end{array}$$

基底変換 (4行4N列) \times (4N行 4N列) \times (4N行 4列)

$$\begin{aligned}
 & \left(\begin{array}{c} \Phi_S^{A^*}(k) \\ \Phi_P^{A^*}(k) \\ \Phi_S^{B^*}(k) \\ \Phi_P^{B^*}(k) \end{array} \right) H \left(\Phi_S^A(k) \Phi_P^A(k) \Phi_S^B(k) \Phi_P^B(k) \right) \\
 &= \left(\begin{array}{c} \Phi_S^{A^*}(k) \\ \Phi_P^{A^*}(k) \\ \Phi_S^{B^*}(k) \\ \Phi_P^{B^*}(k) \end{array} \right) \frac{1}{\sqrt{N}} \left(\begin{array}{cccc} E_S^A e^{ikd} & 0 & V_S(e^{ik2d} + e^{ik2Nd}) & V(e^{ik2d} - e^{ik2Nd}) \\ 0 & E_P^A e^{ikd} & -V'(e^{ik2d} - e^{ik2Nd}) & V_P(e^{ik2d} + e^{ik2Nd}) \\ V_S(e^{ikd} + e^{ik3d}) & -V'(e^{ikd} - e^{ik3d}) & E_S^B e^{ik2d} & 0 \\ V(e^{ikd} - e^{ik3d}) & V_P(e^{ikd} + e^{ik3d}) & 0 & E_P^B e^{ik2d} \\ E_S^A e^{ik3d} & 0 & V_S(e^{ik2d} + e^{ik4d}) & -V(e^{ik2d} - e^{ik4d}) \\ 0 & E_P^A e^{ik3d} & V'(e^{ik2d} - e^{ik4d}) & V_P(e^{ik2d} + e^{ik4d}) \\ V_S(e^{ik3d} + e^{ik5d}) & -V'(e^{ik3d} - e^{ik5d}) & E_S^B e^{ik4d} & 0 \\ V(e^{ik3d} - e^{ik5d}) & V_P(e^{ik3d} + e^{ik5d}) & 0 & E_P^B e^{ik4d} \\ \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots \end{array} \right) \\
 &= \left(\begin{array}{cccc} E_S^A & 0 & V_S(e^{ikd} + e^{-ikd}) & V(e^{ikd} - e^{-ikd}) \\ 0 & E_P^A & -V'(e^{ikd} - e^{-ikd}) & V_P(e^{ikd} + e^{-ikd}) \\ V_S(e^{-ikd} + e^{ikd}) & -V'(e^{-ikd} - e^{ikd}) & E_S^B & 0 \\ V(e^{-ikd} - e^{ikd}) & V_P(e^{-ikd} + e^{ikd}) & 0 & E_P^B \end{array} \right) \\
 &= \left(\begin{array}{cccc} E_S^A & 0 & V_S g & V h \\ 0 & E_P^A & -V' h & V_P g \\ V_S g & V' h & E_S^B & 0 \\ -V h & V_P g & 0 & E_P^B \end{array} \right)
 \end{aligned}$$

ここで

$$g = e^{ikd} + e^{-ikd} = 2\cos kd$$

$$h = e^{ikd} - e^{-ikd} = 2i\sin kd$$

k 空間で対称性のよい点で解ける。

$$k=0 \text{ のとき } g=2 \quad h=0$$

$$\begin{cases} \begin{pmatrix} E_S^A & 0 & 2V_S & 0 \\ 0 & E_P^A & 0 & 2V_P \\ 2V_S & 0 & E_S^B & 0 \\ 0 & 2V_P & 0 & E_P^B \end{pmatrix} & (E_S^A - \lambda)(E_S^B - \lambda) - 4V_S^2 = 0 \quad \lambda = \frac{E_S^A + E_S^B}{2} \pm \sqrt{\left(\frac{E_S^A - E_S^B}{2}\right)^2 + 4V_S^2} \\ & (E_P^A - \lambda)(E_P^B - \lambda) - 4V_P^2 = 0 \quad \lambda = \frac{E_P^A + E_P^B}{2} \pm \sqrt{\left(\frac{E_P^A - E_P^B}{2}\right)^2 + 4V_P^2} \end{cases}$$

$$k = \frac{\pi}{2d} \text{ のとき } g=0 \quad h=2i$$

$$\begin{cases} \begin{pmatrix} E_S^A & 0 & 0 & 2iV \\ 0 & E_P^A & -2iV' & 0 \\ 0 & 2iV' & E_S^B & 0 \\ -2iV & 0 & 0 & E_P^B \end{pmatrix} & (E_P^A - \lambda)(E_S^B - \lambda) - 4V'^2 = 0 \quad \lambda = \frac{E_P^A + E_S^B}{2} \pm \sqrt{\left(\frac{E_P^A - E_S^B}{2}\right)^2 + 4V'^2} \\ & (E_S^A - \lambda)(E_P^B - \lambda) - 4V^2 = 0 \quad \lambda = \frac{E_S^A + E_P^B}{2} \pm \sqrt{\left(\frac{E_S^A - E_P^B}{2}\right)^2 + 4V^2} \end{cases}$$

