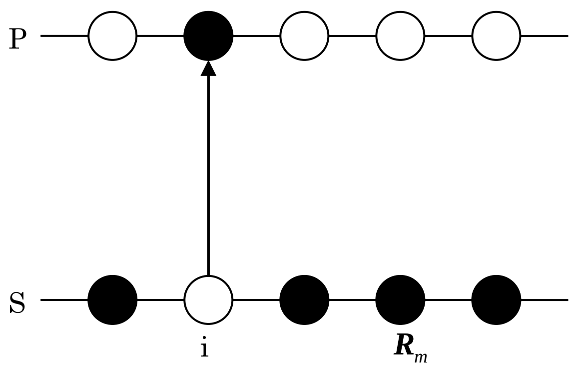
並進対称性を持つ結晶ではある原子(分子)だけを励起しても原子(分子)間相互作用による共鳴効果によって励起は原子から原子へと伝わっていく。結晶内を伝播する電子励起エネルギー　　励起子 exciton

Frenkel 励起子（簡単のためスピンの自由度は考慮しない）



$$\psi_g(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N)=\prod_m \phi_S(\boldsymbol{r}_m-\boldsymbol{R}_m)$$

$$\psi_n=\psi_{\boldsymbol{R}_n,\boldsymbol{R}_n}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N)=\phi_P(\boldsymbol{r}_n-\boldsymbol{R}_n)\prod_{m\neq n}\phi_S(\boldsymbol{r}_m-\boldsymbol{R}_m)$$

$$H=-\sum_i\frac{\hbar^2}{2m}\nabla_i{}^2-\sum_i\sum_I\frac{Ze^2}{4\pi\varepsilon_0|\boldsymbol{r}_i-\boldsymbol{R}_I|}+\sum_{i<j}\sum\frac{e^2}{4\pi\varepsilon_0|\boldsymbol{r}_i-\boldsymbol{r}_j|}$$

$$=\sum_n h_n+\sum_{n<m}\sum v_{nm}$$

$H_{nn}=\langle\psi_n|H|\psi_n\rangle=E_P-E_S$　**基底状態 ψ_g のエネルギー $E_g=NE_S$ を基準**　$E_{nn}=E_P+(N-1)E_S$

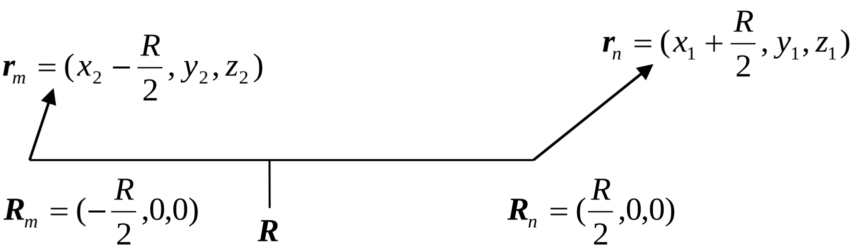
$$H_{nm}=\langle\psi_n|H|\psi_m\rangle=\int d\boldsymbol{r}_n d\boldsymbol{r}_m\phi_P{}^*(\boldsymbol{r}_n-\boldsymbol{R}_n)\phi_S{}^*(\boldsymbol{r}_m-\boldsymbol{R}_m)v_{nm}\phi_S(\boldsymbol{r}_n-\boldsymbol{R}_n)\phi_P(\boldsymbol{r}_m-\boldsymbol{R}_m)\qquad v_{nm}=\frac{e^2}{4\pi\varepsilon_0|\boldsymbol{r}_n-\boldsymbol{r}_m|}$$

$$\boldsymbol{r}_n-\boldsymbol{r}_m=[(\boldsymbol{r}_n-\boldsymbol{R}_n)+\boldsymbol{R}_n]-[(\boldsymbol{r}_m-\boldsymbol{R}_m)+\boldsymbol{R}_m]=(\boldsymbol{r}_n-\boldsymbol{R}_n)-(\boldsymbol{r}_m-\boldsymbol{R}_m)+(\boldsymbol{R}_n-\boldsymbol{R}_m)$$

$$\boldsymbol{r}_n-\boldsymbol{R}_n=(x_1,y_1,z_1)=\boldsymbol{r}_1$$

$$\boldsymbol{r}_m-\boldsymbol{R}_m=(x_2,y_2,z_2)=\boldsymbol{r}_2$$

$$\boldsymbol{R}_n-\boldsymbol{R}_m=\boldsymbol{R}_{nm}=\boldsymbol{R}=(R,0,0)$$



$$\frac{1}{|\boldsymbol{r}_n-\boldsymbol{r}_m|}=\frac{1}{|\boldsymbol{R}+(\boldsymbol{r}_n-\boldsymbol{R}_n)-(\boldsymbol{r}_m-\boldsymbol{R}_m)|}$$

$$=\frac{1}{\sqrt{(x_1-x_2+R)^2+(y_1-y_2)^2+(z_1-z_2)^2}}$$

$$=\frac{1}{R[(1+\frac{x_1-x_2}{R})^2+(\frac{y_1-y_2}{R})^2+(\frac{z_1-z_2}{R})^2]^{1/2}}$$

$$=\frac{1}{R}\left[1+2\frac{(x_1-x_2)}{R}+\frac{(x_1-x_2)^2}{R^2}+\frac{(y_1-y_2)^2}{R^2}+\frac{(z_1-z_2)^2}{R^2}\right]^{-1/2}$$

$$\cong\frac{1}{R}\left\{1-\frac{1}{2}\left[2\frac{(x_1-x_2)}{R}+\frac{(x_1-x_2)^2}{R^2}+\frac{(y_1-y_2)^2}{R^2}+\frac{(z_1-z_2)^2}{R^2}\right]+\frac{3}{8}\left[2\frac{(x_1-x_2)}{R}\right]^2\right\}$$

$$=\frac{1}{R}-\frac{x_1-x_2}{R^2}+\frac{2(x_1{}^2+x_2{}^2)-(y_1{}^2+y_2{}^2)-(z_1{}^2+z_2{}^2)}{2R^3}+\frac{x_1x_2+y_1y_2+z_1z_2}{R^3}-\frac{3x_1x_2}{R^3}$$

$$H_{nm}=\int d\boldsymbol{r}_n d\boldsymbol{r}_m\phi_P{}^*(\boldsymbol{r}_n-\boldsymbol{R}_n)\phi_S{}^*(\boldsymbol{r}_m-\boldsymbol{R}_m)v_{nm}\phi_S(\boldsymbol{r}_n-\boldsymbol{R}_n)\phi_P(\boldsymbol{r}_m-\boldsymbol{R}_m)$$

$$=\int d(\boldsymbol{r}_n-\boldsymbol{R}_n)d(\boldsymbol{r}_m-\boldsymbol{R}_m)\phi_P{}^*(\boldsymbol{r}_n-\boldsymbol{R}_n)\phi_S{}^*(\boldsymbol{r}_m-\boldsymbol{R}_m)v_{nm}\phi_S(\boldsymbol{r}_n-\boldsymbol{R}_n)\phi_P(\boldsymbol{r}_m-\boldsymbol{R}_m)\qquad \boldsymbol{R}_n,\boldsymbol{R}_m:\mathrm{fix}$$

$$=\int d\boldsymbol{r}_1 d\boldsymbol{r}_2\phi_P{}^*(\boldsymbol{r}_1)\phi_S{}^*(\boldsymbol{r}_2)v_{nm}\phi_S(\boldsymbol{r}_1)\phi_P(\boldsymbol{r}_2)$$

$$\langle\psi_n|\frac{1}{R}|\psi_m\rangle=\langle\phi_P(\boldsymbol{r}_1)\phi_S(\boldsymbol{r}_2)|\frac{1}{R}|\phi_S(\boldsymbol{r}_1)\phi_P(\boldsymbol{r}_2)\rangle=0$$

$$\langle\psi_n|-\frac{x_1-x_2}{R^2}|\psi_m\rangle=-\frac{1}{R^2}\langle\psi_n|x_1-x_2|\psi_m\rangle=-\frac{1}{R^2}(\langle\psi_n|x_1|\psi_m\rangle-\langle\psi_n|x_2|\psi_m\rangle)=-\frac{1}{R^2}(0-0)=0$$

$$\langle\psi_n|\frac{x_1{}^2+x_2{}^2}{R^3}|\psi_m\rangle=\frac{1}{R^3}[\langle\psi_n|x_1{}^2|\psi_m\rangle+\langle\psi_n|x_2{}^2|\psi_m\rangle]=\frac{1}{R^3}(0+0)=0$$

$$\left\langle \psi_n \right| \frac{x_1x_2 + y_1y_2 + z_1z_2}{R^3} \left| \psi_m \right\rangle = \frac{1}{R^3} \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \phi_P{}^*(\boldsymbol{r}_1)\phi_S{}^*(\boldsymbol{r}_2)(x_1x_2 + y_1y_2 + z_1z_2)\phi_S(\boldsymbol{r}_1)\phi_P(\boldsymbol{r}_2)$$

$$= \frac{1}{R^3}[\int d\boldsymbol{r}_1\phi_P{}^*(\boldsymbol{r}_1)x_1\phi_S(\boldsymbol{r}_1)\int d\boldsymbol{r}_2\phi_S{}^*(\boldsymbol{r}_2)x_2\phi_P(\boldsymbol{r}_2)$$

$$+ \int d\boldsymbol{r}_1\phi_P{}^*(\boldsymbol{r}_1)y_1\phi_S(\boldsymbol{r}_1)\int d\boldsymbol{r}_2\phi_S{}^*(\boldsymbol{r}_2)y_2\phi_P(\boldsymbol{r}_2)$$

$$+ \int d\boldsymbol{r}_1\phi_P{}^*(\boldsymbol{r}_1)z_1\phi_S(\boldsymbol{r}_1)\int d\boldsymbol{r}_2\phi_S{}^*(\boldsymbol{r}_2)z_2\phi_P(\boldsymbol{r}_2)]$$

$$= \frac{1}{R^3}(x_{PS}^{(1)}x_{SP}^{(2)} + y_{PS}^{(1)}y_{SP}^{(2)} + z_{PS}^{(1)}z_{SP}^{(2)})$$

$$\left\langle \psi_n \right| -\frac{3x_1x_2}{R^3} \left| \psi_m \right\rangle = -\frac{3}{R^3} x_{PS}^{(1)}x_{SP}^{(2)}$$

$$\boldsymbol{M} = -e\boldsymbol{r} = -e(x, y, z) \quad \left\langle \phi_P \middle| \boldsymbol{M} \middle| \phi_S \right\rangle = \boldsymbol{M}_{PS} = -\ e(x_{PS}, y_{PS}, z_{PS})$$

$$\left\langle \psi_n \middle| v_{nm} \middle| \psi_m \right\rangle = \left\langle \psi_n \right| \frac{e^2}{4\pi\varepsilon_0 |\boldsymbol{r}_n - \boldsymbol{r}_m|} \left| \psi_m \right\rangle \cong \frac{1}{4\pi\varepsilon_0 R_{nm}{}^3}\left[\boldsymbol{M}_{PS}^{(1)} \cdot \boldsymbol{M}_{SP}^{(2)} - 3\frac{(\boldsymbol{M}_{PS}^{(1)} \cdot \boldsymbol{R}_{nm})(\boldsymbol{M}_{SP}^{(2)} \cdot \boldsymbol{R}_{nm})}{R_{nm}{}^2} \right]$$

$$= \frac{1}{4\pi\varepsilon_0 R_{nm}{}^3}\left[|\boldsymbol{M}_{PS}|^2 - 3\frac{|\boldsymbol{M}_{PS} \cdot \boldsymbol{R}_{nm}|^2}{R_{nm}{}^2} \right] \equiv D(\boldsymbol{R}_{nm}) \quad (\boldsymbol{M}_{PS}^{(1)}{}^* = \boldsymbol{M}_{SP}^{(2)}\text{のとき})$$

$v_{nm} = v_{mn}$より$\left\langle \psi_n \middle| v_{nm} \middle| \psi_m \right\rangle = \left\langle \psi_m \middle| v_{nm} \middle| \psi_n \right\rangle$

