NO.

ILOC(KTYP) : local potにする軌道角運動量子数 + 1

ILMT(KTYP) : IT種アトムのもつ量子数 lとmの数 (local のぞく)

LMTT(KLMT, KTYP) : IT種アトムの量子数 lとm をもつ軌道の index number

LMTA(KLMT, KATM) : IA アトムの 〃

LTP (KLMT, KTYP) : IT種アトムの 〃 の $\underline{l+1}$

MTP (KLMT, KTYP) 〃 $m+l+1 = \underline{1 \sim 2l+1}$

TAUP (KLMT, KTYP) 〃 $\underline{\tau}$

ILP2(KLMT, KLMT, KTYP) : IT種アトムのガウント系数

Work 領域 NO. ①

PSPOT

CFFT (KFFT)	ALP(2, KTYP), CC(2, KTYP),
	WS(KTYP), WP(KTYP)
	CHGPC(KTYP), EPS(KTAU, KLOC, KTYP)
AFFT(KFFTP)	VHXCR(KMESH, KTYP),
BFFT(KFFTP)	VNLR(KMESH, KTAU, KLOC, KTYP)

EWALD

AFFT(KFFTP)	RR(*)	→ NZIBRD
	RXM	neibrd * NATM2
BFFT(KFFTP)	RYM(*)	〃 〃
	RZM(*)	〃
CFFT(KFFT)	ZSUM(KNG, KIMG)	

XCFFT

X(KNGP)	PCR(KNGP)
Y(KNGP)	PCI(KNGP)

KBINT

X(KNGP)	QX(KNG1)	QY(KNG1)	QZ(KNG1)	AK2(KNG1)
Y(KNGP)	X(KNG1)	Y(KNG1)	YLM(KNG1)	

coop Filing Leaf 7mm・35行

$\boxed{\text{MATRIX}}$

KNG11 OR KNG1

CFFT(KFFT) LDAG (KNGT*KIMG)

AFFT(KFBTP) EKT (KNGT)

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{i,\mathbf{k}+\mathbf{G}} \, e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$= e^{i\mathbf{k}\cdot\mathbf{r}} \underbrace{\sum_{\mathbf{G}} C_{i\mathbf{k}+\mathbf{G}} \, e^{i\mathbf{G}\cdot\mathbf{r}}}_{u_{i\mathbf{k}}(\mathbf{r})}$$

$Y_{lm}(-\hat{r}) = (-1)^l Y_{lm}(\hat{r})$

$$e^{i\mathbf{G}\cdot\mathbf{r}} = 4\pi \sum_{lm} i^l j_l(Gr)\, Y^*_{lm}(\hat{G})\, Y_{lm}(\hat{r})$$

Plane Wave Basis

Jan. 15 '93

NO. 1

" FSR (KEG, KLMTA, KNVJ) $\boxed{\text{SUMSET}}$

FSI

SNL (KNGI, KLMTT, KNV3) $\boxed{\text{EBINT}}$

GSXR (KEG, KLMT) $\boxed{\text{SUMSET}}$

" I

$\langle \varphi_{ilk} | \beta^I_n \rangle \langle \beta^I_{n'} | \varphi_{ilk} \rangle (a-ib)(c+id) = ac+bd+i(ad-bc)$

④ $$h^{IA}_{\tau\ell m,\tau'\ell'm'} \equiv \sum^{\text{occupied}}_{nk} f^{IAn*}_{\tau\ell m}(k)\, f^{IAn}_{\tau'\ell'm'}(k) + f^{IAn*}_{\tau\ell m}(-k)\, f^{IAn}_{\tau'\ell'm'}(-k) \rightarrow \text{実部のみ}$$

$$= h^{IA\,*}_{\tau'\ell'm'\tau\ell m} = (-1)^{\ell+\ell'} h^{-IA\,*}_{\tau\ell m\tau'\ell'm'}$$

〃 HSR(KATM, KLMT, KLMT)

I

⑤ $$\xi^{IA}_{\tau\ell m\tau'\ell'm'} \equiv \sum^{\text{occupied}}_{nk} g^{IAn*}_{\tau\ell m}(k)\, f^{IAn}_{\tau'\ell'm'}(k) + f^{IA*}_{\tau\ell m}(k)\, g^{IAn}_{\tau'\ell'm'}(k)$$

XIXR(IA, KLMT, KLMT)

$$= \xi^{IA\,*}_{\tau'\ell'm'\tau\ell m} = (-1)^{\ell+\ell'+1} \cancel{\xi^{-IA\,n*}_{\tau\ell m\tau'\ell'm'}} = (-1)^{\ell+\ell'+1} \xi^{-IAn}_{\tau'\ell'm'\tau\ell m}$$

⑥ $F^{IA}_{NL} = -$

⑦ $$Q^{It\,\ell''}_{\tau\ell\tau'\ell'}(G) = \frac{4\pi}{\Omega_a} \int_0^\infty Q^{It}_{\tau\tau'\ell\ell'}(r)\, j_{\ell''}(Gr)\, r^2 dr$$

〃 QITG(KNGP, KQITG) ← IQITG

⑧ $$VQ^{IA}_{\tau\ell m\tau'\ell'm'} \equiv \int V_{LHxc}(r)\, Q^{IA}_{\tau\ell m\tau'\ell'm'}(r - R_{IA})\, dr = VQ^{IA}_{\tau'\ell'm'\tau\ell m} = (-1)^{\ell+\ell'} VQ^{-IA}_{\tau\ell m\tau'\ell'm'}$$

〃 VLHxcQ(KLMT, KLMT, KATM2)

$$= \sum_G V_{LHxc}(G)\, e^{iG\cdot R_{IA}} \int Q^{It}_{\tau\ell m\tau'\ell'm'}(r)\, e^{iG\cdot r}\, dr$$

$$= \Omega_a \sum_{\ell''m''} i^{\ell''} d^{\ell''}(\ell m;\ell'm') \sum_G V_{LHxc}(G)\, e^{iG\cdot R_{IA}}\, Q^{It\ell''}_{\tau\ell\tau'\ell'}(G)\, Y_{\ell''m''}(\hat{G})$$

⑨ $$\eta^{IA}_{\tau\ell m\tau'\ell m} = \sum^{\text{occupied}}_{nk} \varepsilon_{nk} \left(g^{IAn*}_{\tau\ell m}(k)\, f^{IAn}_{\tau'\ell m}(k) + f^{IAn*}_{\tau\ell m}(k)\, g^{IAn}_{\tau'\ell m}(k) \right)$$

$$= \eta^{IA\,*}_{\tau\ell m\tau'\ell m}$$

charge density

$$\sum_{LM} d\, Q(|r - R_{I}|)\, Y_{LM}(\widehat{r - R_{IA}})$$

$$n_v(r) = \sum_{nk} \phi^*_{nk}(r)\,\phi_{nk}(r)$$

$$+ \sum_{nk}\sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'} \langle \phi_{nk} | \beta^{IA}_{\tau l m}\rangle\, Q^{It}_{\tau l m \tau' l' m'}(r - R_{IA})\, \langle \beta^{IA}_{\tau' l' m'} | \phi_{nk}\rangle$$

$$= \rho(r) + \sum_{nk}\sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'} f^{IAn*}_{\tau l m}(k)\, f^{IAn}_{\tau' l' m'}(k)\, Q^{It}_{\tau l m \tau' l' m'}(r - R_{IA})$$

$$n_v(G) = \frac{1}{\Omega_a}\int n_v(r)\, e^{-iG\cdot r}\, dr \quad \Longleftrightarrow \quad n_v(r) = \sum_G n_v(G)\, e^{iG\cdot r}$$

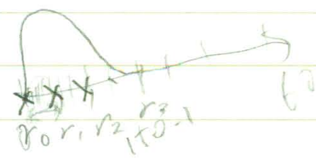
chgq(ig, imag)
KNGP 2

$$= \frac{1}{\Omega_a}\sum_{nk}\sum_{G'} C^{n*}_{k+G'-G}\, C^{n}_{k+G'}$$

$$+ \sum_{nk}\sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'} f^{IAn*}_{\tau l m}(k)\, f^{IAn}_{\tau' l' m'}(k)$$

$$* e^{-iG\cdot R_{IA}}\ \frac{1}{\Omega_a}\int Q^{It}_{\tau l m \tau' l' m'}(r)\, e^{-iG\cdot r}\, dr$$

$i = 1501$
$i_{max} = 96$



$$= \rho(G)$$

$$+ \sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'} h^{IA}_{\tau l m \tau' l' m'} * e^{-iG\cdot R_{IA}}$$

$$Q^{It\, l''}_{\tau l \tau' l'}(G)$$

$$+ \sum_{l'' m''} i^{-l''}\, \frac{4\pi}{\Omega_a}\int_0^\infty dr\ Q^{It}_{\tau l \tau' l'}(r)\, r^2\, j_{l''}(Gr)$$

$$* \underline{\int Y^*_{lm}(\hat r)\, Y_{l'm'}(\hat r)\, Y_{l''m''}(\hat r)\, dr} \quad * \ Y^*_{l''m''}(\hat G)$$

Gaunt 係数 $\equiv d^{l''}(lm; l'm') = d^{l''}(l'm'; lm)$

(Y_{lm} は実数化.)

