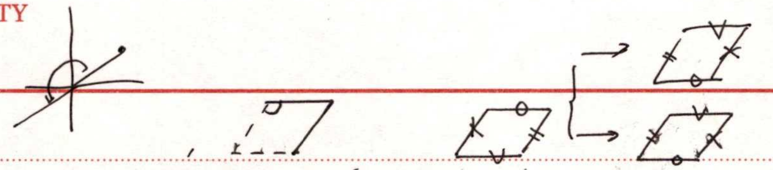
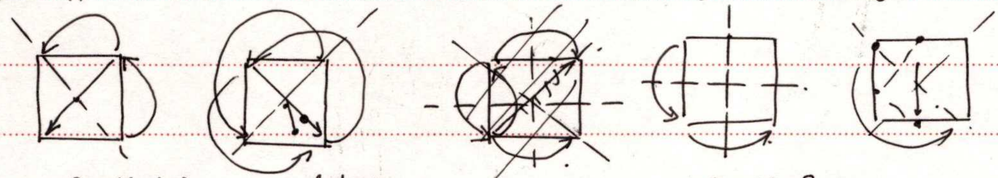
北京大學 PEKING UNIVERSITY

HW5 (3-22)



1. 正方形 C_{4v}



C_4: 旋转　　C_2: 旋转　　　　　2个垂直镜面

正方形二维点群反演操作为两个垂直镜面反射相乘，或是 C_2 轴旋转.

2. (1) 书2.1 Pf:

一对1价的离子势能: $+\sum'_{n_1,n_2,n_3} \frac{q^2}{4\pi\varepsilon_0 r}\frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2+n_2^2+n_3^2}}$

∴ Madlung 常数 $\alpha=\sum' \frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2+n_2^2+n_3^2}}$

$$=2\left(1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\cdots\right)$$

$$=2\ln 2.$$

(2) 书2.2 离子电荷加倍

$$U=\cancel{N\sum_{n_1}}-\frac{q^2\alpha N}{4\pi\varepsilon_0 r}+\frac{B}{r^n}$$

$$\therefore \frac{dU}{dr}=+\frac{q^2\alpha N}{4\pi\varepsilon_0 r^2}-n\frac{B}{r^{n+1}}=0$$

$$\therefore nB=\frac{q^2\alpha N}{4\pi\varepsilon_0}r_0^{n-1}$$

$$r_0=\sqrt[n-1]{nB\cdot\frac{\alpha N q^2}{4\pi\varepsilon_0}}$$

∴ r_0 变为原来 $\sqrt[n-1]{4}$ 倍.

$W=+\frac{q^2\alpha N}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$. 变为原来 $\frac{4}{4^{\frac{1}{n-1}}}=4^{1-\frac{1}{n-1}}$ 倍.

3. $\cancel{\langle c_1 \Psi_1 |}$

(1) $\delta\left\{\langle c_1\varphi_A + c_2\varphi_B|\hat{H}|c_1\varphi_A+c_2\varphi_B\rangle - \lambda(\langle c_1\varphi_A+c_2\varphi_B|c_1\varphi_A+c_2\varphi_B\rangle -1)\right\} = 0$

∴ $\cancel{\langle\varphi_A|\hat{H}}$

$\cancel{\langle c_1\varphi_A+c_2\varphi_B|H}$

$(\langle\varphi_A|\hat{H}|\Psi\rangle - \lambda\langle\varphi_A|\Psi\rangle)\,\delta c_1^* = 0$

$(\langle\varphi_B|\hat{H}|\Psi\rangle - \lambda\langle\varphi_B|\Psi\rangle)\,\delta c_2^* = 0$

∴ $\langle\varphi_A|\left(\hat{H}|\Psi\rangle - \lambda|\Psi\rangle\right) = 0$

$\langle\varphi_B|\left(\hat{H}|\Psi\rangle - \lambda|\Psi\rangle\right) = 0$

∴ $\begin{cases} c_1^* H_{AA} + c_2^* H_{BA} - \lambda c_1^* - \lambda c_2^* S_{BA} = 0 \\ c_2^* H_{BB} + c_1^* H_{AB} - \lambda c_2^* - \lambda c_1^* S_{AB} = 0 \end{cases}$

∴ $\begin{cases} (H_{AA}-E)c_1^* + (H_{BA}-ES_{BA})c_2^* = 0 \\ (H_{BB}-E)c_2^* + (H_{AB}-ES_{AB})c_1^* = 0. \end{cases}$

(2) $E = \frac{1}{\langle\Psi|\Psi\rangle}\left(|c_A|^2H_{AA}+|c_B|^2H_{BB}+c_A^*c_BH_{AB}+c_B^*c_AH_{BA}\right)$

$\langle\Psi|\Psi\rangle \rightarrow |c_A|^2+|c_B|^2+c_A^*c_BS_{AB}+c_B^*c_AS_{BA}$

$\frac{\partial E}{\partial c_1} = 0 \Rightarrow \left(c_1^*H_{AA}+c_2^*H_{BA}\right)\langle\Psi|\Psi\rangle - (\cdots)(c_A^* + c_B^* S_{BA})$

$= \cancel{H_{AA}c_1^*}\ c_1^*H_{AA}(\cancel{|c_A|^2}+|c_B|^2+c_A^*c_BS_{AB}+\cancel{c_B^*c_AS_{BA}})$

$+ c_2^*H_{BA}(\cancel{|c_A|^2}+|c_B|^2+c_A^*c_BS_{AB}+\cancel{c_B^*c_AS_{BA}})$

$- c_A^*(\cancel{|c_A|^2H_{AA}}+|c_B|^2H_{BB}+c_A^*c_BH_{AB}+\cancel{c_B^*c_AH_{BA}})$

$- c_B^*S_{BA}(\cancel{|c_A|^2H_{AA}}+|c_B|^2H_{BB}+c_A^*c_BH_{AB}+\cancel{c_B^*c_AH_{BA}}) = 0$

$\cancel{c_2^* c_1^* H_{BB}}(|c_A|^2+c_B^*c_AS_{BA})\ (c_2^*H_{BB}+c_1^*H_{AB})$

$= c_B^*(|c_A|^2H_{AA}+c_B^*c_AH_{BA}) + c_A^*S_{AB}(|c_A|^2H_{AA}+c_B^*c_AH_{BA})$