フレンケル励起子　　波動関数　　励起波

$$\Psi_{\boldsymbol{K}} = \frac{1}{\sqrt{N}}\sum_n \exp(i\boldsymbol{K}\cdot\boldsymbol{R})\psi_n \qquad (\text{明らかに非対角項}\boldsymbol{K}' \neq \boldsymbol{K} \quad \left\langle \Psi_{\boldsymbol{K}'} \middle| H \middle| \Psi_{\boldsymbol{K}} \right\rangle = 0 \quad \because \sum_n \exp[i(\boldsymbol{K}' - \boldsymbol{K})\cdot\boldsymbol{R}_n] = 0)$$

$$\left\langle \Psi_{\boldsymbol{K}} \middle| H \middle| \Psi_{\boldsymbol{K}} \right\rangle = \frac{1}{N}\sum_n \exp(-i\boldsymbol{K}\cdot\boldsymbol{R}_n)\sum_m \exp(i\boldsymbol{K}\cdot\boldsymbol{R}_m)\left\langle \psi_n \right| \sum_{n'} h_{n'} + \sum_{n'<m'} v_{n'm'} \left| \psi_m \right\rangle$$

$$= \frac{1}{N}\sum_{n,m}\exp[-i\boldsymbol{K}\cdot(\boldsymbol{R}_n - \boldsymbol{R}_m)](E_P - E_S)\delta_{nm} + \frac{1}{N}\sum_{\substack{n,m \\ n\neq m}}\exp[-i\boldsymbol{K}\cdot(\boldsymbol{R}_n - \boldsymbol{R}_m)]D(\boldsymbol{R}_{nm})$$

$$= E_P - E_S + \frac{1}{N}\sum_{\substack{n,m \\ n\neq m}}\exp(-i\boldsymbol{K}\cdot\boldsymbol{R}_{nm})D(\boldsymbol{R}_{nm})$$

$$N = 5 \quad \frac{1}{N}\sum_{n,m}\exp(-i\boldsymbol{K}\cdot\boldsymbol{R}_{nm})\left\langle \psi_n \right| \sum_{n'<m'} v_{n'm'} \left| \psi_m \right\rangle$$

$$= \frac{1}{N}\sum_{n,m}\exp(-i\boldsymbol{K}\cdot\boldsymbol{R}_{nm})\left\langle \psi_n \middle| v_{12} + v_{13} + v_{14} + v_{15} + v_{23} + v_{24} + v_{25} + v_{34} + v_{35} + v_{45} \middle| \psi_m \right\rangle$$

$$= \frac{1}{5}\{ \ \exp[-i\boldsymbol{K}\cdot\boldsymbol{R}_{12}]\left\langle \psi_1 \middle| v_{12} \middle| \psi_2 \right\rangle + \exp[-i\boldsymbol{K}\cdot\boldsymbol{R}_{21}]\left\langle \psi_2 \middle| v_{12} \middle| \psi_1 \right\rangle$$

$$+ \exp[-i\boldsymbol{K}\cdot\boldsymbol{R}_{13}]\left\langle \psi_1 \middle| v_{13} \middle| \psi_3 \right\rangle + \exp[-i\boldsymbol{K}\cdot\boldsymbol{R}_{31}]\left\langle \psi_3 \middle| v_{13} \middle| \psi_1 \right\rangle + \cdots$$

$$+ \exp[-i\boldsymbol{K}\cdot\boldsymbol{R}_{45}]\left\langle \psi_4 \middle| v_{45} \middle| \psi_5 \right\rangle + \exp[-i\boldsymbol{K}\cdot\boldsymbol{R}_{54}]\left\langle \psi_5 \middle| v_{45} \middle| \psi_4 \right\rangle \ \} \quad 20\text{項} = N(N-1)$$

$$= \frac{1}{5}\{ \ [\exp(-i\boldsymbol{K}\cdot\boldsymbol{R}_{12}) + \exp(i\boldsymbol{K}\cdot\boldsymbol{R}_{12})]\left\langle \psi_1 \middle| v_{12} \middle| \psi_2 \right\rangle$$

$$+ [\exp(-i\boldsymbol{K}\cdot\boldsymbol{R}_{13}) + \exp(i\boldsymbol{K}\cdot\boldsymbol{R}_{13})]\left\langle \psi_1 \middle| v_{13} \middle| \psi_3 \right\rangle + \cdots$$

$$+ [\exp(-i\boldsymbol{K}\cdot\boldsymbol{R}_{45}) + \exp(i\boldsymbol{K}\cdot\boldsymbol{R}_{45})]\left\langle \psi_4 \middle| v_{45} \middle| \psi_5 \right\rangle \ \}$$

$$= \frac{1}{5}\{ \ 2\cos(\boldsymbol{K}\cdot\boldsymbol{R}_{12})D(\boldsymbol{R}_{12}) + 2\cos(\boldsymbol{K}\cdot\boldsymbol{R}_{13})D(\boldsymbol{R}_{13}) + \cdots + 2\cos(\boldsymbol{K}\cdot\boldsymbol{R}_{45})D(\boldsymbol{R}_{45}) \ \}$$

直線状　　最近接相互作用のみ　　　（J会合体　$D = J$）

$$= \frac{1}{5}\{ \ 2\cos(\boldsymbol{K}\cdot\boldsymbol{R}_{12})D(\boldsymbol{R}_{12}) + 2\cos(\boldsymbol{K}\cdot\boldsymbol{R}_{23})D(\boldsymbol{R}_{23}) + 2\cos(\boldsymbol{K}\cdot\boldsymbol{R}_{34})D(\boldsymbol{R}_{34}) + 2\cos(\boldsymbol{K}\cdot\boldsymbol{R}_{45})D(\boldsymbol{R}_{45}) \ \}$$

$$= \frac{4}{5}\{ \ 2J\cos(\boldsymbol{K}\cdot\boldsymbol{R}) \ \}$$

Wannier 励起子（簡単のためスピンの自由度は考慮しない）

$$\psi_g(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N)=\prod_k \phi_m(\boldsymbol{r}_k-\boldsymbol{R}_k)$$

Wannier 関数

$$\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N)=\psi_{\boldsymbol{R}_i,\boldsymbol{R}_j}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N)=\phi_n(\boldsymbol{r}_i-\boldsymbol{R}_j)\prod_{k\neq i}\phi_m(\boldsymbol{r}_k-\boldsymbol{R}_k)$$

$$=\phi_m(\boldsymbol{r}_1-\boldsymbol{R}_1)\phi_m(\boldsymbol{r}_2-\boldsymbol{R}_2)\cdots\phi_m(\boldsymbol{r}_{i-1}-\boldsymbol{R}_{i-1})\phi_n(\boldsymbol{r}_i-\boldsymbol{R}_j)\phi_m(\boldsymbol{r}_{i+1}-\boldsymbol{R}_{i+1})\cdots\phi_m(\boldsymbol{r}_N-\boldsymbol{R}_N)$$

$\phi_m(\boldsymbol{r}-\boldsymbol{R}_i)\to\phi_n(\boldsymbol{r}-\boldsymbol{R}_i)$のほかにイオン化状態（電荷移動状態）$\phi_m(\boldsymbol{r}-\boldsymbol{R}_i)\to\phi_n(\boldsymbol{r}-\boldsymbol{R}_j)(i\neq j)$も考える

$$\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta})=\frac{1}{\sqrt{N}}\sum_i \exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}$$

$$\Phi_{mn}(\boldsymbol{K})=\sum_{\boldsymbol{\beta}}F(\boldsymbol{\beta})\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta})\quad \text{Wannier励起子波動関数}$$

$$=\sum_{\boldsymbol{\beta}}F(\boldsymbol{\beta})\frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}_i}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}=\sum_{\boldsymbol{\beta}}\sum_{\boldsymbol{R}_i}\underbrace{\frac{1}{\sqrt{N}}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)F(\boldsymbol{\beta})}_{\text{envelope function}}\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}$$

Wannier function

$$\phi_m(\boldsymbol{r}_i-\boldsymbol{R}_i)\equiv\phi_m(\boldsymbol{R}_i)=\phi^m_{\boldsymbol{R}_i}(\boldsymbol{r}_i)=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_i}\chi^m_{\boldsymbol{k}}(\boldsymbol{r}_i)$$

$$\psi_{\boldsymbol{R}_i,\boldsymbol{R}_j}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N)\equiv\psi_{mn}(\boldsymbol{R}_i,\boldsymbol{R}_j)=\frac{1}{N}\sum_{\boldsymbol{k}_h}\sum_{\boldsymbol{k}_e}\exp[i(\boldsymbol{k}_h\cdot\boldsymbol{R}_i-\boldsymbol{k}_e\cdot\boldsymbol{R}_j)]\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)$$

Bloch関数 $\quad \chi_{\boldsymbol{k}}(\boldsymbol{r})=e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{\boldsymbol{k}}(\boldsymbol{r}) \qquad \chi_{\boldsymbol{k}}(\boldsymbol{r})=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{R}_i}\phi_{\boldsymbol{R}}(\boldsymbol{r})$

Wannier関数 $\quad \phi_{\boldsymbol{R}}(\boldsymbol{r})=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_i}\chi_{\boldsymbol{k}}(\boldsymbol{r})=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{R})_i}u_{\boldsymbol{k}}(\boldsymbol{r})$

$$\Phi_{mn}(\boldsymbol{K})\equiv\Phi_{\boldsymbol{K}}=\sum_{\boldsymbol{\beta}}\sum_{\boldsymbol{R}_i}\frac{1}{\sqrt{N}}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)F(\boldsymbol{\beta})\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}\qquad \boldsymbol{k}_e=\boldsymbol{k}_h+\boldsymbol{K}$$

$$=\sum_{\boldsymbol{\beta}}\sum_{\boldsymbol{R}_i}\frac{1}{\sqrt{N}}\exp[i(\boldsymbol{k}_e-\boldsymbol{k}_h)\cdot\boldsymbol{R}_i]F(\boldsymbol{\beta})\frac{1}{N}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[i(\boldsymbol{k}_h\cdot\boldsymbol{R}_i-\boldsymbol{k}_e\cdot(\boldsymbol{R}_i+\boldsymbol{\beta}))]\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)$$

$$=\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)\frac{1}{\sqrt{N}}\sum_{\boldsymbol{\beta}}\exp[-i\boldsymbol{k}_e\cdot\boldsymbol{\beta}]F(\boldsymbol{\beta})=\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)F(\boldsymbol{k}_e)=\sum_{\boldsymbol{k}_h}\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_h+\boldsymbol{K}}(\boldsymbol{r}_h,\boldsymbol{r}_e)F(\boldsymbol{k}_h+\boldsymbol{K})$$

$$\Phi_{mn}(\boldsymbol{K})\equiv\Phi_{\boldsymbol{K}}=\sum_{\boldsymbol{k}}F(\boldsymbol{k}+\boldsymbol{K})\chi_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{K}}\qquad \chi_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{K}}=\chi^{v*}_{\boldsymbol{k}}(\boldsymbol{r}_1)\chi^c_{\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}_2)$$

$$=\sum_{\boldsymbol{k}}F(\boldsymbol{k}+\boldsymbol{K})\chi^{v*}_{\boldsymbol{k}}(\boldsymbol{r}_1)\chi^c_{\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}_2)=\sum_{\boldsymbol{k}}F(\boldsymbol{k}+\boldsymbol{K})e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_1}u^{v*}_{\boldsymbol{k}}(\boldsymbol{r}_1)e^{i(\boldsymbol{k}+\boldsymbol{K})\cdot\boldsymbol{r}_2}u^c_{\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}_2)$$

$$=\sum_{\boldsymbol{k}+\boldsymbol{K}}F(\boldsymbol{k}+\boldsymbol{K})e^{i(\boldsymbol{k}+\boldsymbol{K})\cdot(\boldsymbol{r}_2-\boldsymbol{r}_1)+i\boldsymbol{K}\cdot\boldsymbol{r}_1}u^{v*}_{\boldsymbol{k}}(\boldsymbol{r}_1)u^c_{\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}_2)$$