$\cancel{\left(\frac{2l''+1}{4\pi}\right)^{1/2}}$

'93/7/8

$$\therefore n(G) = \rho(G)$$

$$+\sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'}\sum_{l'' m''} i^{-l''} d^{l''}(lm;l'm')$$

$$* h^{IA}_{\tau l m \tau' l' m'}\ e^{-iG\cdot R_{IA}}\ Q^{I\tau l''}_{\tau l \tau' l'}(G)\ Y^{*}_{l''m''}(\hat{G})$$ //

$$= \rho(G)$$

$$+\sum_{IA}\sum_{\tau l m}\sum_{l' \geq l}\begin{pmatrix} l'=l \rightarrow & \sum_{\tau' \geq \tau} \\ \text{else} & \sum_{\tau'}\end{pmatrix}\begin{pmatrix} l'\tau'=l\tau \rightarrow & \sum_{m' \geq m} \\ \text{else} & \sum_{m'}\end{pmatrix}\sum_{l''m''}$$

$$i^{-l''} d^{l''}(lm;l'm')\ e^{-iG\cdot R_{IA}}\ Q^{I\tau l''}_{\tau l \tau' l'}(G)\ Y^{*}_{l''m''}(\hat{G})$$

$$* \mathrm{Real}\left(h^{IA}_{\tau l m \tau' l' m'}\right) * \begin{cases} \tau l m = \tau' l' m' & *1 \\ \text{else} & *2 \end{cases}$$ //

inversion center があるとき $i^{-l''}\left(e^{-iGR_{IA}} + (-1)^{l+l'} e^{iGR_{IA}}\right)$

$$= \rho(G)$$

$$+\sum_{\substack{IA \\ 独立}}\sum_{\tau l m}\sum_{l' \geq l}\begin{pmatrix} l'=l \rightarrow & \sum_{\tau' \geq \tau} \\ \text{else} & \sum_{\tau'}\end{pmatrix}\begin{pmatrix} l'\tau'=l\tau \rightarrow & \sum_{m' \geq m} \\ \text{else} & \sum_{m'}\end{pmatrix}\sum_{l''m''} * \begin{cases} \tau l m = \tau l' m' & *1 \\ \text{else} & *2 \end{cases}$$

$$\mathrm{IWEI}(IA) * d^{l''}(lm;l'm')\ Q^{I\tau l''}_{\tau l \tau' l'}(G)\ Y^{*}_{l''m''}(\hat{G})$$

$$* \mathrm{Real}\left(h^{IA}_{\tau l m \tau' l' m'}\right) * \begin{cases} l+l' と l'' 偶数 & * \mathrm{Re}(i^{-l''}) \cos G R_{IA} \\ \quad 奇数 & * \mathrm{Re}(-i^{-l''+1}) \sin G R_{IA} \end{cases}$$ //

$$n(G)^* = \rho(G)^*$$

$$+ \sum_{IA} \sum_{\tau \ell m} \sum_{\tau' \ell' m'} \sum_{\ell'' m''} i^{+\ell''} d^{\ell''}(\ell m; \ell' m')$$

$$* e^{+iG \cdot R_{IA}} Q^{I+\ell'}_{\tau \ell \tau' \ell'}(G) Y_{\ell'' m''}(\hat{G}) \; h^{IA\,*}_{\tau \ell m \tau' \ell' m'}$$

$$\frac{\delta n(G')^*}{\delta C^{n*}_{k+G}} = \frac{1}{\Omega_a} C^{n}_{k+G-G'}$$

$$+ \sum_{IA} \sum_{\tau \ell m} \sum_{\tau' \ell' m'} \sum_{\ell'' m''} i^{+\ell''} d^{\ell''}(\ell m; \ell' m')$$

$$e^{iG' \cdot R_{IA}} Q^{I+\ell''}_{\tau \ell \tau' \ell'}(G') Y_{\ell'' m''}(G')$$

$$* f^{IAn}_{\tau \ell m}(k) \; i^{-\ell'} e^{-iG \cdot R_{IA}} SNL(G, \tau' \ell' m', k)$$

$$\frac{\partial n_v^*(G)}{\partial R_{IA}} = \sum_{\tau\ell m} \sum_{\tau'\ell'm'} \sum_{\ell''m''} i^{\ell''} d^{\ell''}(\ell m; \ell'm') \, e^{iG\cdot R_{IA}} \, Q^{I\tau\ell''}_{\tau\ell\tau'\ell'}(G) \, Y_{\ell''m''}(\hat{G})$$

$$* \left\{ iG \, h^{IA*}_{\tau\ell m\tau'\ell'm'} + \sum_{nk} g^{IAn}_{\tau\ell m}(k) \, f^{IAn*}_{\tau'\ell'm'}(k) + f^{IAn}_{\tau\ell m}(k) \, g^{IAn*}_{\tau'\ell'm'} \right\}$$

$$= \sum_{\tau\ell m} \sum_{\tau'\ell'm'} \sum_{\ell''m''} i^{\ell''} d^{\ell''}(\ell m; \ell'm') \, e^{iG R_{IA}} \, Q^{I\tau\ell''}_{\tau\ell\tau'\ell'}(G) \, Y_{\ell''m''}(\hat{G})$$

$$* \left\{ iG \, h^{IA*}_{\tau\ell m\tau'\ell'm'} + \Xi^{IA*}_{\tau\ell m\tau'\ell'm'} \right\}$$

Kinetic energy

$$E_{kin} = \sum_{n\mathbf{k}} \langle \phi_{n\mathbf{k}} | -\frac{1}{2}\nabla^2 | \phi_{n\mathbf{k}} \rangle$$

$$= +\frac{1}{2} \sum_{n\mathbf{k}} \sum_{\mathbf{G}} |\mathbf{k}+\mathbf{G}|^2 \, |C^n_{\mathbf{k}+\mathbf{G}}|^2$$

$$\frac{\delta E_{kin}}{\delta C^{n*}_{\mathbf{k}+\mathbf{G}}} = \frac{1}{2} |\mathbf{k}+\mathbf{G}|^2 \, C^n_{\mathbf{k}+\mathbf{G}}$$

Hartree energy

$$E_H = \frac{4\pi}{2} \Omega_a \sum_{\mathbf{G}\neq 0} \frac{n_v(\mathbf{G})\, n_v^*(\mathbf{G})}{|\mathbf{G}|^2}$$

$$\frac{\delta E_H}{\delta C^{n*}_{\mathbf{k}+\mathbf{G}}} = 4\pi \Omega_a \sum_{\mathbf{G}'\neq 0} \frac{n_v(\mathbf{G}')}{|\mathbf{G}'|^2} \frac{\delta n_v^*(\mathbf{G}')}{\delta C^{n*}_{\mathbf{k}+\mathbf{G}}}$$

$$\frac{\delta E_H}{\delta \mathbf{R}_{IA}} = 4\pi \Omega_a \sum_{\mathbf{G}'\neq 0} \frac{n_v(\mathbf{G}')}{|\mathbf{G}'|^2} \frac{\delta n_v^*(\mathbf{G})}{\delta \mathbf{R}_{IA}}$$

Exchange Correlation

$$E_{xc} = \Omega_a \sum_{\mathbf{G}} \Big\{ (n_v + n_c(\mathbf{G}))\, \epsilon^*_{xc}[n_v + n_c](\mathbf{G}) - n_c(\mathbf{G}) \cdot \epsilon^*_{xc}[n_c](\mathbf{G}) \Big\}$$

$$\frac{\delta E_{xc}}{\delta C^{n*}_{\mathbf{k}+\mathbf{G}}} = \Omega_a \sum_{\mathbf{G}'} \mu_{xc}[n_v + n_c](\mathbf{G}') \frac{\delta n_v^*(\mathbf{G}')}{\delta C^{nk}_{\mathbf{k}+\mathbf{G}}}$$

$$\frac{\delta E_{xc}}{\delta \mathbf{R}_{IA}} = \Omega_a \sum_{\mathbf{G}'} \mu_{xc}[n_v + n_c](\mathbf{G}') \left(\frac{\delta n_v^*(\mathbf{G}')}{\delta \mathbf{R}_{IA}} + \frac{\delta n_c^*(\mathbf{G}')}{\delta \mathbf{R}_{IA}} \right) - \mu_{xc}[n_c](\mathbf{G}') \frac{\delta n_c^*(\mathbf{G}')}{\delta \mathbf{R}_{IA}}$$

