4. 总能量及作用力

4.1 总能量

$$E_{tot} = E_K + E_{e-c} + E_{e-e} + E_{xc}^{LDA} + E_{c-c}$$

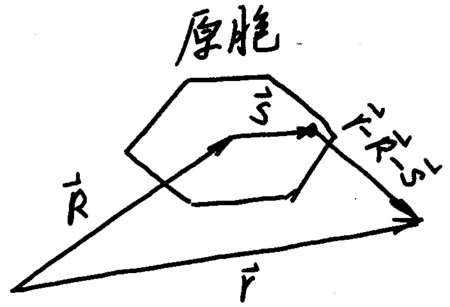
$$E_K = \sum_i \int d\vec{r}\, \phi_i^*(\vec{r}) \left(-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2\right) \phi_i(\vec{r})\, f_i$$

f_i — i态占据几率

$$E_{e-c} = \sum_i \int d\vec{r}\, \phi_i^*(\vec{r})\, v_{ext}(\vec{r})\, \phi_i(\vec{r})\, f_i$$

$$v_{ext}(\vec{r}) = \sum_{\vec{R},\vec{S}} \left[v_S(\vec{r}-\vec{R}-\vec{S}) + \sum_l \delta v_{Sl}(\vec{r}-\vec{R}-\vec{S})\, \hat{P}_l \right]$$

$$= \sum_{\vec{S}} \tilde{v}_S(\vec{r}-\vec{S}) + \sum_{\vec{S}} \sum_l \delta\tilde{v}_{Sl}(\vec{r}-\vec{S})\, \hat{P}_l$$



$$\tilde{v}_S(\vec{r}-\vec{S}) = \sum_{\vec{R}} v_S(\vec{r}-\vec{R}-\vec{S})$$

$$\delta\tilde{v}_{Sl}(\vec{r}-\vec{S}) = \sum_{\vec{R}} \delta v_{Sl}(\vec{r}-\vec{R}-\vec{S})$$

$$E_{e-e} = \frac{e^2}{2} \int \frac{n(\vec{r})\, n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,' , \qquad n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2 f_i$$

$$E_{c-c} = \frac{e^2}{2} \sum_{\substack{\vec{R},\vec{R}' \\ \vec{S},\vec{S}'}}{}' \frac{Z_S^c Z_{S'}^c}{|\vec{R}+\vec{S}-\vec{R}'-\vec{S}'|}$$

$Z_S^c e$ 是 S 原子实的电荷. 原子实近似为点电荷, 原子实电荷之间的重叠忽略不计. $\vec{R}+\vec{S} \neq \vec{R}'+\vec{S}'$

$$E_{xc} = \int n(\vec{r})\, \epsilon_{xc}^{LDA}(\vec{r})\, d\vec{r}$$

平面波展开:

$$\phi_i(\vec{r}) = \phi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}} C_{\vec{G}}(n\vec{k})\, e^{i\vec{G}\cdot\vec{r}}$$

$\vec{k} \in$ 第一布里渊区

n 能带

$\vec{G}$ 倒格矢

$$n(\vec{r}) = \sum_{n\vec{k}} |\phi_{n\vec{k}}(\vec{r})|^2 f_{n\vec{k}} = \sum_{n\vec{k}} n_{n\vec{k}}(\vec{r}) f_{n\vec{k}}$$

$$n_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} n_{n\vec{k}}(\vec{G}) e^{i\vec{G}\cdot\vec{r}} \quad ; \quad n_{n\vec{k}}(\vec{G}) = \sum_{\vec{G}'} C^*_{\vec{G}'-\vec{G}}(n\vec{k}) C_{\vec{G}'}(n\vec{k})$$