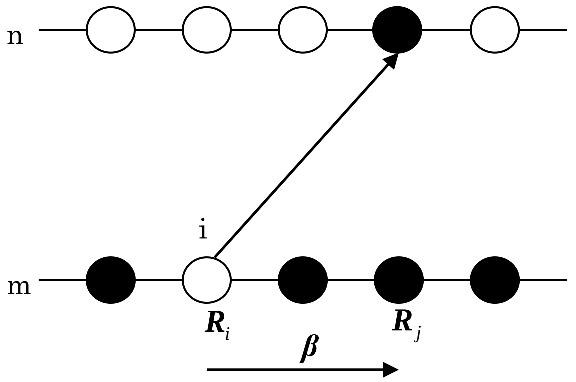
$$=\sqrt{N}F(\boldsymbol{r}_2-\boldsymbol{r}_1)e^{i\boldsymbol{K}\cdot\boldsymbol{r}_1}u^{v*}_{\boldsymbol{k}}(\boldsymbol{r}_1)u^c_{\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}_2)=\sqrt{N}F(\boldsymbol{r})e^{i\boldsymbol{K}\cdot\boldsymbol{r}_1}u^{v*}_{\boldsymbol{k}}(\boldsymbol{r}_1)u^c_{\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}_1+\boldsymbol{r})\qquad \boldsymbol{r}=\boldsymbol{r}_2-\boldsymbol{r}_1$$

$$\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}F(\boldsymbol{k})=\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\frac{1}{\sqrt{N}}\sum_{\boldsymbol{r}'}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}'_i}F(\boldsymbol{r}')=\sum_{\boldsymbol{r}'}\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}F(\boldsymbol{r}')=\sqrt{N}F(\boldsymbol{r})$$

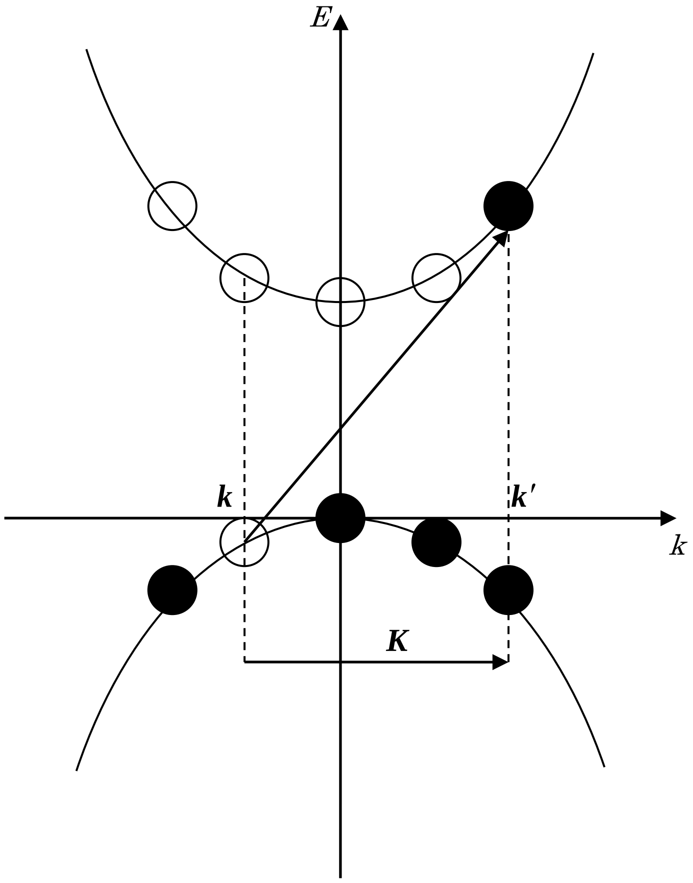
$$H=\sum_i\left[-\frac{\hbar^2}{2m}\nabla_i{}^2+V_{\mathrm{crys}}(\boldsymbol{r}_i)\right]+\sum_{i<j}\frac{e^2}{4\pi\varepsilon\,|\boldsymbol{r}_i-\boldsymbol{r}_j|}=\sum_i H_i+\sum_{i<j}V_{ij}$$

$$\left[-\frac{\hbar^2}{2m}\nabla_1{}^2+V_{\mathrm{crys}}(\boldsymbol{r}_1)\right]\chi^v_{\boldsymbol{k}}(\boldsymbol{r}_1)=E^v_{\boldsymbol{k}}\chi^v_{\boldsymbol{k}}(\boldsymbol{r}_1)\qquad \left[-\frac{\hbar^2}{2m}\nabla_2{}^2+V_{\mathrm{crys}}(\boldsymbol{r}_2)\right]\chi^c_{\boldsymbol{k}}(\boldsymbol{r}_2)=E^c_{\boldsymbol{k}}\chi^c_{\boldsymbol{k}}(\boldsymbol{r}_2)$$

$$H\Phi_{\boldsymbol{K}}=\left[-\frac{\hbar^2}{2m}\nabla_1{}^2+V_{\mathrm{crys}}(\boldsymbol{r}_1)-\frac{\hbar^2}{2m}\nabla_2{}^2+V_{\mathrm{crys}}(\boldsymbol{r}_2)+V(\boldsymbol{r})\right]\Phi_{\boldsymbol{K}}=E\Phi_{\boldsymbol{K}}\qquad \boldsymbol{r}=\boldsymbol{\beta}$$



$\phi_m(\boldsymbol{r}-\boldsymbol{R}_i) \to \phi_n(\boldsymbol{r}-\boldsymbol{R}_i)$のほかにイオン化状態（電荷移動状態）$\phi_m(\boldsymbol{r}-\boldsymbol{R}_i) \to \phi_n(\boldsymbol{r}-\boldsymbol{R}_j)(i \neq j)$も考える



$\boldsymbol{K} = \boldsymbol{k}' - \boldsymbol{k} = \boldsymbol{k}_e - \boldsymbol{k}_h$

励起子波動関数は$\boldsymbol{k}', \boldsymbol{k} \leq \dfrac{1}{a_B}$の範囲のBloch関数で作られる

a_B : 励起子ボーア半径

$$\Phi_{\boldsymbol{K}} = \sum_{\boldsymbol{k}_h,\boldsymbol{k}_e} F(\boldsymbol{k}_e)\chi_{\boldsymbol{k}_h,\boldsymbol{k}_e}\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}} \qquad \chi_{\boldsymbol{k}_h,\boldsymbol{k}_e} = \chi^{v\ *}_{\boldsymbol{k}_h}(\boldsymbol{r}_h)\chi^{c}_{\boldsymbol{k}_e}(\boldsymbol{r}_e)$$

$$H = \sum_i \left[-\frac{\hbar^2}{2m}\nabla_i{}^2 + V_{\text{crys}}(\boldsymbol{r}_i)\right] + \sum_{i<j}\frac{e^2}{4\pi\varepsilon\,|\boldsymbol{r}_i - \boldsymbol{r}_j|} = \sum_i H_i + \sum_{i<j} V_{ij}$$

$$= -\frac{\hbar^2}{2m}\nabla_h{}^2 + V_{\text{crys}}(\boldsymbol{r}_h) - \frac{\hbar^2}{2m}\nabla_e{}^2 + V_{\text{crys}}(\boldsymbol{r}_e) + V_{eh}(\boldsymbol{r}_e - \boldsymbol{r}_h) + \text{others}$$

$$\left[-\frac{\hbar^2}{2m}\nabla_h{}^2 + V_{\text{crys}}(\boldsymbol{r}_h)\right]\chi^v_{\boldsymbol{k}_h}(\boldsymbol{r}_h) = E^v_{\boldsymbol{k}_h}\chi^v_{\boldsymbol{k}_h}(\boldsymbol{r}_h) \qquad \left[-\frac{\hbar^2}{2m}\nabla_e{}^2 + V_{\text{crys}}(\boldsymbol{r}_e)\right]\chi^c_{\boldsymbol{k}_e}(\boldsymbol{r}_e) = E^c_{\boldsymbol{k}_e}\chi^c_{\boldsymbol{k}_e}(\boldsymbol{r}_e)$$

$\left\langle \chi_{\boldsymbol{k},\boldsymbol{k}'}\middle| H \middle| \chi_{\boldsymbol{k}_h,\boldsymbol{k}_e}\right\rangle = \int d\boldsymbol{r}_h d\boldsymbol{r}_e \chi^{v*}_{\boldsymbol{k}}(\boldsymbol{r}_h)\chi^{c\ *}_{\boldsymbol{k}'}(\boldsymbol{r}_e)(E^v_{\boldsymbol{k}_h} + E^c_{\boldsymbol{k}_e} + V_{eh})\chi^v_{\boldsymbol{k}_h}(\boldsymbol{r}_h)\chi^c_{\boldsymbol{k}_e}(\boldsymbol{r}_e)$　結晶の全体積で積分

近似 : V_{eh}がunit cellのサイズで一定とすると(slowly varying function)

$$= \delta_{\boldsymbol{k}\boldsymbol{k}_h}\delta_{\boldsymbol{k}'\boldsymbol{k}_e}(E^v_{\boldsymbol{k}_h} + E^c_{\boldsymbol{k}_e} + V_{eh})$$

$$H\Phi_{\boldsymbol{K}} = E\Phi_{\boldsymbol{K}} \quad H\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e} F(\boldsymbol{k}_e)\chi_{\boldsymbol{k}_h,\boldsymbol{k}_e}\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}} = E\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e} F(\boldsymbol{k}_e)\chi_{\boldsymbol{k}_h,\boldsymbol{k}_e}\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}}$$

$\psi(\boldsymbol{R},\boldsymbol{R}') = \dfrac{1}{N}\sum_{\boldsymbol{k},\boldsymbol{k}'}\exp[i(\boldsymbol{k}\cdot\boldsymbol{R} - \boldsymbol{k}'\cdot\boldsymbol{R}')]\chi_{\boldsymbol{k},\boldsymbol{k}'}$を左からかけて

$$\frac{1}{N}\sum_{\boldsymbol{k},\boldsymbol{k}'}\exp[-i(\boldsymbol{k}\cdot\boldsymbol{R} - \boldsymbol{k}'\cdot\boldsymbol{R}')]\left\langle \chi_{\boldsymbol{k},\boldsymbol{k}'}\middle| H \middle| \sum_{\boldsymbol{k}_h,\boldsymbol{k}_e} F(\boldsymbol{k}_e)\chi_{\boldsymbol{k}_h,\boldsymbol{k}_e}\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}}\right\rangle = E\frac{1}{N}\sum_{\boldsymbol{k},\boldsymbol{k}'}\exp[-i(\boldsymbol{k}\cdot\boldsymbol{R} - \boldsymbol{k}'\cdot\boldsymbol{R}')]\left\langle \chi_{\boldsymbol{k},\boldsymbol{k}'}\middle| \sum_{\boldsymbol{k}_h,\boldsymbol{k}_e} F(\boldsymbol{k}_e)\chi_{\boldsymbol{k}_h,\boldsymbol{k}_e}\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}}\right\rangle$$

$$\frac{1}{N}\sum_{\boldsymbol{k},\boldsymbol{k}'}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[-i(\boldsymbol{k}\cdot\boldsymbol{R} - \boldsymbol{k}'\cdot\boldsymbol{R}')]\left\langle \chi_{\boldsymbol{k},\boldsymbol{k}'}\middle| H \middle| \chi_{\boldsymbol{k}_h,\boldsymbol{k}_e}\right\rangle F(\boldsymbol{k}_e)\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}} = E\frac{1}{N}\sum_{\boldsymbol{k},\boldsymbol{k}'}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[-i(\boldsymbol{k}\cdot\boldsymbol{R} - \boldsymbol{k}'\cdot\boldsymbol{R}')]\left\langle \chi_{\boldsymbol{k},\boldsymbol{k}'}\middle| \chi_{\boldsymbol{k}_h,\boldsymbol{k}_e}\right\rangle F(\boldsymbol{k}_e)\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}}$$

$$\frac{1}{N}\sum_{\boldsymbol{k},\boldsymbol{k}'}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[-i(\boldsymbol{k}\cdot\boldsymbol{R} - \boldsymbol{k}'\cdot\boldsymbol{R}')](E^v_{\boldsymbol{k}_h} + E^c_{\boldsymbol{k}_e} + V_{eh})\delta_{\boldsymbol{k}\boldsymbol{k}_h}\delta_{\boldsymbol{k}'\boldsymbol{k}_e}F(\boldsymbol{k}_e)\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}} = E\frac{1}{N}\sum_{\boldsymbol{k},\boldsymbol{k}'}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[-i(\boldsymbol{k}\cdot\boldsymbol{R} - \boldsymbol{k}'\cdot\boldsymbol{R}')]\delta_{\boldsymbol{k}\boldsymbol{k}_h}\delta_{\boldsymbol{k}'\boldsymbol{k}_e}F(\boldsymbol{k}_e)\delta_{\boldsymbol{k}_e,}$$

$$\frac{1}{N}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[-i(\boldsymbol{k}_h\cdot\boldsymbol{R} - \boldsymbol{k}_e\cdot\boldsymbol{R}')](E^v_{\boldsymbol{k}_h} + E^c_{\boldsymbol{k}_e} + V_{eh})F(\boldsymbol{k}_e)\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}} = E\frac{1}{N}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[-i(\boldsymbol{k}_h\cdot\boldsymbol{R} - \boldsymbol{k}_e\cdot\boldsymbol{R}')]F(\boldsymbol{k}_e)\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}}$$