Local Potential Energy

$$E_{loc} = \int V_{loc}(\mathbf{r})\, n_v(\mathbf{r})\, d\mathbf{r}$$

$$= \sum_{\mathbf{G}} \int V_{loc}(\mathbf{r})\, n_v^*(\mathbf{G})\, e^{-i\mathbf{G}\cdot\mathbf{r}}\, d\mathbf{r}$$

$$= \Omega_a \sum_{\mathbf{G}} V_{loc}(\mathbf{G})\, n_v^*(\mathbf{G}) \;//$$

$$\frac{\delta E_{loc}}{\delta C^{n*}_{\mathbf{k}+\mathbf{G}}} = \Omega_a \sum_{\mathbf{G}'} V_{loc}(\mathbf{G}')\, \frac{\delta n_v^*(\mathbf{G}')}{\delta C^{n*}_{\mathbf{k}+\mathbf{G}}}$$

$$\frac{\delta E_{loc}}{\delta \mathbf{R}_{IA}} = \Omega_a \sum_{\mathbf{G}'} V_{loc}(\mathbf{G}')\, \frac{\delta n_v^*(\mathbf{G}')}{\delta \mathbf{R}_{IA}} \;//$$

$$V_{loc}(\mathbf{G}) = \frac{1}{\Omega_a} \int V_{loc}(\mathbf{r})\, e^{-i\mathbf{G}\cdot\mathbf{r}}\, d\mathbf{r}$$

$$= \frac{1}{\Omega_a} \sum_{IA} e^{-i\mathbf{G}\cdot\mathbf{R}_{IA}} \int V^{IA}_{loc}(r)\, \underbrace{e^{-i\mathbf{G}\cdot\mathbf{r}}}_{} d\mathbf{r}$$

$$4\pi i^l j_l(Gr)\, Y^*_{lm}(\hat{\mathbf{r}})\, Y_{lm}(\hat{\mathbf{G}})$$

$$= \sum_{IA} e^{-i\mathbf{G}\cdot\mathbf{R}_{IA}} \underbrace{\frac{4\pi}{\Omega_a} \int V^{IA}_{loc}(r)\, j_0(Gr)\, r^2 dr}_{\text{PSC (KNG, KTYP)}} \;//$$

NO.

$$\Omega_a \sum_{G} \frac{\delta V_{\mathrm{loc}}(G)}{\delta R_{IA}} n_v^*(G)$$

$$= \Omega_a \sum_{G} (-iG)\, e^{-iGR_{IA}}\, \mathrm{psc}(G, It) * n_v^*(G)$$

$$= \Omega_a \sum_{G} \frac{1}{2} \left\{ -iG e^{-iGR_{IA}} n_v^*(G) + iG e^{iGR_{IA}} n_v(G) \right\} \mathrm{psc}(G, It)$$

$\cos + i\sin$ $\quad x+(y)$

$$= \Omega_a \sum_{G} iG\, i \cdot \mathrm{Im}\left(e^{iGR_{IA}} n_v(G) \right) \mathrm{PSC}(G, It)$$

$$= -\Omega_a \sum_{G} G \left(n_{vx}(G) \sin GR_{IA} + n_{vy}(G) \cos GR_{IA} \right) \mathrm{psc}(G, It)$$

$$\frac{\delta}{\delta R_{IA}}\left(E_H + E_{xc} + E_{loc}\right)$$

省略.

$$= \Omega_a \sum_G V_{LHxc}(G) \frac{\delta n_v^*(G)}{\delta R_{IA}} + \Omega_a \mu_{xc}^{v+c}(G) \frac{\delta n_c^*(G)}{\delta R_{IA}} - \mu_{xc}^{c}(G) \frac{\delta n_c^*(G)}{\partial R_{IA}}$$

$$+ \Omega_a \sum_G \frac{\delta V_{loc}(G)}{\delta R_{IA}} n_v^*(G)$$

$$= \Omega_a \sum_{\tau l m} \sum_{\tau' l' m'} \sum_{l'' m''} i^{l''} d^{l''}(lm; l'm')$$

$$* \sum_G V_{LHxc}(G)\, e^{iG \cdot R_{IA}}\, Q^{I+l''}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})$$

$$* \left\{ iG\, h^{IA*}_{\tau l m \tau' l' m'} + \Xi^{IA\,*}_{\tau l m \tau' l' m'} \right\}$$

$$= \Omega_a \sum_{\tau l m} \sum_{l' \geq l} \begin{pmatrix} l' = l \rightarrow \sum_{\tau' \geq \tau} \\ \text{else} \quad \sum_{\tau'} \end{pmatrix} \begin{pmatrix} l'\tau' = l\tau \rightarrow \sum_{m' \geq m} \\ \text{else} \quad \sum_{m'} \end{pmatrix} \sum_{l'' m''} * \begin{cases} \tau l m = \tau' l' m' & *1 \\ \text{else} & *2 \end{cases} \Bigg\} \equiv \sum_{\substack{\tau l m \\ \tau' l' m' \\ l'' m''}}$$

$$* i^{l''} d^{l''}(lm; l'm') * \sum_G V_{LHxc}(G)\, e^{iG R_{IA}}\, Q^{I+l''}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})$$

$$* \left\{ iG\, \mathrm{Re}\left(h^{IA}_{\tau l m \tau' l' m'}\right) + \mathrm{Re}\left(\Xi^{IA}_{\tau l m \tau' l' m'}\right) \right\}$$

Gと$-G$をたして $\qquad Y_{l''m''}(-\hat{G}) = i^{-2l''}\, Y_{l''m''}(\hat{G})$

$$= \sum_{\substack{\tau l m \\ \tau' l' m' \\ l'' m''}} i^{l''} d^{l''}(lm; l'm') \sum_G Q^{I+l''}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})$$

$$* \Big\{ iG\, \mathrm{Re}\left(h^{IA}_{\tau l m \tau' l' m'}\right) \left(V e^{iG R_{IA}} - (-1)^{l''} V^* e^{-iG R_{IA}} \right)$$

$$+ \mathrm{Re}\left(\Xi^{IA}_{\tau l m \tau' l' m'}\right) \left(V e^{iG R_{IA}} + (-1)^{l''} V^* e^{-iG R_{IA}} \right) \Big\} / 2$$

$$= \sum_{\substack{\tau l m \\ \tau' l' m' \\ \tau'' l'' m''}} d^{l''}(lm;l'm') \sum_{G} Q^{I t l''}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})$$

l'' = 偶数の場合

$$+\mathrm{Re}(i^{l''}) \Big\{ - G\, \mathrm{Re}(h^{IA}_{\tau l m \tau' l' m'}) \left(v_x \sin G R_{IA} + v_y \cos G R_{IA} \right)$$

$$+ \mathrm{Re}(\Xi^{IA}_{\tau l m \tau' l' m'}) \left(v_x \cos G R_{IA} - v_y \sin G R_{IA} \right) \Big\}$$

l'' = 奇数の場合

[redacted]

$$\frac{\delta}{\delta C^{n*}_{k+G}}\left(E_H + E_{xc} + E_{loc}\right)$$

$$= \Omega_a \sum_{G'} V_{LHxc}(G') \frac{\delta n_v^*(G')}{\delta C^{n*}_{k+G}}$$

$$= \sum_{G'} V_{LHxc}(G')\, C^{n}_{k+G-G'}$$

$$+\,\Omega_a \sum_{IA} \sum_{\tau l m} \sum_{\tau' l' m'} \sum_{l'' m''} i^{l''}\, d^{l''}(lm; l'm')$$

$$\sum_{G'} V_{LHxc}(G')\, e^{iG' R_{IA}}\, Q^{It\,l''}_{\tau l \tau' l'}(G')\, Y_{l''m''}(G')$$

$$* f^{IAn}_{\tau l m}(k)\, i^{-l'}\, e^{-iG R_{IA}}\, S_{NL}(G, \tau' l' m'; k)$$

$$\int V_{LHxc}(r)\, Q^{IA}_{\tau l m \tau' l' m'}(r - R_{IA})\, dr$$

$$Q^{Itl''}_{\tau l \tau' l'}\, Y^*_{lm}\, Y_{l'm'} \qquad 4\pi\, i^{l''} j_{l''}\, Y_{l''m''}(\hat{G})\, Y^*_{lm} Y_{l'm'}$$