A と B が同じ種類の原子のとき厳密に解ける。

$$E_S^A = E_S^B = E_S \quad E_P^A = E_P^B = E_P \quad V = V'$$

$$\begin{aligned} & \frac{1}{\sqrt{2}} \begin{pmatrix} (1 & 0 & 1 & 0) \\ (0 & 1 & 0 & 1) \\ (1 & 0 & -1 & 0) \\ (0 & 1 & 0 & -1) \end{pmatrix} \begin{pmatrix} E_S & 0 & V_S g & Vh \\ 0 & E_P & -Vh & V_P g \\ V_S g & Vh & E_S & 0 \\ -Vh & V_P g & 0 & E_P \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} (1) \\ (0) \\ (1) \\ (0) \end{pmatrix} \begin{pmatrix} (0) \\ (1) \\ (0) \\ (-1) \end{pmatrix} \begin{pmatrix} (1) \\ (0) \\ (-1) \\ (0) \end{pmatrix} \begin{pmatrix} (0) \\ (1) \\ (1) \\ (-1) \end{pmatrix} \\ &= \frac{1}{\sqrt{2}} \begin{pmatrix} (1 & 0 & 1 & 0) \\ (0 & 1 & 0 & 1) \\ (1 & 0 & -1 & 0) \\ (0 & 1 & 0 & -1) \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} E_S + V_S g & Vh & E_S - V_S g & -Vh \\ -Vh & E_P + V_P g & Vh & E_P - V_P g \\ E_S + V_S g & Vh & -E_S + V_S g & Vh \\ -Vh & E_P + V_P g & -Vh & -E_P + V_P g \end{pmatrix} \\ &= \begin{pmatrix} E_S + V_S g & Vh & 0 & 0 \\ -Vh & E_P + V_P g & 0 & 0 \\ 0 & 0 & E_S - V_S g & -Vh \\ 0 & 0 & Vh & E_P - V_P g \end{pmatrix} \end{aligned}$$

固有値

$$(E_S + V_S g - \lambda)(E_P + V_P g - \lambda) + V^2 h^2 = 0 \quad \lambda_{S\pm} = \frac{E_P + E_S + V_P + V_S}{2} g \pm \sqrt{\left(\frac{E_P - E_S + V_P - V_S}{2} g\right)^2 - V^2 h^2}$$

$$(E_S - V_S g - \lambda)(E_P - V_P g - \lambda) + V^2 h^2 = 0 \quad \lambda_{A\pm} = \frac{E_P + E_S - V_P - V_S}{2} g \pm \sqrt{\left(\frac{E_P - E_S - V_P - V_S}{2} g\right)^2 - V^2 h^2}$$

$$\frac{E_P + E_S}{2} = E_0 \quad \frac{V_P + V_S}{2} = V_0 \quad \frac{E_P - E_S}{2} = \Delta > 0 \quad \frac{V_P - V_S}{2} = W > 0 \quad -V^2 h^2 = |Vh|^2$$