$\boldsymbol{R}' = \boldsymbol{R} + \boldsymbol{\beta} \quad \boldsymbol{\beta} = \boldsymbol{R}' - \boldsymbol{R} \quad \delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}}$より$\boldsymbol{k}_e = \boldsymbol{k}_h + \boldsymbol{K} \rightarrow \boldsymbol{k}_h = \boldsymbol{k}_e - \boldsymbol{K} \quad \delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}} = \delta_{\boldsymbol{k}_h,\boldsymbol{k}_e-\boldsymbol{K}}$

$e \quad h$

$$\boldsymbol{k}_h\cdot\boldsymbol{R} - \boldsymbol{k}_e\cdot\boldsymbol{R}' = \boldsymbol{k}_h\cdot\boldsymbol{R} - \boldsymbol{k}_e\cdot(\boldsymbol{R}+\boldsymbol{\beta}) = (\boldsymbol{k}_e - \boldsymbol{K})\cdot\boldsymbol{R} - \boldsymbol{k}_e\cdot(\boldsymbol{R}+\boldsymbol{\beta})$$

$E^v_{\boldsymbol{k}_h} = \dfrac{\hbar^2}{2m_h}k_h{}^2 \quad E^c_{\boldsymbol{k}_e} = E_g + \dfrac{\hbar^2}{2m_e}k_e{}^2$　価電子帯のtopをエネルギーの原点

$$\frac{1}{N}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[-i(\boldsymbol{k}_h\cdot\boldsymbol{R} - \boldsymbol{k}_e\cdot\boldsymbol{R}')](E^v_{\boldsymbol{k}_h} + E^c_{\boldsymbol{k}_e} + V_{eh})F(\boldsymbol{k}_e)\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}}$$

$$= \frac{1}{N}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[-i(\boldsymbol{k}_h\cdot\boldsymbol{R} - \boldsymbol{k}_e\cdot\boldsymbol{R}')](\frac{\hbar^2}{2m_h}k_h{}^2 + E_g + \frac{\hbar^2}{2m_e}k_e{}^2 + V_{eh})F(\boldsymbol{k}_e)\delta_{\boldsymbol{k}_h,\boldsymbol{k}_e-\boldsymbol{K}}$$

$$= \frac{1}{N}\sum_{\boldsymbol{k}_e}[E_g + \frac{\hbar^2}{2m_h}(\boldsymbol{k}_e - \boldsymbol{K})^2 + \frac{\hbar^2}{2m_e}k_e{}^2 + V_{eh}]\exp[-i(\boldsymbol{k}_e - \boldsymbol{K})\cdot\boldsymbol{R} + i\boldsymbol{k}_e\cdot(\boldsymbol{R}+\boldsymbol{\beta})]F(\boldsymbol{k}_e)$$

$$= \frac{1}{N}\sum_{\boldsymbol{k}_e}[E_g + \frac{\hbar^2}{2}(\frac{1}{m_h} + \frac{1}{m_e})k_e{}^2 + \frac{\hbar^2}{2m_h}K^2 - \frac{\hbar^2}{m_h}\boldsymbol{k}_e\cdot\boldsymbol{K} + V_{eh}]\exp[i\boldsymbol{K}\cdot\boldsymbol{R} + i\boldsymbol{k}_e\cdot\boldsymbol{\beta}]F(\boldsymbol{k}_e)$$

$$=\frac{1}{\sqrt{N}}[E_g-\frac{\hbar^2}{2}(\frac{1}{m_h}+\frac{1}{m_e})\frac{\partial^2}{\partial\boldsymbol{\beta}^2}+\frac{\hbar^2}{2m_h}K^2+i\frac{\hbar^2}{m_h}\boldsymbol{K}\cdot\frac{\partial}{\partial\boldsymbol{\beta}}+V_{eh}]\exp[i\boldsymbol{K}\cdot\boldsymbol{R}]\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}_e}\exp[i\boldsymbol{k}_e\cdot\boldsymbol{\beta}]F(\boldsymbol{k}_e)$$

$$=\frac{1}{\sqrt{N}}[E_g-\frac{\hbar^2}{2}(\frac{1}{m_h}+\frac{1}{m_e})\frac{\partial^2}{\partial\boldsymbol{\beta}^2}+\frac{\hbar^2}{2m_h}K^2+i\frac{\hbar^2}{m_h}\boldsymbol{K}\cdot\frac{\partial}{\partial\boldsymbol{\beta}}+V_{eh}]\exp[i\boldsymbol{K}\cdot\boldsymbol{R}]F(\boldsymbol{\beta})$$

$$\text{右辺}=E\frac{1}{N}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[-i(\boldsymbol{k}_h\cdot\boldsymbol{R}-\boldsymbol{k}_e\cdot\boldsymbol{R}')]F(\boldsymbol{k}_e)\delta_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{K}}=\frac{1}{\sqrt{N}}E\exp[i\boldsymbol{K}\cdot\boldsymbol{R}]F(\boldsymbol{\beta})$$

$$[E_g-\frac{\hbar^2}{2}(\frac{1}{m_h}+\frac{1}{m_e})\frac{\partial^2}{\partial\boldsymbol{\beta}^2}+\frac{\hbar^2}{2m_h}K^2+i\frac{\hbar^2}{m_h}\boldsymbol{K}\cdot\frac{\partial}{\partial\boldsymbol{\beta}}+V_{eh}]F(\boldsymbol{\beta})=EF(\boldsymbol{\beta})$$

$F(\boldsymbol{\beta})=e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})$とおく

$$\frac{\partial^2}{\partial\boldsymbol{\beta}^2}[e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})]=-\alpha^2K^2e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})+2i\alpha\boldsymbol{K}e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial}{\partial\boldsymbol{\beta}}F'(\boldsymbol{\beta})+e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial^2}{\partial\boldsymbol{\beta}^2}F'(\boldsymbol{\beta})$$

$$\frac{\partial}{\partial\boldsymbol{\beta}}[e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})]=i\alpha\boldsymbol{K}e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})+e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial}{\partial\boldsymbol{\beta}}F'(\boldsymbol{\beta})$$

$e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial}{\partial\boldsymbol{\beta}}F'(\boldsymbol{\beta})$の係数が0になるように$\alpha$を定める

$$-\frac{\hbar^2}{2}(\frac{1}{m_h}+\frac{1}{m_e})2i\alpha\boldsymbol{K}+i\frac{\hbar^2}{m_h}\boldsymbol{K}=0\quad\frac{1}{m_h}+\frac{1}{m_e}=\frac{1}{\mu}$$

$-i\hbar^2\frac{\alpha}{\mu}=-i\frac{\hbar^2}{m_h}\quad\therefore\alpha=\frac{\mu}{m_h}$とおけばよい

$$[E_g-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\boldsymbol{\beta}^2}+\frac{\hbar^2}{2m_h}K^2+i\frac{\hbar^2}{m_h}\boldsymbol{K}\cdot\frac{\partial}{\partial\boldsymbol{\beta}}+V_{eh}][e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})]=E[e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})]$$

$$e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}[E_g-\frac{\hbar^2}{2\mu}(-\alpha^2K^2)+\frac{\hbar^2}{2m_h}K^2+i\frac{\hbar^2}{m_h}\boldsymbol{K}\cdot(i\alpha\boldsymbol{K})+V_{eh}]F'(\boldsymbol{\beta})-e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\boldsymbol{\beta}^2}F'(\boldsymbol{\beta})=e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}EF'(\boldsymbol{\beta})$$

$$[E_g+\frac{\hbar^2}{2\mu}(\frac{\mu}{m_h})^2K^2+\frac{\hbar^2}{2m_h}K^2-\frac{\hbar^2}{m_h}(\frac{\mu}{m_h})K^2+V_{eh}]F'(\boldsymbol{\beta})-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\boldsymbol{\beta}^2}F'(\boldsymbol{\beta})=EF'(\boldsymbol{\beta})$$

$$[E_g-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\boldsymbol{\beta}^2}-\frac{\hbar^2}{2}\frac{\mu}{m_h{}^2}K^2+\frac{\hbar^2}{2m_h}K^2+V_{eh}]F'(\boldsymbol{\beta})=EF'(\boldsymbol{\beta})$$

$$-\frac{\hbar^2}{2}\frac{\mu}{m_h{}^2}K^2+\frac{\hbar^2}{2m_h}K^2=\frac{\hbar^2}{2m_h}K^2(-\frac{\mu}{m_h}+1)=\frac{\hbar^2}{2m_h}K^2(-\frac{1}{m_h}\frac{1}{\frac{1}{m_h}+\frac{1}{m_e}}+1)=\frac{\hbar^2}{2m_h}K^2(-\frac{m_e}{m_e+m_h}+1)=\frac{\hbar^2K^2}{2(m_e+m_h)}$$

励起子の重心の運動エネルギー

最終表式　$[E_g+\frac{\hbar^2K^2}{2(m_e+m_h)}-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\boldsymbol{\beta}^2}+V_{eh}]F'(\boldsymbol{\beta})=EF'(\boldsymbol{\beta})$

電子eと正孔hの有効質量m_e,m_h

eとhの相対運動の軌道半径a, 格子定数dとしたとき、$a>>d$のときに成り立つ

包絡波動関数$F'(\boldsymbol{\beta})$の満たす式　水素原子の問題と相似

$a\leq d\rightarrow$ Frenkel励起子

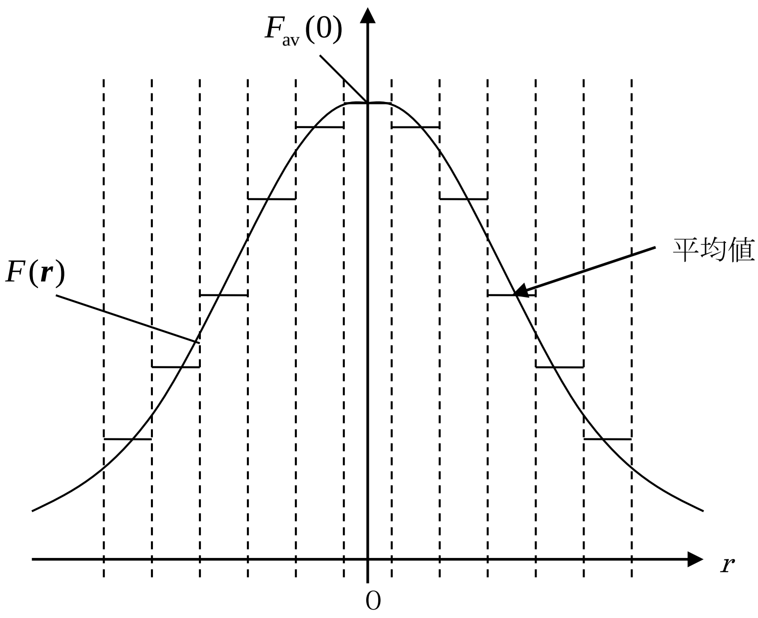
$$E = E_g + \frac{\hbar^2 K^2}{2M} - \frac{R}{n^2} \qquad M = m_e + m_h \quad R = \frac{\mu e^4}{2(4\pi\varepsilon)^2 \hbar^2} = \frac{e^2}{2(4\pi\varepsilon)a} = \frac{1}{(4\pi\varepsilon)^2}\frac{\mu}{m_0} R_H$$

$$a = \frac{(4\pi\varepsilon)\hbar^2}{\mu e^2} = (4\pi\varepsilon)\frac{m_0}{\mu} a_H \qquad R_H = 13.6\mathrm{eV} \quad a_H = 0.53\mathrm{A} \ \ (\varepsilon = \varepsilon_0, \mu = m_0)$$

ns波動関数 $F(r) = \frac{1}{\sqrt{\pi} a^{3/2}} \frac{1}{n^{3/2}} e^{-\frac{r}{na}}$ $\qquad \int |F(\boldsymbol{r})|^2 \, d\boldsymbol{r} = 1 \quad \left(\int |F(\boldsymbol{\beta})|^2 \, d\boldsymbol{\beta} = 1 \right)$