$$= \sum_{G'} V_{LHxc}(G')\, e^{iG' R_{IA}} \int Q^{It}_{\tau l m \tau' l' m'}(r)\, e^{iG' r}\, dr$$

$$= \Omega_a \sum_{l''m''} \underbrace{\frac{4\pi}{\Omega_a}\, i^{l''}}_{d^{l''}(lm;l'm')} \sum_{G'} V_{LHxc}(G')\, e^{iG' R_{IA}} \int Q^{Itl''}_{\tau l \tau' l'}(r)\, j_{l''}(Gr)\, r^2 dr\, Y_{l''m''}(\hat{G}')$$

$$= \Omega_a \sum_{l''m''} i^{l''} d^{l''}(lm; l'm') \sum_{G} V_{LHxc}(G')\, e^{iG' R_{IA}}$$

$$* Q^{Itl''}_{\tau l \tau l}(G')\, Y_{l''m''}(\hat{G}')$$

$$= \sum_{G'} V_{LHxc}(G')\, C^{n}_{k+G-G'}$$

$$+ \sum_{IA} \sum_{\tau l m} \sum_{\tau' l' m'} VQ^{IA}_{\tau l m \tau' l' m'} * f^{IAn}_{\tau l m}(k)\, i^{-l'} e^{-iG R_{IA}}$$

$$* S_{NL}(G, \tau' l' m'; k)$$

$$VQ^{IA}_{\tau l m \tau' l' m'} \equiv \int V_{LHxc}(\mathbf{r})\, Q^{IA}_{\tau l m \tau' l' m'}(\mathbf{r}-\mathbf{R}_{IA})\, d\mathbf{r}$$

$$= \Omega_a \sum_{l''m''} i^{l''} d^{l''}(lm;l'm') \sum_{G} V_{LHxc}(G)\, e^{iG R_{IA}}\, Q^{I\tau l''}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})$$

Gと$-G$で和　$Y_{l''m''}(-\hat{G}) = (-1)^{l''} Y_{l''m''}(\hat{G})$

$$= \Omega_a \sum_{l''m''} i^{l''} d^{l''}(lm;l'm') \sum_{G} Q^{I\tau l''}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})$$

$$* \left(V e^{iG R_{IA}} + (-1)^{l''} V^* e^{-iG R_{IA}} \right) / 2$$

$$= \Omega_a \sum_{l''m''} d^{l''}(lm;l'm') \sum_{G} Q^{I\tau l''}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})$$

l''＝偶数

$$* \, \mathrm{Re}(i^{l''}) * \left(V_x \cos G R_{IA} - V_y \sin G R_{IA} \right)$$

l''＝奇数

$$* - \mathrm{Im}(i^{l''}) * \left(V_x \sin G R_{IA} + V_y \cos G R_{IA} \right)$$

$d^{l''}(lm;l'm')\, Y_{l''m''}(\hat{G})$ の計算を必要とする項 NO. 13.

$M(G) = P(G)$

$$+\sum_{IA}\sum_{\tau l m}\sum_{l' \geq l} \begin{pmatrix} l'=l \to \sum_{\tau' \geq \tau} \\ \text{else} \sum_{\tau'} \end{pmatrix} \begin{pmatrix} l'\tau'=l\tau \to \sum_{m' \geq m} \\ \text{else} \sum_{m'} \end{pmatrix} \sum_{l''m''} \begin{cases} \tau l m = \tau' l' m' & *1 \\ \text{else} & *2 \end{cases}$$

l'' = 偶数

$$* \mathrm{Re}(i^{-l''})\, d^{l''}(lm;l'm') * \mathrm{Real}\left(h^{IA}_{\tau l m \tau' l' m'}\right) * Q^{I\tau l'}_{\tau l \tau' l'}(G)\, Y^{*}_{l''m''}(\hat{G}) \quad e^{iGR_{IA}}$$

l'' = 奇数

$$* \mathrm{Im}(i^{-l''})\, d^{l''}(lm;l'm') * \mathrm{Real}\left(h^{IA}_{\tau l m \tau' l' m'}\right) * Q^{I\tau l'}_{\tau l \tau' l'}(G)\, Y^{*}_{l''m''}(\hat{G}) \begin{pmatrix} \sin GR_{IA} \\ \cos GR_{IA} \end{pmatrix}$$

$\begin{pmatrix} \cos \\ -\sin \end{pmatrix}$

inversion center があるとき

$= P(G)$

$$+\sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'} \begin{pmatrix} l'=l \to \sum_{\tau' \geq \tau} \\ \text{else} \sum_{\tau'} \end{pmatrix} \begin{pmatrix} l'\tau'=l\tau \to \sum_{m' \geq m} \\ \text{else} \sum_{m'} \end{pmatrix} \sum_{l''m''} \mathrm{IWei}(IA) * \begin{cases} \tau l m = \tau' l' m' & *1 \\ \text{else} & *2 \end{cases}$$

l'' = 偶数

$$* \mathrm{Re}(i^{-l''})\, d^{l''}(lm;l'm') * \mathrm{Real}\left(h^{IA}_{\tau l m \tau' l' m'}\right) * Q^{I\tau l'}_{\tau l \tau' l'}(G)\, Y^{*}_{l''m''}(\hat{G}) * \cos GR_{IA}$$

l'' = 奇数

$$* \mathrm{Im}(i^{-l''})\, d^{l''}(lm;l'm') * \mathrm{Real}\left(h^{IA}_{\tau l m \tau' l' m'}\right) * Q^{I\tau l'}_{\tau l \tau' l'}(G)\, Y^{*}_{l''m''}(\hat{G}) * \sin GR_{IA}$$

$\sum_{l''m''} d^{l''}(lm;l'm')\, Q^{IAl''}_{\tau l \tau' l'}(r)\, Y_{l''m''}(\hat{r})$

$$VQ^{IA}_{\tau l m \tau' l' m'} \equiv \int V_{LHXC}(r)\, Q^{IA}_{\tau l m \tau' l' m'}(r - R_{IA})\, dr$$

$$= \sum_{l''m''} d^{l''}(lm;l'm') \sum_{G} V(G)\, e^{iGR_{IA}} \int Q^{I\tau l''}_{\tau l \tau' l'}(r)\, Y_{l''m''}(\hat{r})\, e^{iGr}\, dr$$

$$= \Omega a \sum_{l''m''} i^{l''} d^{l''}(lm;l'm') \sum_{G} V(G)\, e^{iGR_{IA}} \frac{4\pi}{\Omega a} \int j_{l''}(Gr)\, Q^{I\tau l'}_{\tau l \tau' l'}(r)\, r^2 dr\, Y_{l''m''}(\hat{G})$$

$$= \Omega a \sum_{l''m''} i^{l''} d^{l''}(lm;l'm') \sum_{G} Q^{I\tau l''}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})\, V(G)\, e^{iGR_{IA}}$$

$l''=$偶数

$Y_{l''m''}(-\hat{G})$

$-(-1)^{l''} Y_{l''m''}(\hat{G})$

$$= \Omega a \sum_{l''m''} \mathrm{Re}(i^{l''})\, d^{l''}(lm;l'm') \sum_{G} Q^{I\tau l''}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})$$

$$* \left(v_x \cos GR_{IA} - v_y \sin GR_{IA} \right)$$

$l''=$奇数

$$= \Omega a \sum_{l''m''} (-1)\, \mathrm{Im}(i^{l''})\, d^{l''}(lm;l'm') \sum_{G} Q^{I\tau l'}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})$$

$$* \left(v_x \sin GR_{IA} + v_y \cos GR_{IA} \right)$$

P16 参照

$$\Omega a \sum_{G} V(G) \frac{\partial n^{*}(G)}{\partial R_{IA}}$$

略

$$V(Q^{IA}_{\tau l m \tau' l' m'})$$

$$= \Omega a \sum_{\substack{\tau l m \\ \tau' l' m'}} \xi^{IA}_{\tau l m \tau' l' m'} \sum_{l'' m''} i^{l''} d^{l''}(lm; l'm') \sum_{G} Q^{I \tau l''}_{\tau l \tau' l'}(G) Y_{l'' m''}(\hat{G}) V(G) e^{iGR_{IA}}$$

$$+ \Omega a \sum_{\substack{\tau l m \\ \tau' l' m'}} h^{IA}_{\tau l m \tau' l' m'} \sum_{l'' m''} i^{l''+1} d^{l''}(lm; l'm') \sum_{G} Q^{I \tau l''}_{\tau l \tau' l'}(G) Y_{l'' m''}(\hat{G}) V(G) e^{iGR_{IA}} G$$