E_{e-c}，E_{e-e} 和 E_{c-c} 分别都发散，将 E_{e-c} 改写为：

$$v_{ext}(\vec{r}) = \sum_{\vec{s}} \sum_{\vec{R}} \frac{-e^2 Z_s^c}{|\vec{r}-\vec{R}-\vec{s}|} + \sum_{\vec{s}} \Big\{ \underbrace{\sum_{\vec{R}} v_s(\vec{r}-\vec{R}-\vec{s})}_{\widetilde{v}_s(\vec{r}-\vec{s})} + \sum_{\vec{R}} \frac{+e^2 Z_s^c}{|\vec{r}-\vec{R}-\vec{s}|} \Big\} + \sum_{\vec{s}} \sum_{l} \delta v_{sl}(\vec{r}-\vec{s}) \hat{P}_l$$

$$E_{e-c} = E_{e-c}^{coul} + \Delta E_{e-c}$$

$$E_{e-c}^{coul} = \int d\vec{r}\, n(\vec{r}) \sum_{\vec{s}\vec{R}} \frac{-e^2 Z_s^c}{|\vec{r}-\vec{R}-\vec{s}|}$$

$E_{e-c}^{coul} + E_{e-e} + E_{c-c} = E_{coul}$ 是一个周期分布的正点电荷与一个连续周期分布的负电荷组成系统的库仑能，正、负电荷量相同。由静电问题的可叠加性，可在上述系统中加入一个均匀分布的负电荷和正电荷。原来的系统可看作由 A，B 两个新子系统组成：

A：在均匀分布的负电荷中周期分布的正点电荷；

B：在均匀分布的正电荷中周期连续分布的负电荷.

所以

$E_{coul} = E_A + E_B + E_{A-B}$　　发散项可明显抵消，见附录.

总能量可改写为： $E_{tot} = E_K + E'_{e-c} + E'_{e-e} + E^{LDA}_{xc} + E'_{c-c}$

$$E_K = V_0 \sum_{n\vec{k}} \sum_{\vec{G}} \frac{\hbar^2(\vec{k}+\vec{G})^2}{2m} |C_{\vec{G}}(n\vec{k})|^2 f_{n\vec{k}}$$

$$E'_{e-c} = E_{A-B} + \Delta E_{e-c} = V_0 \sum_{n\vec{k}} \sum_{\vec{G}\vec{S}} n^*_{n\vec{k}}(\vec{G}) e^{-i\vec{G}\cdot\vec{S}} v_s(\vec{G}) f_{n\vec{k}} +$$

$$+ V_0 \sum_{n\vec{k}} \sum_{\vec{G}'\vec{G}} \sum_{\vec{S}l} C^*_{\vec{G}'}(n\vec{k}) C_{\vec{G}}(n\vec{k}) e^{-i(\vec{G}'-\vec{G})\cdot\vec{S}} \delta v_{sl}(\vec{k}+\vec{G}', \vec{k}+\vec{G}) f_{n\vec{k}}$$

$$E'_{e-e} = E_B = V_0 \frac{1}{2} \sum_{\vec{G}\neq 0} \frac{4\pi e^2}{|\vec{G}|^2} |n(\vec{G})|^2 , \quad n(\vec{G}) = \int d\vec{r}\, n(\vec{r}) \frac{e^{-i\vec{G}\cdot\vec{r}}}{V_0} = \sum_{n\vec{k}} n_{n\vec{k}}(\vec{G}) f_{n\vec{k}}$$

$$E^{LDA}_{xc} = V_0 \sum_{\vec{G}} n^*(\vec{G})\, \epsilon^{LDA}_{xc}(\vec{G}) , \quad n^*(\vec{G}) = n(-\vec{G}) . \quad n^*_{n\vec{k}}(\vec{G}) = n_{n\vec{k}}(-\vec{G}) ,$$

$$\epsilon^{LDA}_{xc}(\vec{G}) = \int \frac{d\vec{r}}{\Omega_c} e^{-i\vec{G}\cdot\vec{r}} \epsilon^{LDA}_{xc}(\vec{r})$$

$$E'_{c-c} = E_A = \frac{e^2}{2} \sum_{SS'} Z^c_S \gamma_{SS'} Z^c_{S'} ,$$

其中：

$$v_s(\vec{G}) = \begin{cases} \frac{1}{\Omega_c} \int d\vec{r}\, e^{-i\vec{G}\cdot\vec{r}} v_s(\vec{r}) & (\vec{G}\neq 0,\ \Omega_c \text{原胞体积}) \\ \frac{1}{\Omega_c} \int d\vec{r} \left[v_s(\vec{r}) + \frac{Z^c_S e^2}{r} \right] & (\vec{G}=0,\ v_s(r) \xrightarrow{r\to\infty} -\frac{Z^c_S e^2}{r}) \end{cases}$$