$$\lambda_{S\pm} = E_0 + V_0 g \pm \sqrt{(\Delta + Wg)^2 - V^2 h^2}$$

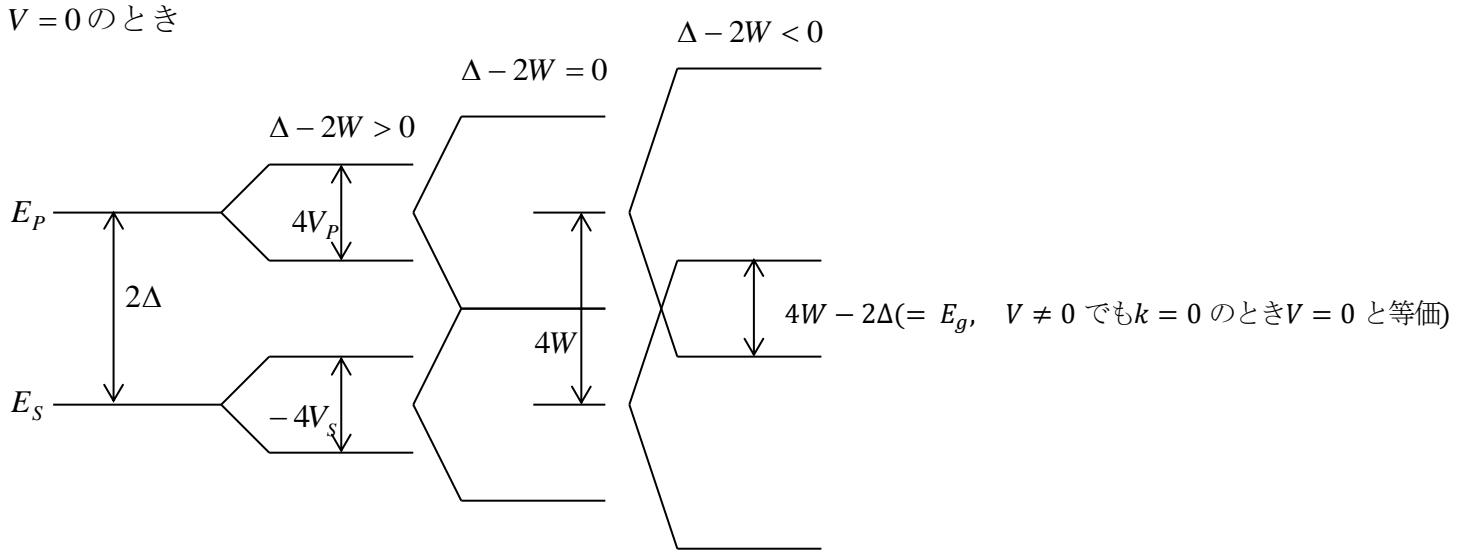
$$\lambda_{A\pm} = E_0 - V_0 g \pm \sqrt{(\Delta - Wg)^2 - V^2 h^2}$$

$A=B$ より周期 d なので、 $-\frac{\pi}{d} < k \leq \frac{\pi}{d}$ このとき $-2 \leq g \leq 2$ なので、この k の範囲では各 k に対し固有値は 2 つ、

つまり $\lambda_{S\pm} = \lambda_{A\pm}$ 。しかし、以降 $A \neq B$ の場合のイメージをつかむために周期 $2d$ 、 $-\frac{\pi}{2d} < k \leq \frac{\pi}{2d}$ とする。

このとき $0 \leq g \leq 2$ なので つねに $\Delta + Wg > 0$

$V=0$ のとき



S P相互作用がなし($V = 0$)とき

$$g = 2\cos kd \quad h = 2i\sin kd \quad 0 \leq g \leq 2$$

$\Delta - 2W > 0$ のとき $\Delta + Wg > 0$ より

$$\lambda_{S+} = E_0 + V_0g + (\Delta + Wg) = E_p + 2V_p \cos kd$$

$$\lambda_{S-} = E_0 + V_0g - (\Delta + Wg) = E_s + 2V_s \cos kd$$

$$E_p - E_s + (V_p - V_s)g > 0 \quad \text{したがって } \lambda_{S+} > \lambda_{S-}$$

$\Delta - Wg > 0$ より

$$\lambda_{A+} = E_0 - V_0g + (\Delta - Wg) = E_p - 2V_p \cos kd$$

$$\lambda_{A-} = E_0 - V_0g - (\Delta - Wg) = E_s - 2V_s \cos kd$$

$$E_p - E_s - (V_p - V_s)g = 2(\Delta - Wg) > 0 \quad \text{したがって } \lambda_{A+} > \lambda_{A-}$$

$\Delta - 2W < 0$ のとき

つねに $\Delta + Wg > 0$ なので $\lambda_{S+}, \lambda_{S-}$ は上と同じ

$\Delta - Wg > 0 (g < \Delta/W)$ のとき $\lambda_{A+} = E_p - 2V_p \cos kd \quad \lambda_{A-} = E_s - 2V_s \cos kd$

$$\Delta - Wg > 0 \text{ より } E_p - E_s - (V_p - V_s)g > 0 \quad \text{したがって } \lambda_{A+} > \lambda_{A-}$$