l'' = 偶

$$= -\Omega a \sum_{\substack{\tau l m \\ \tau' l' m'}} h^{IA}_{\tau l m \tau' l' m'} \sum_{l'' m''} \mathrm{Re}(i^{l''}) d^{l''}(lm; l'm') \sum_{G} Q^{I \tau l''}_{\tau l \tau' l'}(G) Y_{l'' m''}(\hat{G})$$

$$* (v_x \sin GR_{IA} + v_y \cos GR_{IA}) * G$$

l'' = 奇

$$= -\Omega a \sum_{\substack{\tau l m \\ \tau' l' m'}} h^{IA}_{\tau l m \tau' l' m'} \sum_{l'' m''} \mathrm{Im}(i^{l''}) d^{l''}(lm; l'm') \sum_{G} Q^{I \tau l''}_{\tau l \tau' l'}(G) Y_{l'' m''}(\hat{G})$$

$$* (v_x \cos GR_{IA} - v_y \sin GR_{IA}) * G$$

non-local part

$$E_{NL} = \sum_{n\mathbf{k}} \langle \phi_{n\mathbf{k}} | V_{NL}^{ion} | \phi_{n\mathbf{k}} \rangle$$

$$= \sum_{n\mathbf{k}} \sum_{IA} \sum_{lm} \sum_{\tau\tau'} D^{ion\,I}_{\tau\tau' l} \langle \phi_{n\mathbf{k}} | \beta^{IA}_{\tau lm} \rangle \langle \beta^{I}_{\tau' lm} | \phi_{n\mathbf{k}} \rangle$$

$$= \sum_{IA} \sum_{lm} \sum_{\tau\tau'} D^{ion\,I}_{\tau\tau' l} \, h^{IA}_{\tau lm \tau' lm}$$

$$\frac{\delta E_{NL}}{\delta C^{n*}_{\mathbf{k}+\mathbf{G}}} = \sum_{IA} \sum_{lm} \sum_{\tau\tau'} D^{ion\,I}_{\tau\tau' l}$$

$$* i^{-l} * e^{-i\mathbf{G}\cdot\mathbf{R}_{IA}} \; SNL(\mathbf{G}, \tau lm, \mathbf{k}) * f^{IA\,n}_{\tau' lm}(\mathbf{k})$$

—

$(x-iy)$ $(a+ib)$

$(ax+yb)+i(xb-ya)$

$$\frac{\delta E_{NL}}{\delta \mathbf{R}_{IA}} = \sum_{n\mathbf{k}} \sum_{\tau\tau'} \sum_{lm} D^{ion}_{\tau\tau' l} \left(g^{IA\,n*}_{\tau lm}(\mathbf{k}) \, f^{IA\,n}_{\tau' lm}(\mathbf{k}) + f^{IA\,n*}_{\tau lm}(\mathbf{k}) \, g^{IA\,n*}_{\tau' lm}(\mathbf{k}) \right)$$

$$= \sum_{lm} \sum_{\tau\tau'} D^{ion}_{\tau\tau' l} \, \Xi^{IA}_{\tau lm \tau' lm}$$

← ττ'で対称化

$$= \sum_{lm} \sum_{\tau\tau'} D^{ion}_{\tau\tau' l} \, \mathrm{Re}\left(\Xi^{IA}_{\tau lm \tau' lm} \right)$$

Total Energy

$$E_{tot} = \sum \langle \phi_{nk} | -\frac{1}{2}\Delta + V_{ion} | \phi_{nk} \rangle$$

NO.

$$\sum_{IA}\sum_{\ell m}\sum_{\tau\tau'} Q^{z\ell}_{\tau\tau'\ell}\, f^{IAn*}_{\tau\ell m}(k)\, f^{IAn'}_{\tau'\ell m}(k)$$

inversion center があるとき

$$\sum_{IA}\sum_{\ell m}\sum_{\tau\tau'} \frac{1}{2}\, Iwei(IA) * Q^{z\ell}_{\tau\tau'\ell}$$

$$* \left(f^{IAn*}_{\tau\ell m}(k)\, f^{IAn'}_{\tau'\ell m}(k) + f^{IAn}_{\tau\ell m} * f^{IAn'*}_{\tau'\ell m}(k) \right)$$

$$= \sum_{IA}\sum_{\ell m}\sum_{\tau\tau'} Iwei(IA) * Q^{z\ell}_{\tau\tau'\ell} * Re\left(f^{IAn*}_{\tau\ell m}(k)\, f^{IAn'}_{\tau'\ell m}(k) \right)$$

$$\mathbb{F} = -\frac{\partial E}{\partial \mathbb{R}} \Rightarrow \mathbb{F} = -\frac{\partial}{\partial \mathbb{R}} \left\{ E - \sum_{ik}^{occ} f_{ik} \epsilon_{ik} \langle \phi_{ik} | S | \phi_{ik} \rangle \right\}$$

Orthogonality Conditions

NO. 18

$$\langle \phi_{nk} | S | \phi_{n'k} \rangle = \delta_{nn'}$$

$$= \langle \phi_{nk} | \phi_{n'k} \rangle + \sum_{IA} \sum_{\ell m} \sum_{\tau\tau'} Q^{It}_{\tau\tau'\ell} \langle \phi_{nk} | \beta^{IA}_{\tau\ell m} \rangle \langle \beta^{IA}_{\tau'\ell m} | \phi_{n'k} \rangle$$

$$= \sum_{G} C^{n*}_{k+G} C^{n'}_{k+G}$$

$$+ \sum_{IA} \sum_{\ell m} \sum_{\tau\tau'} Q^{It}_{\tau\tau'\ell} f^{IAn*}_{\tau\ell m}(k) f^{IAn'}_{\tau'\ell m}(k)$$

$$\frac{\delta}{\delta C^{n*}_{k+G}} \langle \phi_{nk} | s | \phi_{n'k} \rangle$$

$$= C^{n'}_{k+G}$$

$$+ \sum_{IA} \sum_{\ell m} \sum_{\tau\tau'} Q^{It}_{\tau\tau'\ell} * i^{-\ell} e^{-iGR_{IA}} SNL(G, \tau\ell m, k) \; f^{IAn'}_{\tau'\ell m}(k)$$

$$\sum_{nk} \epsilon_{nk} \frac{\partial}{\partial R_{IA}} \langle \phi_{nk} | S | \phi_{nk} \rangle$$

$$= \sum_{\ell m} \sum_{\tau\tau'} Q^{It}_{\tau\tau'\ell} \sum_{nk}^{occupied} \epsilon_{nk} \Big(\ldots$$

Car-Parrinello equation of motion

$$-\frac{\delta E_{tot}}{\delta C^{n*}_{k+G}} + \epsilon_{nk} \frac{\delta}{\delta C^{n*}_{k+G}} \langle \phi_{nk} | S | \phi_{nk} \rangle$$

$$= -\cancel{\sum_{G}} \frac{1}{2} |k+G|^2 C^{n}_{k+G}$$

$$- \sum_{IA} \sum_{\ell m} \sum_{\tau\tau'} D^{ion\, It}_{\tau\tau'\ell} \, i^{-\ell} \, e^{-iG R_{IA}} \, SNL(G, \tau\ell m, k) \, f^{IAn}_{\tau'\ell m}(k)$$

$$- \Omega_a \sum_{G'} V_{LHxc}(G') \frac{\delta n_a^*(G')}{\delta C_{k+G}} + \epsilon_{nk} \frac{\delta}{\delta C^{n*}_{k+G}} \langle \phi_{nk} | S | \phi_{nk} \rangle$$

$$= -\cancel{\sum_{G}} \left(\frac{1}{2} |k+G|^2 - \epsilon_{nk} \right) C^{n}_{k+G}$$

$$- \sum_{IA} \sum_{\ell m} \sum_{\tau\tau'} D^{ion\, It}_{\tau\tau'\ell} \, i^{-\ell} \, e^{-iG R_{IA}} \, SNL(G, \tau\ell m, k) \, f^{IAn}_{\tau'\ell m}(k)$$

$$+ \sum_{IA} \sum_{\ell m} \sum_{\tau\tau'} \epsilon_{nk} Q^{It}_{\tau\tau'\ell} \, i^{-\ell} \, e^{-iG R_{IA}} \, SNL(G, \tau\ell m, k) \, f^{IAn}_{\tau'\ell m}(k)$$

$$- \sum_{G'} V_{LHxc}(G') \, C^{n}_{k+G-G'}$$

$$- \Omega_a \sum_{IA} \sum_{\tau\ell m} \sum_{\tau'\ell' m'} \sum_{\ell'' m''} i^{\ell''} d^{\ell''}(\ell m ; \ell' m')$$

$$= VQ^{IA}_{\tau\ell m \tau'\ell' m'} = VQ^{IA}_{\tau'\ell' m' \tau\ell m}$$

$$\| $$

$$(-1)^{\ell''} VQ^{-IA}_{\tau\ell m \tau'\ell' m'}$$

$$* \sum_{G'} V_{LHxc}(G') \, e^{iG' \cdot R_{IA}} \, Q^{It\, \ell''}_{\tau\ell\tau'\ell'}(G') \, Y_{\ell'' m''}(G')$$

$$* f^{IAn}_{\tau\ell m}(k) \, i^{-\ell'} e^{-iG R_{IA}} \, SNL(G, \tau'\ell' m', k)$$