0点の振幅$F(0) = \frac{1}{\sqrt{\pi} a^{3/2}} \frac{1}{n^{3/2}} \Omega_{\boldsymbol{\beta}}{}^{1/2}$ $\qquad \Omega_{\boldsymbol{\beta}}$: 単位胞の体積

ns励起子の振動子強度 $f_{ns} \propto F^2(0) \propto \frac{1}{a^3}\frac{1}{n^3}$



規格化

$$1 = \int |F(\boldsymbol{r})|^2 \, dV = \sum_{\boldsymbol{\beta}} \int_{\Omega_{\boldsymbol{\beta}}} |F(\boldsymbol{r})|^2 \, dV = \sum_{\boldsymbol{\beta}} |F_{\mathrm{ex}}(\boldsymbol{\beta})|^2 = 1$$

$|F_{\mathrm{ex}}(\boldsymbol{\beta} = 0)|^2 = \int_{\Omega_{\boldsymbol{\beta}=0}} |F(\boldsymbol{r})|^2 \, dV = |F_{\mathrm{av}}(0)|^2 \, \Omega_{\boldsymbol{\beta}}$ $\qquad \Omega_{\boldsymbol{\beta}}$: 単位胞の体積 $\qquad F_{\mathrm{ex}}(0) = F_{\mathrm{av}}(0)\Omega_{\boldsymbol{\beta}}{}^{1/2}$

-----------------メモ

$$\Phi_{mn}(\boldsymbol{K}) \equiv \Phi_{\boldsymbol{K}} = \sum_{\boldsymbol{k}} F(\boldsymbol{k} + \boldsymbol{K}) \chi_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{K}} \qquad \chi_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{K}} = \chi_{\boldsymbol{k}}^{v*}(\boldsymbol{r}_1) \chi_{\boldsymbol{k}+\boldsymbol{K}}^{c}(\boldsymbol{r}_2)$$

$$= \sum_{\boldsymbol{k}} F(\boldsymbol{k} + \boldsymbol{K}) \chi_{\boldsymbol{k}}^{v*}(\boldsymbol{r}_1) \chi_{\boldsymbol{k}+\boldsymbol{K}}^{c}(\boldsymbol{r}_2) = \sum_{\boldsymbol{k}} F(\boldsymbol{k} + \boldsymbol{K}) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_1} u_{\boldsymbol{k}}^{v*}(\boldsymbol{r}_1) e^{i(\boldsymbol{k}+\boldsymbol{K})\cdot\boldsymbol{r}_2} u_{\boldsymbol{k}+\boldsymbol{K}}^{c}(\boldsymbol{r}_2)$$

$$= \sum_{\boldsymbol{k}+\boldsymbol{K}} F(\boldsymbol{k} + \boldsymbol{K}) e^{i(\boldsymbol{k}+\boldsymbol{K})\cdot(\boldsymbol{r}_2 - \boldsymbol{r}_1) + i\boldsymbol{K}\cdot\boldsymbol{r}_1} u_{\boldsymbol{k}}^{v*}(\boldsymbol{r}_1) u_{\boldsymbol{k}+\boldsymbol{K}}^{c}(\boldsymbol{r}_2)$$

$$= \sqrt{N} F(\boldsymbol{r}_2 - \boldsymbol{r}_1) e^{i\boldsymbol{K}\cdot\boldsymbol{r}_1} u_{\boldsymbol{k}}^{v*}(\boldsymbol{r}_1) u_{\boldsymbol{k}+\boldsymbol{K}}^{c}(\boldsymbol{r}_2) = \sqrt{N} F(\boldsymbol{r}) e^{i\boldsymbol{K}\cdot\boldsymbol{r}_1} u_{\boldsymbol{k}}^{v*}(\boldsymbol{r}_1) u_{\boldsymbol{k}+\boldsymbol{K}}^{c}(\boldsymbol{r}_1 + \boldsymbol{r}) \qquad \boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \boldsymbol{r}_{cm} = \frac{m_1 \boldsymbol{r}_1 + m_2 \boldsymbol{r}_2}{m_1 + m_2} = \mu(\boldsymbol{r}_1 / m_2 + \boldsymbol{r}_2 / m_1) \quad e^{i\boldsymbol{k}\cdot\boldsymbol{r}_1} e^{i(\boldsymbol{k}+\boldsymbol{K})\cdot\boldsymbol{r}_2} \quad e^{i(\boldsymbol{k}+\boldsymbol{K})\cdot(\boldsymbol{r}_2 - \boldsymbol{r}_1)} e^{i\boldsymbol{K}\cdot\boldsymbol{r}_{cm}} = (\boldsymbol{k} + \boldsymbol{K}) \cdot (\boldsymbol{r}_2 - \boldsymbol{r}_1) + \boldsymbol{K} \cdot \boldsymbol{r}_{cm}$$

$$= (\boldsymbol{k} + \boldsymbol{K}) \cdot (\boldsymbol{r}_2 - \boldsymbol{r}_1) + \boldsymbol{K} \cdot \frac{m_1 \boldsymbol{r}_1 + m_2 \boldsymbol{r}_2}{m_1 + m_2} = \boldsymbol{K} \cdot \left(\frac{(m_1 + m_2)\boldsymbol{r}_2 - (m_1 + m_2)\boldsymbol{r}_1}{m_1 + m_2} + \frac{m_1 \boldsymbol{r}_1 + m_2 \boldsymbol{r}_2}{m_1 + m_2}\right) + \boldsymbol{k} \cdot (\boldsymbol{r}_2 - \boldsymbol{r}_1)$$

----------------メモ

Wannier 励起子（簡単のためスピンの自由度は考慮しない）

$$\psi_g(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N)=\prod_k \phi_m(\boldsymbol{r}_k-\boldsymbol{R}_k)$$

$$\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N)=\psi_{\boldsymbol{R}_i,\boldsymbol{R}_j}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N)=\phi_n(\boldsymbol{r}_i-\boldsymbol{R}_j)\prod_{k\neq i}\phi_m(\boldsymbol{r}_k-\boldsymbol{R}_k)$$

$$=\phi_m(\boldsymbol{r}_1-\boldsymbol{R}_1)\phi_m(\boldsymbol{r}_2-\boldsymbol{R}_2)\cdots\phi_m(\boldsymbol{r}_{i-1}-\boldsymbol{R}_{i-1})\phi_n(\boldsymbol{r}_i-\boldsymbol{R}_j)\phi_m(\boldsymbol{r}_{i+1}-\boldsymbol{R}_{i+1})\cdots\phi_m(\boldsymbol{r}_N-\boldsymbol{R}_N)$$

$\phi_m(\boldsymbol{r}-\boldsymbol{R}_i)\to\phi_n(\boldsymbol{r}-\boldsymbol{R}_i)$のほかにイオン化状態（電荷移動状態）$\phi_m(\boldsymbol{r}-\boldsymbol{R}_i)\to\phi_n(\boldsymbol{r}-\boldsymbol{R}_j)(i\neq j)$も考える

$$\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta})=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}_i}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}$$

$$\Phi_{mn}(\boldsymbol{K})=\sum_{\boldsymbol{\beta}}F(\boldsymbol{\beta})\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta})\quad \text{Wannier励起子波動関数}$$

$$=\sum_{\boldsymbol{\beta}}F(\boldsymbol{\beta})\frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}_i}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}=\sum_{\boldsymbol{\beta}}\sum_{\boldsymbol{R}_i}\frac{1}{\sqrt{N}}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)F(\boldsymbol{\beta})\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}$$

envelope function　　Wannier function

$$\phi_m(\boldsymbol{r}_i-\boldsymbol{R}_i)=\phi_m(\boldsymbol{R}_i)=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_i}\chi_{\boldsymbol{k}}^m(\boldsymbol{r}_i)$$

$$\psi_{\boldsymbol{R}_i,\boldsymbol{R}_j}(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N)\equiv\psi_{mn}(\boldsymbol{R}_i,\boldsymbol{R}_j)=\frac{1}{N}\sum_{\boldsymbol{k}_h}\sum_{\boldsymbol{k}_e}\exp[i(\boldsymbol{k}_h\cdot\boldsymbol{R}_i-\boldsymbol{k}_e\cdot\boldsymbol{R}_j)]\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)$$

Bloch関数　$\chi_{\boldsymbol{k}}(\boldsymbol{r})=e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{\boldsymbol{k}}(\boldsymbol{r})$

Wannier関数　$\phi_{\boldsymbol{R}}(\boldsymbol{r})=\dfrac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_i}\chi_{\boldsymbol{k}}(\boldsymbol{r})=\dfrac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{R})_i}u_{\boldsymbol{k}}(\boldsymbol{r})$

$$\chi_{\boldsymbol{k}}(\boldsymbol{r})=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{R}_i}\phi_{\boldsymbol{R}}(\boldsymbol{r})$$

$$\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta})=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}_i}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}_i}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)\frac{1}{N}\sum_{\boldsymbol{k}_h}\sum_{\boldsymbol{k}_e}\exp[i(\boldsymbol{k}_h\cdot\boldsymbol{R}_i-\boldsymbol{k}_e\cdot\boldsymbol{R}_j)]\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)$$

$$=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}_i}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)\frac{1}{N}\sum_{\boldsymbol{k}_e}\exp[i((\boldsymbol{k}_e-\boldsymbol{K})\cdot\boldsymbol{R}_i-\boldsymbol{k}_e\cdot(\boldsymbol{R}_i+\boldsymbol{\beta}))]\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)\quad \boldsymbol{R}_j=\boldsymbol{R}_i+\boldsymbol{\beta}\quad \boldsymbol{k}_e=\boldsymbol{k}_h+\boldsymbol{K}$$

$$=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}_i}\frac{1}{N}\sum_{\boldsymbol{k}_e}\exp[-i\boldsymbol{k}_e\cdot\boldsymbol{\beta}]\chi^n_{\boldsymbol{k}_e-\boldsymbol{K},\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}_e}\exp[-i\boldsymbol{k}_e\cdot\boldsymbol{\beta}]\chi^n_{\boldsymbol{k}_e-\boldsymbol{K},\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)$$

$$\Phi_{mn}(\boldsymbol{K})\equiv\Phi_{\boldsymbol{K}}=\sum_{\boldsymbol{\beta}}\sum_{\boldsymbol{R}_i}\frac{1}{\sqrt{N}}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)F(\boldsymbol{\beta})\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}\quad \boldsymbol{k}_e=\boldsymbol{k}_h+\boldsymbol{K}$$

$$=\sum_{\boldsymbol{\beta}}\sum_{\boldsymbol{R}_i}\frac{1}{\sqrt{N}}\exp[i(\boldsymbol{k}_e-\boldsymbol{k}_h)\cdot\boldsymbol{R}_i]F(\boldsymbol{\beta})\frac{1}{N}\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\exp[i(\boldsymbol{k}_h\cdot\boldsymbol{R}_i-\boldsymbol{k}_e\cdot(\boldsymbol{R}_i+\boldsymbol{\beta})]\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)$$

$$=\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)\frac{1}{\sqrt{N}}\sum_{\boldsymbol{\beta}}\exp[-i\boldsymbol{k}_e\cdot\boldsymbol{\beta}]F(\boldsymbol{\beta})=\sum_{\boldsymbol{k}_h,\boldsymbol{k}_e}\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)F(\boldsymbol{k}_e)=\sum_{\boldsymbol{k}_h}\chi^n_{\boldsymbol{k}_h,\boldsymbol{k}_h+\boldsymbol{K}}(\boldsymbol{r}_h,\boldsymbol{r}_e)F(\boldsymbol{k}_h+\boldsymbol{K})$$