$$\delta v_{sl}(\vec{k}+\vec{G}', \vec{k}+\vec{G}) = \frac{1}{\Omega_c} \int d\vec{r}\, e^{-i(\vec{k}+\vec{G}')\cdot\vec{r}} \delta v_{sl}(r) \hat{P}_l\, e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$$

$$= \frac{4\pi}{\Omega_c} (2l+1) P_l \left[\frac{(\vec{k}+\vec{G}')\cdot(\vec{k}+\vec{G})}{|\vec{k}+\vec{G}'|\,|\vec{k}+\vec{G}|} \right] \int_0^\infty \delta v_{sl}(r)\, j_l(|\vec{k}+\vec{G}'|r)\, j_l(|\vec{k}+\vec{G}|r)\, r^2 dr$$

非K-B赝势

$$\gamma_{SS'}\ (\text{Ewald常数}) = \frac{4\pi}{V_0} \sum_{\vec{G}\neq 0} \left\{ \frac{1}{|\vec{G}|^2} \cos[\vec{G}\cdot(\vec{S}-\vec{S}')] \exp\left[-\frac{|\vec{G}|^2}{4\eta^2}\right] - \right.$$

$$-\frac{\pi}{\eta^2 V_0} + \sum_{\substack{\vec R \\ (\vec R+\vec s-\vec s'\neq 0)}} \left[\frac{\mathrm{erfc}(\eta x)}{x}\right]_{x=|\vec R+\vec s-\vec s'|} - \frac{2\eta}{\sqrt{\pi}}\delta_{ss'}\Big\}$$

η: Ewald求和的收敛因子.

动量空间的本征值方程:

$$\frac{dE_{tot}}{dC^*_{\vec G}(n\vec k)} - \epsilon\frac{dI_{n\vec k}}{dC^*_{\vec G}(n\vec k)} = 0 \Rightarrow \sum_{\vec G'} H_{\vec G\vec G'}(\vec k)\, C_{\vec G'}(n\vec k) = \epsilon_{n\vec k}\, C_{\vec G}(n\vec k)$$

$$I_{n\vec k} = \int |\varphi_{n\vec k}(\vec r)|^2 d\vec r = V_0 \sum_{\vec G} |C_{\vec G}(n\vec k)|^2 = 1$$

$$H_{\vec G\vec G'}(\vec k) = \frac{\hbar^2(\vec k+\vec G)^2}{2m}\delta_{\vec G,\vec G'} + \sum_{\vec s} e^{-i(\vec G-\vec G')\cdot\vec s}\, v_s(\vec G-\vec G') +$$

$$+\sum_{\vec s\, l} e^{-i(\vec G-\vec G')\cdot\vec s}\,\delta v_{sl}(\vec k+\vec G, \vec k+\vec G') + (1-\delta_{\vec G,\vec G'})\frac{4\pi e^2}{|\vec G-\vec G'|^2} n^*(\vec G-\vec G') +$$

$$+\epsilon_{xc}^{LDA}(\vec G-\vec G')$$

4.2 作用力.

Hellmann - Feynman 定理 (1937 & 1939):

$$\vec f_s = -\nabla_{\vec s} E_{tot} = -\sum_{n\vec k}\sum_{\vec G}\nabla_{\vec s} C^*_{\vec G}(n\vec k)\frac{\partial E_{tot}}{\partial C^*_{\vec G}(n\vec k)} - \sum_{n\vec k}\sum_{\vec G}\frac{\partial E_{tot}}{\partial C_{\vec G}(n\vec k)}\nabla_{\vec s} C_{\vec G}(n\vec k) -$$