← $\tau\ell m$ と $\tau'\ell' m'$ を 入れかえ

NO.

$$V_{NL} = \sum_{ij} D_{ij} |\beta_i\rangle\langle\beta_j|$$

$$S = 1 + \sum_{ij} Q_{ij} |\beta_i\rangle\langle\beta_j|$$

$$(T + V_{loc} + V_{NL}) |\psi\rangle = \epsilon S |\psi\rangle$$

$$\mu |\dot{\psi}\rangle = -(T + V_{loc} + V_{NL} - \epsilon S) |\psi\rangle$$

$$= -(T + V_{loc} - \epsilon) |\psi\rangle - \sum_{ij} (D_{ij} - \epsilon Q_{ij}) |\beta_i\rangle\langle\beta_j|\psi\rangle$$

$(x+iy)(c-is) = xc+ys+i(yc-xs)$

$V_{NL}\,\phi_{nk}$

NO. 20

$$-(H-\epsilon_{nk}S)\,C^{n}_{k+G}$$

$$= -\left(\tfrac{1}{2}|k+G|^2-\epsilon_{nk}\right)C^{n}_{k+G} - \sum_{G'} V_{LHxc}(G')\,C^{n}_{k+G-G'}$$

$$-\sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'}\left\{\left(D^{ion\,I}_{\tau\tau' l}-\epsilon_{nk}Q^{I}_{\tau\tau' l}\right)\delta_{ll'}\delta_{mm'}+VQ^{IA}_{\tau l m \tau' l' m'}\right\}$$

$$* i^{-l}\,e^{-iG R_{IA}}\,SNL(G,\tau l m,k)\,f^{IAn}_{\tau' l' m'}(k)$$

VNLPH

(KNG1

KEG

KZM(s))

$$VNLPH(G,n) = -\sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'}\left\{\left(D^{ion\,I}_{\tau\tau' l}-\epsilon_{nk}Q^{I}_{\tau\tau' l}\right)\delta_{ll'}\delta_{mm'}+VQ^{IA}_{\tau l m \tau' l' m'}\right\}$$

VNLPH(G,n) の高速化について

$$\mathrm{VNLPH}(G,n)$$

$$= -\sum_{IA}\sum_{\tau\ell m}\sum_{\tau'\ell'm'} \Big(\underbrace{(D^{ion\,It}_{\tau\tau'\ell} - \epsilon_{nk} Q^{It}_{\tau\tau'\ell})\delta_{\ell\ell'}\delta_{mm'} + VQ^{IA}_{\tau\ell m\tau'\ell'm'}}_{g^{IAn}_{\tau\ell m\tau'\ell'm'}} \Big)$$

$$* i^{-l} SNL(G, \tau\ell m, k)$$

$$* \Big\{ \cos G R_{IA} \cdot \mathrm{Re}(f^{IAn}_{\tau'\ell'm'}(k)) + \sin G R_{IA} \cdot \mathrm{Im}(f^{IAn}_{\tau'\ell'm'}(k))$$

$$+ i \cos G R_{IA} \cdot \mathrm{Im}(f^{IAn}_{\tau'\ell'm'}(k)) - i \sin G R_{IA} \cdot \mathrm{Re}(f^{IAn}_{\tau'\ell'm'}(k)) \Big\}$$

$$= -\sum_{IA}\sum_{\tau\ell m} i^{-l} SNL(G, \tau\ell m, k)$$

$$* \Big\{ \cos G R_{IA} \cdot \sum_{\tau'\ell'm'} g^{IAn}_{\tau\ell m\tau'\ell'm'} \mathrm{Re}(f^{IAn}_{\tau'\ell'm'}(k))$$

$$+ \sin G R_{IA} \cdot \sum_{\tau'\ell'm'} g^{IAn}_{\tau\ell m\tau'\ell'm'} \mathrm{Im}(f^{IAn}_{\tau'\ell'm'}(k))$$

$$+ i \cos G R_{IA} \cdot \sum_{\tau'\ell'm'} g^{IAn}_{\tau\ell m\tau'\ell'm'} \mathrm{Im}(f^{IAn}_{\tau'\ell'm'}(k))$$

$$- i \sin G R_{IA} \sum_{\tau'\ell'm'} g^{IAn}_{\tau\ell m\tau'\ell'm'} \mathrm{Re}(f^{IAn}_{\tau'\ell'm'}(k)) \Big\}$$

$$-\frac{\delta}{\delta R_{IA}}\left(E_H + E_{XC} + E_{loc} + E_{NL} - \sum_{nk} \epsilon_{nk} \langle \phi_{nk} | S | \phi_{nk} \rangle\right)$$

$$= -\Omega_a \sum_{\tau \ell m} \sum_{\tau' \ell' m'} \sum_{\ell'' m''} i^{\ell''} d^{\ell''}(\ell m; \ell' m') \qquad \text{“} VQ^{IA}_{\tau \ell m \tau' \ell' m'}$$

$$\times \sum_{G} V_{LHXC}(G)\, e^{iG R_{IA}}\, Q^{I t \ell''}_{\tau \tau' \ell'}(G)\, Y_{\ell'' m''}(\hat{G}) + \Xi^{IA*}_{\tau \ell m \tau' \ell' m'}$$

$$-\Omega_a \sum_{\tau \ell m} \sum_{\tau' \ell' m'} \sum_{\ell'' m''} i^{\ell''} d^{\ell''}(\ell m; \ell' m')$$

$$\times \sum_{G} V_{LHXC}(G)\, e^{iG R_{IA}}\, Q^{I t \ell''}_{\tau \tau' \ell'}(G)\, Y_{\ell'' m''}(\hat{G})\; iG\; h^{IA*}_{\tau \ell m \tau' \ell' m'}$$

$$-\sum_{\ell m} \sum_{\tau \tau'} D^{I t\, ion}_{\tau \tau' \ell}\; \Xi^{IA}_{\tau \ell m \tau' \ell m}$$

$$+\sum_{\ell m} \sum_{\tau \tau'} Q^{It}_{\tau \tau' \ell}\; \mathcal{E}^{IA}_{\tau \ell m \tau' \ell m}$$

$$= -\Omega_a \sum_{\tau \ell m} \sum_{\tau' \ell' m'} \sum_{\ell'' m''} i^{\ell''} d^{\ell''}(\ell m; \ell m')$$

$$\times \sum_{G} V_{LHXC}(G)\, e^{iG R_{IA}}\, Q^{It\ell''}_{\tau \tau' \ell'}(G)\, Y_{\ell'' m''}(\hat{G})\; iG\; h^{IA*}_{\tau \ell m \tau' \ell' m'}$$

$$-\sum_{\tau \ell m} \sum_{\tau' \ell' m'} \Big\{ \left(D^{It\, ion}_{\tau \tau' \ell}\, \delta_{\ell \ell'} \delta_{m m'} + VQ^{IA}_{\tau \ell m \tau' \ell' m'} \right) \mathrm{Re}\left(\Xi^{IA}_{\tau \ell m \tau' \ell' m'} \right)$$

$$- Q^{It}_{\tau \tau' \ell}\, \delta_{\ell \ell'} \delta_{m m'}\, \mathrm{Re}\left(\mathcal{E}^{IA}_{\tau \ell m \tau' \ell m}\right) \Big\}$$

$(c - is)(x + iy) = xc + ys + i(cy - xs)$

inversion center

VNLPH(G,n)

$$= -\sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'} \{ (D^{ion\,I t}_{\tau\tau' l} - \epsilon_{nk} Q^{It}_{\tau\tau' l}) \delta_{ll'}\delta_{mm'} + VQ^{IA}_{\tau l m \tau' l' m'} \} * IWEI(IA)$$

$$* \{ i^{-l} e^{-iGR_{IA}} SNL(G,\tau l m,k) f^{IA\,n}_{\tau' l' m'}(k)$$

$$+ i^{-l} (-1)^l e^{iGR_{IA}} SNL(G,\tau l m,k) f^{IA\,n\,*}_{\tau' l' m'}(k) \} / 2$$

$$= -\sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'} \{ (D^{ion\,I t}_{\tau\tau' l} - \epsilon_{nk} Q^{It}_{\tau\tau' l}) \delta_{ll'}\delta_{mm'} + VQ^{IA}_{\tau l m \tau' l' m'} \} * IWEI(IA)$$

l= 偶数のとき

$$* Re(i^{-l}) SNL(G,\tau l m,k) * \left(Re(f^{IA\,n}_{\tau' l' m'}(k)) \cos GR_{IA} + Im(f^{IA\,n}_{\tau' l' m'}(k)) \sin GR_{IA} \right)$$

l= 奇数のとき

$$* -Im(i^{-l}) SNL(G,\tau l m,k) * \left(Im(f^{IA\,n}_{\tau' l' m'}(k)) \cos GR_{IA} - Re(f^{IA\,n}_{\tau' l' m'}(k)) \sin GR_{IA} \right)$$