$$\Phi_{mn}(\boldsymbol{K})\equiv\Phi_{\boldsymbol{K}}=\sum_{\boldsymbol{k}}F(\boldsymbol{k}+\boldsymbol{K})\chi_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{K}}\qquad \chi_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{K}}=\chi_{\boldsymbol{k}}^{v^*}(\boldsymbol{r}_1)\chi^c_{\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}_2)$$

$$\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}F(\boldsymbol{k})=\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\frac{1}{\sqrt{N}}\sum_{\boldsymbol{r}'}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}'_i}F(\boldsymbol{r}')=\sum_{\boldsymbol{r}'}\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}F(\boldsymbol{r}')=\sqrt{N}F(\boldsymbol{r})$$

$$H=\sum_i\left[-\frac{\hbar^2}{2m}\nabla_i{}^2+V_{\text{crys}}(\boldsymbol{r}_i)\right]+\sum_{i<j}\frac{e^2}{4\pi\varepsilon\,|\,\boldsymbol{r}_i-\boldsymbol{r}_j\,|}=\sum_i H_i+\sum_{i<j}V_{ij}$$

$$\left[-\frac{\hbar^2}{2m}\nabla_1{}^2+V_{\text{crys}}(\boldsymbol{r}_1)\right]\chi_{\boldsymbol{k}}^v(\boldsymbol{r}_1)=E_{\boldsymbol{k}}^v\chi_{\boldsymbol{k}}^v(\boldsymbol{r}_1)\quad\left[-\frac{\hbar^2}{2m}\nabla_2{}^2+V_{\text{crys}}(\boldsymbol{r}_2)\right]\chi_{\boldsymbol{k}}^c(\boldsymbol{r}_2)=E_{\boldsymbol{k}}^c\chi_{\boldsymbol{k}}^c(\boldsymbol{r}_2)$$

$$H\Phi_{\boldsymbol{K}}=\left[-\frac{\hbar^2}{2m}\nabla_1{}^2+V_{\text{crys}}(\boldsymbol{r}_1)-\frac{\hbar^2}{2m}\nabla_2{}^2+V_{\text{crys}}(\boldsymbol{r}_2)+V(\boldsymbol{r})\right]\Phi_{\boldsymbol{K}}=E\Phi_{\boldsymbol{K}}\qquad \boldsymbol{r}=\boldsymbol{\beta}$$

$$\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta})=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}_i}\exp(i\boldsymbol{K}\cdot\boldsymbol{R}_i)\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}_e}\exp[-i\boldsymbol{k}_e\cdot\boldsymbol{\beta}]\chi^n_{\boldsymbol{k}_e-\boldsymbol{K},\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)\quad \boldsymbol{R}_j=\boldsymbol{R}_i+\boldsymbol{\beta}\quad \boldsymbol{k}_e=\boldsymbol{k}_h+\boldsymbol{K}$$

$$\left\langle\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta})\right|H\left|\Lambda_{mn}(\boldsymbol{K}',\boldsymbol{\beta}')\right\rangle=\frac{1}{N}\sum_{\boldsymbol{R}_i,\boldsymbol{R}_i'}\exp[i(\boldsymbol{K}'\cdot\boldsymbol{R}_i'-\boldsymbol{K}\cdot\boldsymbol{R}_i)]\left\langle\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}\right|H\left|\psi_{\boldsymbol{R}_i',\boldsymbol{R}_i'+\boldsymbol{\beta}'}\right\rangle$$

$$=\frac{1}{N}\sum_{\boldsymbol{k}_e,\boldsymbol{k}_e'}\exp[i(\boldsymbol{k}_e\cdot\boldsymbol{\beta}-\boldsymbol{k}_e'\cdot\boldsymbol{\beta}')]\left\langle\chi^n_{\boldsymbol{k}_e-\boldsymbol{K},\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e)\right|H\left|\chi^n_{\boldsymbol{k}_e'-\boldsymbol{K}',\boldsymbol{k}_e'}(\boldsymbol{r}_h,\boldsymbol{r}_e)\right\rangle$$

$$\left\langle\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}\right|H\left|\psi_{\boldsymbol{R}_j,\boldsymbol{R}_j+\boldsymbol{\beta}'}\right\rangle=\int d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N\phi_m^*(\boldsymbol{r}_1-\boldsymbol{R}_1)\cdots\phi_m^*(\boldsymbol{r}_{i-1}-\boldsymbol{R}_{i-1})\phi_n^*(\boldsymbol{r}_i-(\boldsymbol{R}_i+\boldsymbol{\beta}))\phi_m^*(\boldsymbol{r}_{i+1}-\boldsymbol{R}_{i+1})\cdots\phi_m^*(\boldsymbol{r}_N-\boldsymbol{R}_N)$$

$$(\sum_p H_p+\sum_{\substack{p,q\\p<q}}V_{pq})\phi_m(\boldsymbol{r}_1-\boldsymbol{R}_1)\cdots\phi_m(\boldsymbol{r}_{j-1}-\boldsymbol{R}_{j-1})\phi_n(\boldsymbol{r}_j-(\boldsymbol{R}_j+\boldsymbol{\beta}'))\phi_m(\boldsymbol{r}_{j+1}-\boldsymbol{R}_{j+1})\cdots\phi_m(\boldsymbol{r}_N-\boldsymbol{R}_N)$$

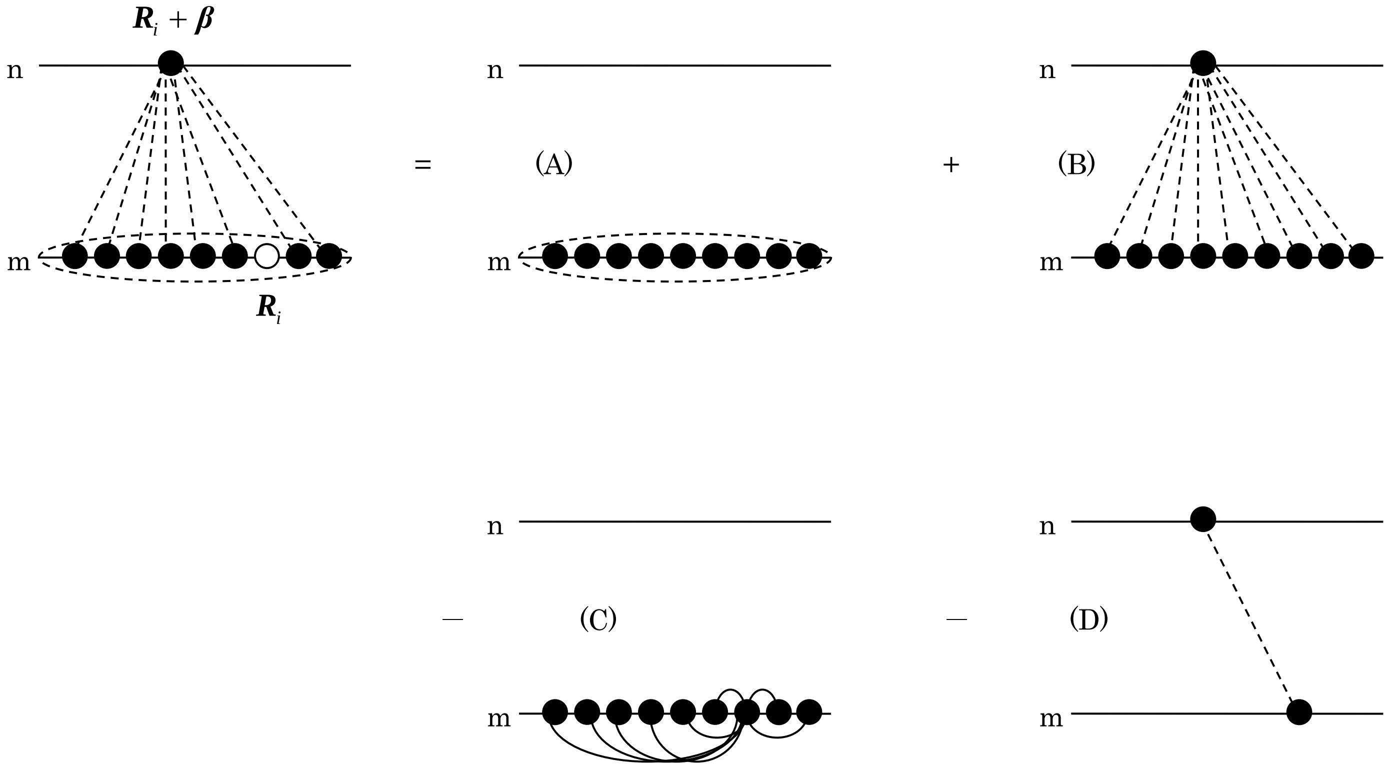
$$=\sum_p\int d\boldsymbol{r}_p\phi_m^*(\boldsymbol{r}_p-\boldsymbol{R}_p)H_p\phi_m(\boldsymbol{r}_p-\boldsymbol{R}_p)+\sum_{\substack{p,q\\p<q}}\int d\boldsymbol{r}_pd\boldsymbol{r}_q\phi_m^*(\boldsymbol{r}_p-\boldsymbol{R}_p)\phi_m^*(\boldsymbol{r}_q-\boldsymbol{R}_q)V_{pq}\phi_m(\boldsymbol{r}_p-\boldsymbol{R}_p)\phi_m(\boldsymbol{r}_q-\boldsymbol{R}_q)\quad\cdots(\text{A})$$

$$+\delta_{ij}\delta_{\boldsymbol{\beta}\boldsymbol{\beta}'}[\int d\boldsymbol{r}_i\phi_n^*(\boldsymbol{r}_i-(\boldsymbol{R}_i+\boldsymbol{\beta}))H_i\phi_n(\boldsymbol{r}_j-(\boldsymbol{R}_j+\boldsymbol{\beta}'))$$

$$+\sum_q\int d\boldsymbol{r}_id\boldsymbol{r}_q\phi_n^*(\boldsymbol{r}_i-(\boldsymbol{R}_i+\boldsymbol{\beta}))\phi_m^*(\boldsymbol{r}_q-\boldsymbol{R}_q)V_{iq}\phi_n(\boldsymbol{r}_j-(\boldsymbol{R}_j+\boldsymbol{\beta}'))\phi_m(\boldsymbol{r}_q-\boldsymbol{R}_q)]\quad\cdots(\text{B})$$

$$-\delta_{ij}[\int d\boldsymbol{r}_i\phi_m^*(\boldsymbol{r}_i-\boldsymbol{R}_i)H_i\phi_m(\boldsymbol{r}_j-\boldsymbol{R}_j)+\sum_{\substack{q\\i\neq q}}\int d\boldsymbol{r}_id\boldsymbol{r}_q\phi_m^*(\boldsymbol{r}_i-\boldsymbol{R}_i)\phi_m^*(\boldsymbol{r}_q-\boldsymbol{R}_q)V_{iq}\phi_m(\boldsymbol{r}_j-\boldsymbol{R}_j)\phi_m(\boldsymbol{r}_q-\boldsymbol{R}_q)]\quad\cdots(\text{C})$$

$$-\delta_{ij}\delta_{\boldsymbol{\beta}\boldsymbol{\beta}'}\int d\boldsymbol{r}_id\boldsymbol{r}_s\phi_n^*(\boldsymbol{r}_s-(\boldsymbol{R}_i+\boldsymbol{\beta}))\phi_m^*(\boldsymbol{r}_i-\boldsymbol{R}_i)V_{is}\phi_n(\boldsymbol{r}_s-(\boldsymbol{R}_j+\boldsymbol{\beta}'))\phi_m(\boldsymbol{r}_j-\boldsymbol{R}_j)\qquad \boldsymbol{R}_i+\boldsymbol{\beta}=\boldsymbol{R}_s\quad\cdots(\text{D})$$


$\boldsymbol{R}_i + \boldsymbol{\beta}$
n
m
$\boldsymbol{R}_i$
=
(A)
+
(B)
—
(C)
—
(D)

$$\phi_m(\boldsymbol{r}_i-\boldsymbol{R}_i)=\phi_m(\boldsymbol{R}_i)=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_i}\chi^m_{\boldsymbol{k}}(\boldsymbol{r}_i)\quad \phi_n(\boldsymbol{r}_i-(\boldsymbol{R}_i+\boldsymbol{\beta}))=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}e^{-i\boldsymbol{k}\cdot(\boldsymbol{R}_i+\boldsymbol{\beta})}\chi^n_{\boldsymbol{k}}(\boldsymbol{r}_i)$$