$$-\nabla_{\vec s} E_{tot}\big|_{\psi} = -\sum_{n\vec k}\sum_{\vec G} V_0\Big\{\nabla_{\vec s} C^*_{\vec G}(n\vec k)\,\epsilon_{n\vec k}\, C_{\vec G}(n\vec k) + \epsilon_{n\vec k}\, C^*_{\vec G}(n\vec k)\nabla_{\vec s} C_{\vec G}(n\vec k)\Big\} -$$

$$-\nabla_{\vec s} E_{tot}\big|_{\psi} = -V_0\sum_{n\vec k}\epsilon_{n\vec k}\cdot\nabla_{\vec s}\underbrace{\sum_{\vec G} C^*_{\vec G}(n\vec k)\, C_{\vec G}(n\vec k)}_{=1} - \nabla_{\vec s} E_{tot}\big|_{\psi}$$

$$= -\nabla_{\vec s} E_{tot}\big|_{\psi}$$

$$= V_0 i \sum_{n\vec{k}} \sum_{\vec{G}} \vec{G}\, n^*_{n\vec{k}}(\vec{G})\, e^{-i\vec{G}\cdot\vec{s}}\, v_s(\vec{G})\, f_{n\vec{k}} + V_0 i \sum_{n\vec{k}} \sum_{\vec{G}'\vec{G}} \sum_{l} (\vec{G}'-\vec{G})\, C^*_{\vec{G}'}(n\vec{k})\, C_{\vec{G}}(n\vec{k}) \,*$$

$$* \, e^{-i(\vec{G}'-\vec{G})\cdot\vec{s}}\, \delta v_{sl}(\vec{k}+\vec{G}', \vec{k}+\vec{G})\, f_{n\vec{k}} + e^2 Z_s^c \sum_{s'\neq s} Z_{s'}^c \Big\{ \frac{4\pi}{V_0} \sum_{\vec{G}\neq 0} \frac{\vec{G}}{|\vec{G}|^2} \sin[\vec{G}\cdot(\vec{s}-\vec{s}')] \,*$$

$$* \exp\left[-\frac{|\vec{G}|^2}{4\eta^2}\right] + \sum_{\vec{R}} \left[\frac{\vec{x}\, \mathrm{erfc}(\eta|\vec{x}|)}{|\vec{x}|^3} + \frac{2\eta\vec{x}}{\sqrt{\pi}\,|\vec{x}|^2}\, e^{-|\vec{x}|^2} \right]_{\vec{x}=\vec{R}+\vec{s}-\vec{s}'} \Big\}$$

4.3 附录

$$E_A = \frac{e^2}{2} \sum_{ss'} Z_s^c\, \gamma_{ss'}\, Z_{s'}^c \qquad (\text{Ewald energy}, 1935)$$

$$E_B = \frac{V_0}{2} \sum_{\vec{G}\neq 0} \frac{\vec{E}_B^*(\vec{G})\cdot\vec{E}_B(\vec{G})}{4\pi}, \qquad E_{A-B} = V_0 \sum_{\vec{G}\neq 0} \frac{\vec{E}_A^*(\vec{G})\cdot\vec{E}_B(\vec{G})}{4\pi}$$

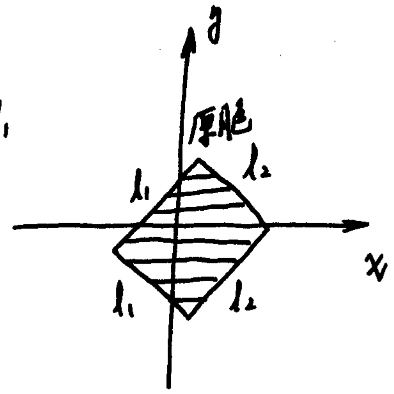
由于 $\vec{E}_A$ 和 $\vec{E}_B$ 是周期分布的电荷产生的电场场强.

$$\vec{E}_{A,B}(\vec{G}=0) = \int_{\Omega_c} \frac{d\vec{r}}{\Omega_c}\, e^{-i\vec{G}\cdot\vec{r}}\, \vec{E}_{A,B}(\vec{r})\Big|_{\vec{G}=0} = \int_{\Omega_c} \frac{d\vec{r}}{\Omega_c}\, \vec{E}_{A,B}(\vec{r}) = \int \frac{d\vec{r}}{\Omega_c} \left[-\nabla_{\vec{r}} U_{A,B}(\vec{r})\right]$$