//

Diagonal part

$$= -\sum_{IA}\sum_{\tau l m}\sum_{l' \geq l} \begin{pmatrix} l' = l & \sum_{\tau' \geq \tau} \\ \text{else} & \sum_{\tau'} \end{pmatrix} \begin{pmatrix} l'\tau' = l\tau \rightarrow \sum_{m' \geq m} \\ \text{else} \quad \sum_{m'} \end{pmatrix} \begin{cases} \tau l m = \tau' l' m' \rightarrow *1 \\ \text{else} \quad *2 \end{cases}$$

$$* \{ (D^{ion\,I t}_{\tau\tau' l} - \epsilon_{nk} Q^{It}_{\tau\tau' l}) \delta_{ll'}\delta_{mm'} + VQ^{IA}_{\tau l m \tau' l' m'} \}$$

$$* \{ Re(i^{-l+l'}) SNL(G,\tau l m,k) \cdot SNL(G,\tau' l' m',k) \}$$

$$* \frac{1}{2}(1 + (-1)^{l+l'})$$ *IWEI(IA

//

$$VNLPH(G,n) = -\sum_{IA}\sum_{\tau l m}\sum_{\tau' l' m'} \left\{ \left(D^{IAn\,ZA}_{\tau\tau' l} - \epsilon_{nk}\, Q^{ZA}_{\tau\tau' l} \right) \delta_{ll'}\delta_{mm'} + VQ^{ZA}_{\tau l m \tau' l' m'} \right\}$$

$l=$ 偶数

$$* \mathrm{Re}(i^{-l})\, SNL(G,\tau l m, k) * \left\{ \mathrm{Re}\left(f^{ZAn}_{\tau l' m'}(k)\right) \cos G R_{ZA} + \mathrm{Im}\left(f^{ZAn}_{\tau' l' m'}(k)\right) \sin G R_{ZA} \right.$$

$$\left. + i\left(\mathrm{Im}\left(f^{ZAn}_{\tau' l' m'}(k)\right) \cos G R_{ZA} - \mathrm{Re}\left(f^{ZAn}_{\tau' l' m'}(k)\right) \sin G R_{ZA} \right) \right\}$$

$l=$ 奇数

$$* \mathrm{Im}(i^{-l})\, SNL(G,\tau l m, k) * \left\{ -\left(\mathrm{Im}\left(f^{ZAn}_{\tau' l' m'}(k)\right) \cos G R_{ZA} - \mathrm{Re}\left(f^{ZAn}_{\tau' l' m'}(k)\right) \sin G R_{ZA} \right) \right.$$

$$\left. + i\left(\mathrm{Re}\left(f^{ZAn}_{\tau' l' m'}(k)\right) \cos G R_{ZA} + \mathrm{Im}\left(f^{ZAn}_{\tau' l' m'}(k)\right) \sin G R_{ZA} \right) \right\}$$

NO.

$$(T + V_{LHxc} + V_{NL}) |\psi\rangle = \epsilon S |\psi\rangle$$

$$\sum_{n\mathbf{k}} \langle \psi_{n\mathbf{k}} | T + V_{NL} | \psi_{n\mathbf{k}} \rangle + \sum_{n\mathbf{k}} \int |\psi_{n\mathbf{k}}|^2 V_{LHxc} \, d\mathbf{r}$$

Eigen value Estimation

NO.

$$\lambda^{n}_{k}(t+\Delta t) = \langle \phi_{nk}(t+\Delta t) | H(t) | \phi_{nk}(t+\Delta t) \rangle$$

$$= \langle \phi_{nk}(t+\Delta t) | \lambda_{nk}(t) S + (H(t) - \lambda_{nk}(t) S) | \phi_{nk}(t+\Delta t) \rangle$$

$$= \lambda_{nk}(t) + \langle \phi_{nk}(t) | \mathcal{H}(t) - \lambda_{nk}(t) S | \phi_{nk}(t) \rangle$$

$$+ \langle \delta\phi_{nk}(t) | \mathcal{H}(t) - \lambda_{nk}(t) S | \phi_{nk}(t) \rangle$$

$$+ \langle \phi_{nk}(t) | \mathcal{H}(t) - \lambda_{nk}(t) S | \delta\phi_{nk}(t) \rangle + O(\Delta t^2)$$

$$= \lambda_{nk}(t) - \nu \{ \langle \dot{\phi}_{nk}(t) | \phi_{nk}(t) \rangle + \langle \phi_{nk}(t+\Delta t) | \dot{\phi}_{nk}(t) \rangle + \langle \dot{\phi}_{nk}(t) | \phi_{nk}(t+\Delta t) \rangle$$

$$- \langle \phi_{nk}(t) | \dot{\phi}_{nk}(t) \rangle - \langle \dot{\phi}_{nk}(t) | \phi_{nk}(t) \rangle \}$$

$$= \lambda_{nk}(t) - 2\nu \, \mathrm{Re} (\langle \phi_{nk}(t+\Delta t) | \dot{\phi}_{nk}(t) \rangle)$$

$$+ \nu \langle \phi_{nk}(t) | \dot{\phi}_{nk}(t) \rangle$$

$$= \lambda_{nk}(t) - 2\nu \sum_{G} \mathrm{Re} (C^{*}_{nk}(t+\Delta t) \, \dot{C}_{nk}(t))$$

$$+ \nu \sum_{G} C^{*}_{nk}(t) \, \dot{C}_{nk}(t)$$

Extrapolation

NO. 9th Sep. '93

$$H' = H(t_n) + \alpha\left(H(t_n) - H(t_{n-1})\right) + \beta\left(H(t_{n-1}) - H(t_{n-2})\right)$$

$$|H(t_{n-1}) - H'|^2$$

$$= \sum \{\alpha^2 (r_{ix}(t_n) - r_{ix}(t_{n-1}))^2$$

$$) - r_{ix}(t_{n-1}))(r_{ix}(t_{n+1}) - r_{ix}(t_n))$$

$$) - r_{ix}(t_{n-2}))^2$$

$$) - r_{ix}(t_{n-2}))(r_{ix}(t_{n+1}) - r_{ix}(t_n))$$

$$) - r_{ix}(t_{n-1}))(r_{ix}(t_{n-1}) - r_{ix}(t_{n-2}))$$

$$) - r_{ix}(t_n))^2 \}$$

$$C\beta^2 - 2D\beta + 2E\alpha\beta + F$$

$$\frac{\partial^2 f}{\partial \beta^2}$$

$$= B$$

$$= D$$

$$\begin{matrix} -E \\ +A \end{matrix} \Big) \begin{pmatrix} B \\ D \end{pmatrix}$$

$$\sum_{ix} \{ \ldots r_{ix}(t_n)$$

$$-2\alpha (r_{ix}(t_n$$

$$+\beta^2 (r_{ix}(t_{n-}$$

$$-2\beta (r_{ix}(t_n$$

$$+2\alpha\beta (r_{ix}(t_n$$

$$+ (r_{ix}(t_{n+1}$$

$$= A\alpha^2 - 2B\alpha +$$

$$\frac{\partial f}{\partial \alpha} = \frac{\partial f}{\partial \beta} = 0$$

かつ

$$\left(\frac{\partial^2 f}{\partial \alpha \partial \beta}\right)^2 \le \frac{\partial^2 f}{\partial \alpha^2} \frac{\partial}{\partial}$$

$$\alpha A + E\beta$$

$$\alpha E + C\beta$$

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \frac{1}{AC - E^2} \Big(\begin{matrix} C \\ -E \end{matrix}$$