(A) = 基底状態エネルギー $= E_0$

$$(\mathrm{B})=\delta_{ij}\delta_{\boldsymbol{\beta}\boldsymbol{\beta}'}\int d\boldsymbol{r}_i\phi^*_n(\boldsymbol{r}_i-(\boldsymbol{R}_i+\boldsymbol{\beta}))H_i{}'\phi_n(\boldsymbol{r}_j-(\boldsymbol{R}_j+\boldsymbol{\beta}'))$$

$$H_i{}'=H_i+\sum_q\int d\boldsymbol{r}_q\phi^*_m(\boldsymbol{r}_q-\boldsymbol{R}_q)V_{iq}\phi_m(\boldsymbol{r}_q-\boldsymbol{R}_q)$$

$$=\int d\boldsymbol{r}_i\phi^*_n(\boldsymbol{r}_i-(\boldsymbol{R}_i+\boldsymbol{\beta}))H_i{}'\phi_n(\boldsymbol{r}_i-(\boldsymbol{R}_i+\boldsymbol{\beta}))=\frac{1}{N}\sum_{\boldsymbol{k}_e,\boldsymbol{k}'_e}e^{i(\boldsymbol{k}_e-\boldsymbol{k}'_e)\cdot(\boldsymbol{R}_i+\boldsymbol{\beta})}\int d\boldsymbol{r}_i\chi^{n\,*}_{\boldsymbol{k}_e}(\boldsymbol{r}_i)H_i{}'\chi^n_{\boldsymbol{k}'_e}(\boldsymbol{r}_i)=\frac{1}{N}\sum_{\boldsymbol{k}_e,\boldsymbol{k}'_e}e^{i(\boldsymbol{k}_e-\boldsymbol{k}'_e)\cdot(\boldsymbol{R}_i+\boldsymbol{\beta})}E_n(\boldsymbol{k}'_e)\delta_{\boldsymbol{k}_e,\boldsymbol{k}'_e}$$

$$=\frac{1}{N}\sum_{\boldsymbol{k}_e}E_n(\boldsymbol{k}_e)=E_n(\boldsymbol{k}_e)$$ 伝導帯電子エネルギー（1電子エネルギー）

$$(\mathrm{C})=-\delta_{ij}\int d\boldsymbol{r}_i\phi^*_m(\boldsymbol{r}_i-\boldsymbol{R}_i)H_i{}'\phi_m(\boldsymbol{r}_j-\boldsymbol{R}_j)=-\int d\boldsymbol{r}_i\phi^*_m(\boldsymbol{r}_i-\boldsymbol{R}_i)H_i{}'\phi_m(\boldsymbol{r}_i-\boldsymbol{R}_i)$$

$$H_i{}'=H_i+\sum_{\substack{q\\ i\neq q}}\int d\boldsymbol{r}_q\phi^*_m(\boldsymbol{r}_q-\boldsymbol{R}_q)V_{iq}\phi_m(\boldsymbol{r}_q-\boldsymbol{R}_q)$$

$$=-\frac{1}{N}\sum_{\boldsymbol{k}_h,\boldsymbol{k}'_h}e^{i(\boldsymbol{k}_h-\boldsymbol{k}'_h)\cdot\boldsymbol{R}_i}\int d\boldsymbol{r}_i\chi^{m\,*}_{\boldsymbol{k}_h}(\boldsymbol{r}_i)H_i{}'\chi^m_{\boldsymbol{k}'_h}(\boldsymbol{r}_i)=-\frac{1}{N}\sum_{\boldsymbol{k}_h,\boldsymbol{k}'_h}e^{i(\boldsymbol{k}_h-\boldsymbol{k}'_h)\cdot\boldsymbol{R}_i}E_m(\boldsymbol{k}'_h)\delta_{\boldsymbol{k}_h,\boldsymbol{k}'_h}$$

$$=-E_m(\boldsymbol{k}_h)=-E_m(\boldsymbol{k}_e-\boldsymbol{K})\quad \boldsymbol{k}_e=\boldsymbol{k}_h+\boldsymbol{K}$$ 価電子帯正孔エネルギー（1電子エネルギー）

$$(\mathrm{D})=-\int d\boldsymbol{r}_id\boldsymbol{r}_s\phi^*_n(\boldsymbol{r}_s-(\boldsymbol{R}_i+\boldsymbol{\beta}))\phi^*_m(\boldsymbol{r}_i-\boldsymbol{R}_i)V_{is}\phi_n(\boldsymbol{r}_s-(\boldsymbol{R}_i+\boldsymbol{\beta}))\phi_m(\boldsymbol{r}_i-\boldsymbol{R}_i)$$

$$=-\int d\boldsymbol{r}_hd\boldsymbol{r}_e\phi^*_n(\boldsymbol{r}_e-(\boldsymbol{R}_h+\boldsymbol{\beta}))\phi^*_m(\boldsymbol{r}_h-\boldsymbol{R}_h)V_{he}\phi_n(\boldsymbol{r}_e-(\boldsymbol{R}_h+\boldsymbol{\beta}))\phi_m(\boldsymbol{r}_h-\boldsymbol{R}_h)\quad \boldsymbol{R}_h+\boldsymbol{\beta}=\boldsymbol{R}_e$$

$$=-\frac{1}{N^2}\sum_{\boldsymbol{k}_e,\boldsymbol{k}'_e,\boldsymbol{k}_h,\boldsymbol{k}'_h}e^{i(\boldsymbol{k}_e-\boldsymbol{k}'_e)\cdot(\boldsymbol{R}_h+\boldsymbol{\beta})}e^{i(\boldsymbol{k}_h-\boldsymbol{k}'_h)\cdot\boldsymbol{R}_h}\int d\boldsymbol{r}_hd\boldsymbol{r}_e\chi^{m\,*}_{\boldsymbol{k}_h}(\boldsymbol{r}_h)\chi^{n\,*}_{\boldsymbol{k}_e}(\boldsymbol{r}_e)V_{he}\chi^m_{\boldsymbol{k}'_h}(\boldsymbol{r}_h)\chi^n_{\boldsymbol{k}'_e}(\boldsymbol{r}_e)\quad V_{he}\cong V_{\boldsymbol{\beta}}=\frac{e^2}{4\pi\varepsilon|\boldsymbol{\beta}|}$$ と近似

$$\cong-\frac{1}{N^2}\sum_{\boldsymbol{k}_e,\boldsymbol{k}'_e,\boldsymbol{k}_h,\boldsymbol{k}'_h}e^{i(\boldsymbol{k}_e-\boldsymbol{k}'_e)\cdot(\boldsymbol{R}_h+\boldsymbol{\beta})}e^{i(\boldsymbol{k}_h-\boldsymbol{k}'_h)\cdot\boldsymbol{R}_h}V_{\boldsymbol{\beta}}\int d\boldsymbol{r}_hd\boldsymbol{r}_e\chi^{m\,*}_{\boldsymbol{k}_h}(\boldsymbol{r}_h)\chi^{n\,*}_{\boldsymbol{k}_e}(\boldsymbol{r}_e)\chi^m_{\boldsymbol{k}'_h}(\boldsymbol{r}_h)\chi^n_{\boldsymbol{k}'_e}(\boldsymbol{r}_e)$$

$$\cong-\frac{1}{N^2}\sum_{\boldsymbol{k}_e,\boldsymbol{k}'_e,\boldsymbol{k}_h,\boldsymbol{k}'_h}e^{i(\boldsymbol{k}_e-\boldsymbol{k}'_e)\cdot(\boldsymbol{R}_h+\boldsymbol{\beta})}e^{i(\boldsymbol{k}_h-\boldsymbol{k}'_h)\cdot\boldsymbol{R}_h}V_{\boldsymbol{\beta}}\delta_{\boldsymbol{k}_e,\boldsymbol{k}'_e}\delta_{\boldsymbol{k}_h,\boldsymbol{k}'_h}=-V_{\boldsymbol{\beta}}$$

$$\left\langle\psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}}\middle|H\middle|\psi_{\boldsymbol{R}_j,\boldsymbol{R}_j+\boldsymbol{\beta}'}\right\rangle=[E_0+E_n(\boldsymbol{k}_e)-E_m(\boldsymbol{k}_h)-V_\beta]\delta_{ij}\delta_{\boldsymbol{\beta}\boldsymbol{\beta}'}$$

注：$-\delta_{ij}\delta_{\boldsymbol{\beta}\boldsymbol{\beta}'}\int d\boldsymbol{r}_id\boldsymbol{r}_j\phi^*_n(\boldsymbol{r}_i-(\boldsymbol{R}_i+\boldsymbol{\beta}))\phi^*_m(\boldsymbol{r}_i-\boldsymbol{R}_i)V_{\boldsymbol{\beta}}\phi_n(\boldsymbol{r}_j-(\boldsymbol{R}_j+\boldsymbol{\beta}'))\phi_m(\boldsymbol{r}_j-\boldsymbol{R}_j)\qquad V_{\boldsymbol{\beta}}=\dfrac{e^2}{4\pi\varepsilon|\boldsymbol{\beta}|}\quad\cdots(\mathrm{D})?$

$$\left\langle \Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta}) \middle| H \middle| \Lambda_{mn}(\boldsymbol{K}',\boldsymbol{\beta}') \right\rangle = \frac{1}{N}\sum_{\boldsymbol{R}_i,\boldsymbol{R}_i'} \exp[i(\boldsymbol{K}'\cdot\boldsymbol{R}_i' - \boldsymbol{K}\cdot\boldsymbol{R}_i)] \left\langle \psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}} \middle| H \middle| \psi_{\boldsymbol{R}_i',\boldsymbol{R}_i'+\boldsymbol{\beta}'} \right\rangle$$

$$= \frac{1}{N}\sum_{\boldsymbol{k}_e,\boldsymbol{k}_e'} \exp[i(\boldsymbol{k}_e\cdot\boldsymbol{\beta} - \boldsymbol{k}_e'\cdot\boldsymbol{\beta}')] \left\langle \chi^n_{\boldsymbol{k}_e-\boldsymbol{K},\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e) \middle| H \middle| \chi^n_{\boldsymbol{k}_e'-\boldsymbol{K}',\boldsymbol{k}_e'}(\boldsymbol{r}_h,\boldsymbol{r}_e) \right\rangle$$

$H=1$ならば$\left\langle \Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta}) \middle| \Lambda_{mn}(\boldsymbol{K}',\boldsymbol{\beta}') \right\rangle = \frac{1}{N}\sum_{\boldsymbol{k}_e,\boldsymbol{k}_e'} \exp[i(\boldsymbol{k}_e\cdot\boldsymbol{\beta} - \boldsymbol{k}_e'\cdot\boldsymbol{\beta}')] \left\langle \chi^n_{\boldsymbol{k}_e-\boldsymbol{K},\boldsymbol{k}_e}(\boldsymbol{r}_h,\boldsymbol{r}_e) \middle| \chi^n_{\boldsymbol{k}_e'-\boldsymbol{K}',\boldsymbol{k}_e'}(\boldsymbol{r}_h,\boldsymbol{r}_e) \right\rangle$

$$= \frac{1}{N}\sum_{\boldsymbol{k}_e,\boldsymbol{k}_e'} \exp[i(\boldsymbol{k}_e\cdot\boldsymbol{\beta} - \boldsymbol{k}_e'\cdot\boldsymbol{\beta}')] \delta_{\boldsymbol{k}_e-\boldsymbol{K},\boldsymbol{k}_e'-\boldsymbol{K}'} \delta_{\boldsymbol{k}_e,\boldsymbol{k}_e'} = \delta_{\boldsymbol{K},\boldsymbol{K}'}\delta_{\boldsymbol{\beta},\boldsymbol{\beta}'}$$

$\Phi_{mn}(\boldsymbol{K}) = \sum_{\boldsymbol{\beta}} F(\boldsymbol{\beta})\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta})$　Wannier励起子波動関数

$$H\Phi_{mn}(\boldsymbol{K}) = E\Phi_{mn}(\boldsymbol{K})$$

$$H\sum_{\boldsymbol{\beta}} F(\boldsymbol{\beta})\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta}) = E\sum_{\boldsymbol{\beta}} F(\boldsymbol{\beta})\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta})$$