如

$$E_x(\vec{G}=0) = \int \frac{d\vec{r}}{\Omega_c} \left[-\frac{\partial}{\partial x} U(\vec{r})\right] \overset{\text{二维举例}}{=\!=\!=} -\int \frac{dy}{\Omega_c} U(\vec{r})\Big|_{\vec{r}\in l_1}$$

$$+ \int \frac{dy}{\Omega_c} U(\vec{r})\Big|_{\vec{r}\in l_2} = 0 \qquad (U(\vec{r})\text{具有周期性})$$



所以

$$\vec{E}_{A,B}(\vec{G}=0) = 0.$$

$$U_B(\vec r) = \int_{V_0} \frac{-e\, n(\vec r\,')}{|\vec r - \vec r\,'|} d\vec r\,' + \int_{V_0} \frac{\rho_+}{|\vec r - \vec r\,'|} d\vec r\,' = \int_{V_0} \frac{-e\, n(\vec r\,')}{|\vec r - \vec r\,'|} d\vec r\,' + C_+$$

$$U_A(\vec r) = \sum_{\vec R, \vec S} \frac{e Z_s^c}{|\vec r - \vec R - \vec S|} + \int_{V_0} \frac{\rho_-}{|\vec r - \vec r\,'|} d\vec r\,' = \sum_{\vec R, \vec S} \frac{e Z_s^c}{|\vec r - \vec R - \vec S|} + C_-$$

$$\vec E_A(\vec G) = \int_{V_0} \frac{d\vec r}{V_0} e^{-i\vec G\cdot\vec r} \left(-\nabla_{\vec r} U_A(\vec r)\right) = -i\vec G \int_{V_0} \frac{d\vec r}{V_0} e^{-i\vec G\cdot\vec r} U_A(\vec r)$$

$$= -i\vec G \int_{\Omega_c} \frac{d\vec r}{\Omega_c} e^{-i\vec G\cdot\vec r} U_A(\vec r) = -i\vec G \cdot U_A(\vec G) \qquad (\vec G \neq 0)$$

$$\vec E_B(\vec G) = \int_{V_0} \frac{d\vec r}{V_0} e^{-i\vec G\cdot\vec r} \left\{ -\nabla_{\vec r} \int_{V_0} \frac{-e\, n(\vec r\,')}{|\vec r - \vec r\,'|} d\vec r\,' \right\}$$

$$= i\vec G \int_{V_0} \frac{d\vec r}{V_0} e^{-i\vec G\cdot\vec r} \int \frac{e\, n(\vec r\,')}{|\vec r - \vec r\,'|} d\vec r\,' = i\vec G \int_{V_0} dr \frac{e^{-i\vec G\cdot\vec r}}{|\vec r|} \int \frac{d\vec r\,'}{V_0} e\, n(\vec r\,') e^{-i\vec G\cdot\vec r\,'}$$

$$= i\vec G \frac{4\pi e}{|\vec G|^2} n(\vec G)$$

$$E_{A-B} = V_0 \sum_{\vec G \neq 0} \frac{\vec E_A(\vec G)\cdot \vec E_B^*(\vec G)}{4\pi} = -V_0 \sum_{\vec G \neq 0} n^*(\vec G)\, V_A(\vec G)$$

$$V_A(\vec G) = e\, U_A(\vec G) = \int_{\Omega_c} \frac{d\vec r}{\Omega_c} \sum_{\vec R, \vec S} \frac{e^2 Z_s}{|\vec r - \vec R - \vec S|} e^{-i\vec G\cdot\vec r} \qquad (\vec G \neq 0)$$

$$E_B = \frac{V_0}{2} \sum_{\vec G \neq 0} \frac{4\pi e^2}{|\vec G|^2} |n(\vec G)|^2$$

注：E_{A-B} 与 ΔE_{e-c} 中的部分项相互抵消.