$\Delta - Wg < 0 (g > \Delta/W)$ のとき $\lambda_{A+} = E_s - 2V_s \cos kd \quad \lambda_{A-} = E_p - 2V_p \cos kd$

$$\Delta - Wg < 0 \text{ より } E_p - E_s - (V_p - V_s)g < 0 \quad \text{したがって } \lambda_{A+} > \lambda_{A-}$$

S P相互作用がある($V \neq 0$)とき

$k = 0$ のとき $g = 2 \quad h = 0$

$$\lambda_{S\pm} = E_0 + 2V_0 \pm (\Delta + 2W) = \begin{cases} E_p + 2V_p \\ E_s + 2V_s \end{cases}$$

$$\lambda_{A\pm} = E_0 - 2V_0 \pm \sqrt{(\Delta - 2W)^2}$$

$$\Delta - 2W > 0 \text{ のとき } E_0 - 2V_0 \pm (\Delta - 2W) = \begin{cases} E_p - 2V_p \\ E_s - 2V_s \end{cases}$$

$$\Delta - 2W < 0 \text{ のとき } E_0 - 2V_0 \pm (2W - \Delta) = \begin{cases} E_s - 2V_s \\ E_p - 2V_p \end{cases}$$

$k = \frac{\pi}{2d}$ のとき $g = 0 \quad h = 2i$

$$\lambda_{S\pm} = E_0 \pm \sqrt{\Delta^2 + 4V^2}$$

$$\lambda_{A\pm} = E_0 \pm \sqrt{\Delta^2 + 4V^2}$$

$g = \Delta/W$ のとき

$$\lambda_{A\pm} = E_0 - V_0g \pm \sqrt{(\Delta - Wg)^2 - V^2 h^2} = E_0 - V_0 \frac{\Delta}{W} \pm \sqrt{-V^2 h^2}$$

$$\boxed{\begin{aligned} E_g &= \lambda_{A+} - \lambda_{A-} = 2\sqrt{(\Delta - 2W)^2} \\ &= -2(\Delta - 2W) \\ &= 2(2W - \Delta) \\ &= 2(V_p - V_s - \frac{E_p - E_s}{2}) \end{aligned}}$$

Δ/W が2より大きい場合はどうなる？

固有関数

$$\Psi_k^{\lambda_{S+}} = \frac{1}{\sqrt{2N}} \sum_{n=1}^{2N} e^{iknd} [A(k)S^{nd} + B(k)P^{nd}]$$

$$\Psi_k^{\lambda_{S-}} = \frac{1}{\sqrt{2N}} \sum_{n=1}^{2N} e^{iknd} [B(k)S^{nd} + A(k)P^{nd}]$$

$$\Psi_k^{\lambda_{A+}} = \frac{1}{\sqrt{2N}} \sum_{n=1}^{2N} (-e^{ikd})^n [-C(k)S^{nd} + D(k)P^{nd}] = \Psi_{k+\pi/d}^{\lambda_{S+}} \quad e^{i(k+\pi/d)nd} = e^{iknd+in\pi} = e^{iknd} (\cos n\pi + i \sin n\pi) = \begin{cases} e^{iknd} & (n: even) \\ -e^{iknd} & (n: odd) \end{cases}$$

$$\Psi_k^{\lambda_{A-}} = \frac{1}{\sqrt{2N}} \sum_{n=1}^{2N} (-e^{ikd})^n [D(k)S^{nd} - C(k)P^{nd}] = \Psi_{k+\pi/d}^{\lambda_{S-}}$$

$$\Phi_S^A(k) = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ik(2n-1)d} S_A^{(2n-1)d} \quad \Phi_P^A(k) = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ik(2n-1)d} P_A^{(2n-1)d}$$

$$\Phi_S^B(k) = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ik2nd} S_B^{2nd} \quad \Phi_P^B(k) = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ik2nd} P_B^{2nd}$$

$$\text{A=B のとき} \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2N}} \sum_{n=1}^{2N} e^{iknd} S^{nd} \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2N}} \sum_{n=1}^{2N} e^{iknd} P^{nd}$$