$C^{l''}(lm;l'm')\, Y_{l''m''}(\hat{\mathbf{G}})$ の計算を必要とする項　NO. ①

$$VQ^{IA}_{\tau lm\tau' l'm'} \equiv \int V_{Hxc}(\mathbf{r})\, Q^{IA}_{\tau lm \tau' l'm'}(\mathbf{r}-\mathbf{R}_{IA})$$

$$= \Omega_a \sum_{l''m''} i^{l''} d^{l''}(lm;l'm') \sum_{\mathbf{G}} V_{Hxc}(\mathbf{G})\, e^{i\mathbf{G}\cdot\mathbf{R}_{IA}} * Y^{*}_{l''m''}(\hat{\mathbf{G}})$$

$$* \frac{4\pi}{\Omega_a} \int_0^{\infty} Q^{I}_{\tau l\tau' l'}(r)\, j_{l''}(Gr)\, r^2 dr$$ ← $\mathbf{G}$と$-\mathbf{G}$について対称

$$= \Omega_a \sum_{l''m''} d^{l''}(lm;l'm') * \sum_{\mathbf{G}} Q^{I\tau l''}_{\tau l\tau' l'}(G)\, Y^{*}_{l''m''}(\hat{\mathbf{G}})$$

$$* \{ (v_x \cos \mathbf{G}\mathbf{R}_{IA} - v_y \sin \mathbf{G}\mathbf{R}_{IA})\, \mathrm{Re}(i^{l''})$$
$$- (v_x \sin \mathbf{G}\mathbf{R}_{IA} + v_y \cos \mathbf{G}\mathbf{R}_{IA})\, \mathrm{Im}(i^{l''}) \}$$

$$= \Omega_a \sum_{l''m''} \underline{d^{l''}(lm;l'm')} * \sum_{\mathbf{G}} Q^{I\tau l''}_{\tau l\tau' l'}\, Y^{*}_{l''m''}(\hat{\mathbf{G}})$$

$$\begin{cases} \text{if } l+l' = \text{even then} \\ \quad * (v_x \cos \mathbf{G}\mathbf{R}_{IA} - v_y \sin \mathbf{G}\mathbf{R}_{IA})\, \underline{\mathrm{Re}(i^{l''})} \\ \text{else} \\ \quad * -(v_x \sin \mathbf{G}\mathbf{R}_{IA} + v_y \cos \mathbf{G}\mathbf{R}_{IA})\, \mathrm{Im}(i^{l''}) \end{cases}$$

inversion center があると

$$\begin{cases} l+l' = \text{even} \\ \quad * \ v_x \cos \mathbf{G}\mathbf{R}_{IA} * \underline{\mathrm{Re}(i^{l''})} \\ \text{else.} \\ \quad * -v_x \sin \mathbf{G}\mathbf{R}_{IA} * \mathrm{Im}(i^{l''}) \end{cases}$$

VQ^{-IA}

$$\begin{cases} l+l' = \text{even} & = VQ^{IA} \\ \text{else} & = -VQ^{IA} \end{cases}$$

$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\,dy\,dz$

$dx = -dx$

$+\infty$ が $-\infty$

$$VQ^{IA} = \int V(\mathbf{r})\, Q(\mathbf{r}-\mathbf{R}_{IA})\, d\mathbf{r} = \int V(-\mathbf{r})\, Q(\underbrace{\mathbf{r}-\mathbf{R}_{IA}}_{=-\tau})\, d\mathbf{r} = \int V(\tau-\mathbf{R}_{IA})\, Q(-\tau)\, d\tau$$
$$= (-1)^{l+l'} \int V(\tau-\mathbf{R}_{IA})\, Q(\tau)\, d\mathbf{r}$$

$$VQ^{-IA} = \int V(\mathbf{r})\, Q(\underbrace{\mathbf{r}+\mathbf{R}_{IA}}_{=+\tau})\, d\mathbf{r} = \int V(\tau-\mathbf{R}_{IA})\, Q(\tau)\, d\tau$$

NO. 2

$n_\alpha(G) = \rho(G)$

$$\sum_{IA} \sum_{\tau\ell m} \sum_{\tau'\ell'm' \geq \tau\ell m} \sum_{\ell''m''} g^{\ell''}(\ell m, \ell'm') \; Q^{\tau\ell\tau'\ell'}_{\ell''} \; Q^{I\tau\ell''}_{\ell''m''}(G) \times Y^*_{\ell''m''}(\hat{G})$$

if $\ell+\ell'$: even then

$* \; e^{-iG\cdot R_{IA}} * Re(h^{IA}_{\tau\ell m\tau'\ell'm'}) \; * Re(i^{-\ell''}) \, Re(i^{\ell'-\ell}) \, w(IA)$

else

$* \; i e^{-iG\cdot R_{IA}} * Im(h^{IA}_{\tau\ell m\tau'\ell'm'}) \; * Im(i^{-\ell''}) \, Im(i^{\ell'-\ell}) \, w(IA)$

$*$ $\tau\ell m = \tau'\ell'm'$ $\rightarrow *1$

else $*2$

inversion center がある

$\ell+\ell'$ = even

$* \cos G\cdot R_{IA} * Re(h^{IA}_{\tau\ell m\tau'\ell'm'}) \; * Re(i^{-\ell'}) \, Re(i^{\ell'-\ell}) \, w(IA)$

else

$* \sin G\cdot R_{IA} * Im(h^{IA}_{\tau\ell m\tau'\ell'm'}) \; * Im(i^{\ell'}) \, Im(i^{\ell'-\ell}) \, w(IA)$

$*$ $\tau\ell m = \tau'\ell'm'$ $\rightarrow *1$

else $*2$

$$\frac{\delta(E_H + E_{xc})}{\delta R_{IA}}$$

$$\Rightarrow \sum_{\tau l m} \sum_{\tau' l' m' \geq \tau l m} \sum_{l'' m''} \underline{d^{l''}(lm; l'm')} \sum_{G} Q^{I \tau l''}_{\tau l \tau' l'}(G)\, Y_{l''m''}(\hat{G})$$

$$\begin{cases} \text{if } l+l' = \text{even then} \\ \quad * \left\{ (v_x \cos G R_{IA} - v_y \sin G R_{IA}) \,\mathrm{Im}\left(\Xi^{IA}_{\tau l m \tau' l' m'}\right) \right. \\ \quad\quad \left. - (v_x \sin G R_{IA} + v_y \cos G R_{IA}) * G * \mathrm{Re}\left(h^{IA}_{\tau l m \tau' l' m'}\right) \right\} \underline{\mathrm{Re}(i^{l'-l})}\, \underline{\mathrm{Re}(i^{l''})} \\ \text{else} \\ \quad * \left\{ -(v_x \sin G R_{IA} + v_y \cos G R_{IA}) \,\mathrm{Re}\left(\Xi^{IA}_{\tau l m \tau' l' m'}\right) \right. \\ \quad\quad \left. + (v_x \cos G R_{IA} - v_y \sin G R_{IA}) * G * \mathrm{Im}\left(h^{IA}_{\tau l m \tau' l' m'}\right) \right\} \mathrm{Im}(i^{l'-l})\, \mathrm{Im}(i^{l''}) \end{cases}$$

$$* \begin{cases} \tau l m = \tau' l' m' & \rightarrow \underline{*1} \\ \text{else} & \underline{*2} \end{cases}$$

inversion center がある場合

$$\begin{cases} l+l' = \text{even} \\ \quad * \, v_x \left\{ \cos G R_{IA} \,\mathrm{Im}\left(\Xi^{IA}_{\tau l m \tau' l' m'}\right) \right. \\ \quad\quad \left. - \sin G R_{IA} * G * \mathrm{Re}\left(h^{IA}_{\tau l m \tau' l' m'}\right) \right\} \underline{\mathrm{Re}(i^{l'-l})}\, \underline{\mathrm{Re}(i^{l''})} \\ \text{else} \\ \quad * \cdot v_x \left\{ -\sin G R_{IA} \,\mathrm{Re}\left(\Xi^{IA}_{\tau l m \tau' l' m'}\right) \right. \\ \quad\quad \left. + \cos G R_{IA} * G * \mathrm{Im}\left(h^{IA}_{\tau l m \tau' l' m'}\right) \right\} \mathrm{Im}(i^{l'-l})\, \mathrm{Im}(i^{l''}) \end{cases}$$

$$* \begin{cases} \tau l m = \tau' l' m' & \rightarrow \underline{*1} \\ \text{else} & \underline{*2} \end{cases}$$

NO.

本来

$$f^{IAn}_{\tau\ell m}(-\mathbf{k}) = (-1)^m f^{IAn\,*}_{\tau\ell -m}(\mathbf{k})$$

$$f^{-IAn}_{\tau\ell m}(\mathbf{k}) = (-1)^{\ell+m} f^{IAn\,*}_{\tau\ell -m}(\mathbf{k})$$

$$Y^{*}_{\ell m}(\theta,\varphi) = (-1)^m Y_{\ell -m}(\theta,\varphi)$$