両辺に左から$\Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta})$　(明らかに$\boldsymbol{K}'\neq\boldsymbol{K}$の非対角項$\left\langle \Lambda_{mn}(\boldsymbol{K}',\boldsymbol{\beta}) \middle| H \middle| \Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta}') \right\rangle = 0$　$\because \sum_n \exp[i(\boldsymbol{K}'-\boldsymbol{K})\cdot\boldsymbol{R}_n] = 0$)

$$\sum_{\boldsymbol{\beta}'} F(\boldsymbol{\beta}') \left\langle \Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta}) \middle| H \middle| \Lambda_{mn}(\boldsymbol{K},\boldsymbol{\beta}') \right\rangle = E\sum_{\boldsymbol{\beta}'} F(\boldsymbol{\beta}')\delta_{\boldsymbol{\beta},\boldsymbol{\beta}'}$$

$$\sum_{\boldsymbol{\beta}'} F(\boldsymbol{\beta}') \left\{ \frac{1}{N}\sum_{\boldsymbol{R}_i,\boldsymbol{R}_j} \exp[-i\boldsymbol{K}\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)] \left\langle \psi_{\boldsymbol{R}_i,\boldsymbol{R}_i+\boldsymbol{\beta}} \middle| H \middle| \psi_{\boldsymbol{R}_j,\boldsymbol{R}_j+\boldsymbol{\beta}'} \right\rangle \right\} = EF(\boldsymbol{\beta})$$

$$\sum_{\boldsymbol{\beta}'} F(\boldsymbol{\beta}') \left\{ \frac{1}{N}\sum_{\boldsymbol{R}_i,\boldsymbol{R}_j} \exp[-i\boldsymbol{K}\cdot(\boldsymbol{R}_i-\boldsymbol{R}_j)] [E_0 + E_n(\boldsymbol{k}_e) - E_m(\boldsymbol{k}_h) - V_{\beta}]\delta_{ij}\delta_{\boldsymbol{\beta}\boldsymbol{\beta}'} \right\} = EF(\boldsymbol{\beta})$$

$$\sum_{\boldsymbol{\beta}'} F(\boldsymbol{\beta}') \left\{ \frac{1}{N}\sum_{\boldsymbol{R}_i} [E_0 + E_n(\boldsymbol{k}_e) - E_m(\boldsymbol{k}_h) - V_{\beta}]\delta_{\boldsymbol{\beta}\boldsymbol{\beta}'} \right\} = EF(\boldsymbol{\beta})$$

$$[E_0 + E_n(\boldsymbol{k}_e) - E_m(\boldsymbol{k}_h) - V_{\beta}]F(\boldsymbol{\beta}) = EF(\boldsymbol{\beta})$$

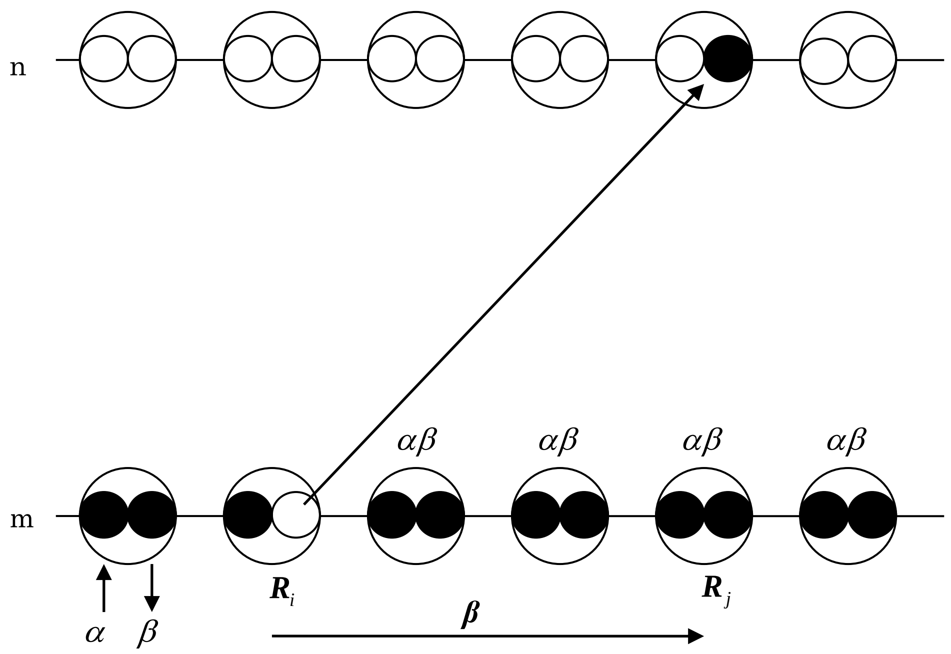
$E_0 - E_m(\boldsymbol{k}_e - \boldsymbol{K}) = \frac{\hbar^2}{2m_h}(\boldsymbol{k}_e-\boldsymbol{K})^2$　$E_n(\boldsymbol{k}_e) = E_g + \frac{\hbar^2}{2m_e}k_e{}^2$　価電子帯のtopをエネルギーの原点

$$\left(E_g + \frac{\hbar^2}{2m_e}k_e{}^2 + \frac{\hbar^2}{2m_h}k_e{}^2 - \frac{\hbar^2}{m_h}\boldsymbol{k}_e\cdot\boldsymbol{K} + \frac{\hbar^2}{2m_h}K^2 - \frac{e^2}{4\pi\varepsilon|\boldsymbol{\beta}|} \right) F(\boldsymbol{\beta}) = EF(\boldsymbol{\beta})$$

$F(\boldsymbol{\beta}) = e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta}),$　$k_e \to -i\frac{\partial}{\partial\boldsymbol{\beta}}$とおいて　p.6参照

$$[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\boldsymbol{\beta}^2} - \frac{e^2}{4\pi\varepsilon|\boldsymbol{\beta}|}]F'(\boldsymbol{\beta}) = [E - E_g - \frac{\hbar^2K^2}{2(m_e+m_h)}]F'(\boldsymbol{\beta})$$

実際は、スピンを考慮しなければならない



$$\phi_m(\boldsymbol{r}_i - \boldsymbol{R}_i) = \phi_m(\boldsymbol{R}_i) = \phi^m_{\boldsymbol{R}_i}(\boldsymbol{r}_i)$$

もっと厳密な基底状態

$$\psi_g(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) = \frac{1}{\sqrt{(2N)!}} \begin{vmatrix} \phi^m_{\boldsymbol{R}_1}(\boldsymbol{r}_1)\alpha & \phi^m_{\boldsymbol{R}_1}(\boldsymbol{r}_2)\alpha & \phi^m_{\boldsymbol{R}_1}(\boldsymbol{r}_3)\alpha & \cdots & \phi^m_{\boldsymbol{R}_1}(\boldsymbol{r}_{2N})\alpha \\ \phi^m_{\boldsymbol{R}_1}(\boldsymbol{r}_1)\beta & \phi^m_{\boldsymbol{R}_1}(\boldsymbol{r}_2)\beta & \phi^m_{\boldsymbol{R}_1}(\boldsymbol{r}_3)\beta & \cdots & \phi^m_{\boldsymbol{R}_1}(\boldsymbol{r}_{2N})\beta \\ \phi^m_{\boldsymbol{R}_2}(\boldsymbol{r}_1)\alpha & \phi^m_{\boldsymbol{R}_2}(\boldsymbol{r}_2)\alpha & \phi^m_{\boldsymbol{R}_2}(\boldsymbol{r}_3)\alpha & \cdots & \phi^m_{\boldsymbol{R}_2}(\boldsymbol{r}_{2N})\alpha \\ \vdots & & & & \\ \phi^m_{\boldsymbol{R}_N}(\boldsymbol{r}_1)\beta & \phi^m_{\boldsymbol{R}_N}(\boldsymbol{r}_2)\beta & \phi^m_{\boldsymbol{R}_N}(\boldsymbol{r}_3)\beta & \cdots & \phi^m_{\boldsymbol{R}_N}(\boldsymbol{r}_{2N})\beta \end{vmatrix}$$

スレーター行列式　全体として反対称な波動関数

励起状態はもっと複雑になる

励起状態をもっと厳密にやれば

一重項励起子の縦横分裂（縦波励起子と横波励起子）や三重項励起子が出てくる

$$-\delta_{ij}\delta_{\boldsymbol{\beta}\boldsymbol{\beta}'}\int d\boldsymbol{r}_i d\boldsymbol{r}_j \phi_n^*(\boldsymbol{r}_i-(\boldsymbol{R}_i+\boldsymbol{\beta}))\phi_m^*(\boldsymbol{r}_i-\boldsymbol{R}_i)V_{\boldsymbol{\beta}}\phi_n(\boldsymbol{r}_j-(\boldsymbol{R}_j+\boldsymbol{\beta}'))\phi_m(\boldsymbol{r}_j-\boldsymbol{R}_j) \qquad V_{\boldsymbol{\beta}}=\frac{e^2}{4\pi\varepsilon|\boldsymbol{\beta}|} \quad \cdots(\mathrm{D})?$$

３次元で等方的な場合　$\nabla_{\boldsymbol{\beta}}^2=\frac{1}{\beta^2}\frac{\partial}{\partial\beta}(\beta^2\frac{\partial}{\partial\beta})=\frac{2}{\beta}\frac{\partial}{\partial\beta}+\frac{\partial^2}{\partial\beta^2}$

$$[E_g-\frac{\hbar^2}{2}(\frac{1}{m_h}+\frac{1}{m_e})\frac{\partial^2}{\partial\boldsymbol{\beta}^2}+\frac{\hbar^2}{2m_h}K^2+i\frac{\hbar^2}{m_h}\boldsymbol{K}\cdot\frac{\partial}{\partial\boldsymbol{\beta}}+V_{eh}]F(\boldsymbol{\beta})=EF(\boldsymbol{\beta})$$

$F(\boldsymbol{\beta})=e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})$とおく

$$\frac{\partial}{\partial\boldsymbol{\beta}}[e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})]=i\alpha\boldsymbol{K}e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})+e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial}{\partial\boldsymbol{\beta}}F'(\boldsymbol{\beta})$$

$$\frac{\partial^2}{\partial\boldsymbol{\beta}^2}[e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})]=-\alpha^2K^2e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})+2i\alpha\boldsymbol{K}e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial}{\partial\boldsymbol{\beta}}F'(\boldsymbol{\beta})+e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial^2}{\partial\boldsymbol{\beta}^2}F'(\boldsymbol{\beta})+\frac{2}{\beta}\frac{\partial}{\partial\boldsymbol{\beta}}[e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})]$$

$$=-\alpha^2K^2e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})+2i\alpha\boldsymbol{K}e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial}{\partial\boldsymbol{\beta}}F'(\boldsymbol{\beta})+e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial^2}{\partial\boldsymbol{\beta}^2}F'(\boldsymbol{\beta})+\frac{2}{\beta}[i\alpha\boldsymbol{K}e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}F'(\boldsymbol{\beta})+e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial}{\partial\boldsymbol{\beta}}F'(\boldsymbol{\beta})]$$

$e^{i\alpha\boldsymbol{K}\cdot\boldsymbol{\beta}}\frac{\partial}{\partial\boldsymbol{\beta}}F'(\boldsymbol{\beta})$の係数が0になるように$\alpha$を定める?

$$-\frac{\hbar^2}{2}(\frac{1}{m_h}+\frac{1}{m_e})(2i\alpha\boldsymbol{K}+\frac{2}{\beta})+i\frac{\hbar^2}{m_h}\boldsymbol{K}=0 \quad \frac{1}{m_h}+\frac{1}{m_e}=\frac{1}{\mu} \quad -\frac{\hbar^2}{2\mu}(2i\alpha\boldsymbol{K}+\frac{2}{\beta})=-i\frac{\hbar^2}{m_h}\boldsymbol{K} \quad -\frac{\hbar^2}{\mu}(i\alpha\boldsymbol{K}+\frac{1}{\beta})=-i\frac{\hbar^2}{m_h}\boldsymbol{K}$$