$k=0$ のとき ($g=2, h=0$)

$$\Psi_{k=0}^{\lambda_{S+}} = \frac{1}{\sqrt{2N}} \sum_{n=1}^{2N} P^{nd} \quad \text{anti-bonding P}$$

$$\Psi_{k=0}^{\lambda_{S-}} = \frac{1}{\sqrt{2N}} \sum_{n=1}^{2N} S^{nd} \quad \text{bonding S}$$

$$\Psi_{k=0}^{\lambda_{A+}} = \frac{1}{\sqrt{2N}} \sum_{n=1}^{2N} (-1)^n P^{nd} = \Psi_{\pi/d}^{\lambda_{S+}} \quad \text{bonding P} \quad (\Delta - 2W > 0 \text{ のとき}) \quad (\Delta - 2W < 0 \text{ のときは anti-bonding S})$$

$$\Psi_{k=0}^{\lambda_{A-}} = \frac{1}{\sqrt{2N}} \sum_{n=1}^{2N} (-1)^n S^{nd} = \Psi_{\pi/d}^{\lambda_{S-}} \quad \text{anti-bonding S} \quad (\Delta - 2W > 0 \text{ のとき}) \quad (\Delta - 2W < 0 \text{ のときは bonding P})$$

異種原子A,Bの場合もS軌道,P軌道のみの重ね合わせ。ただしAとBは混じる。

$$A(k) = \frac{Vh}{E} \quad B(k) = \frac{1}{E} [\Delta + Wg + \sqrt{(\Delta + Wg)^2 - V^2 h^2}]$$

$$C(k) = \frac{Vh}{F} \quad D(k) = \frac{1}{F} [\Delta - Wg + \sqrt{(\Delta - Wg)^2 - V^2 h^2}]$$

$$E = \sqrt{2[(\Delta + Wg)^2 - V^2 h^2]} + 2(\Delta + Wg) \sqrt{(\Delta + Wg)^2 - V^2 h^2}$$

$$F = \sqrt{2[(\Delta - Wg)^2 - V^2 h^2]} + 2(\Delta - Wg) \sqrt{(\Delta - Wg)^2 - V^2 h^2}$$

$$|A(k)|^2 + |B(k)|^2 = 1, \quad A(k)B^*(k) + B(k)A^*(k) = 0, \quad A^*(k) = -A(k) \quad B^*(k) = B(k) \quad \left\langle \Psi_{k=0}^{\lambda_{A+}} \left| \sum_{n=1}^{2N} x_n \right| \Psi_{k=0}^{\lambda_{A-}} \right\rangle = \langle P | x | S \rangle$$

$k \rightarrow k + \pi/d$
$g \rightarrow -g$
$h \rightarrow -h$
$A \rightarrow -C$
$B \rightarrow D$

$$\langle S^{nd} | x | P^{md} \rangle = \delta_{mn} \langle S | x | P \rangle$$

$$\langle S^{nd} | S^{md} \rangle = \delta_{mn} \quad \langle P^{nd} | P^{md} \rangle = \delta_{mn} \quad (n = m \pm 1 の場合でも…重なり積分無視)$$

$$H' = -\mathbf{M} \cdot \mathbf{E}_0 \cos(\omega t - kX)$$

$$M = -\sum_j e \mathbf{r}_j \quad \theta_j : \mathbf{r}_j \text{ と } \mathbf{E}_0 \text{ のなす角}$$

$$H' = \sum_j e(r_j \cos \theta_j) E_0 \cos(\omega t - k X_j)$$

$$= \sum_j \frac{e x_j E_0}{2} (e^{i(\omega t - k X_j)} + e^{-i(\omega t - k X_j)})$$

$$\begin{aligned} \langle \Psi_{k_2}^{\lambda_{A+}} | \sum_n x_n e^{ikX_n} | \Psi_{k_1}^{\lambda_{A-}} \rangle &= \frac{1}{2N} \left\langle \sum_{m=1}^{2N} (-e^{ik_2 d})^m [-C(k_2)S^{md} + D(k_2)P^{md}] \right| \sum_{n=1}^{2N} x_n e^{iknd} \left| \sum_{l=1}^{2N} (-e^{ik_1 d})^l [D(k_1)S^{ld} - C(k_1)P^{ld}] \right\rangle \\ &= \frac{1}{2N} \sum_{n=1}^{2N} e^{i(-k_2 + k + k_1)nd} [C^*(k_2)C(k_1) \langle S^{nd} | x_n | P^{nd} \rangle + D^*(k_2)D(k_1) \langle P^{nd} | x_n | S^{nd} \rangle] \\ &= [C^*(k_2)C(k_1) + D^*(k_2)D(k_1)] \langle S | x | P \rangle \quad \text{for } k_2 = k_1 + k \\ &\approx \langle S | x | P \rangle \quad \text{for } k_1 \approx k_2 \end{aligned}$$

(修正 $\langle \sum (e^{-ik_2 d})^m [] | \sum e^{-ikX_n} | \sum (e^{-ik_1 d})^l [] \rangle X_n = nd$ より $k_2 = k_1 + k$)