Divide-and-Conquer Method for Nonlocal Pseudopotentials

1/2/04

$$E_{NL} = \sum_{\alpha}\sum_{m} f(\epsilon_m^{\alpha}) \sum_{I}\sum_{L} \times \frac{1}{2}\Big[\int d\mathbf{r}\, P^{\alpha}(\mathbf{r})\, \psi_m^{\alpha *}(\mathbf{r})\, \xi_L^{I}(\mathbf{r}-\mathbf{R}_I) \int d\mathbf{r}'\, \xi_L^{I*}(\mathbf{r}'-\mathbf{R}_I)\, \psi_m^{\alpha}(\mathbf{r}')$$

$\updownarrow$ c.c.

$$+ \int d\mathbf{r}\, \psi_m^{\alpha *}(\mathbf{r})\, \xi_L^{I}(\mathbf{r}-\mathbf{R}_I) \int d\mathbf{r}'\, \xi_L^{I*}(\mathbf{r}'-\mathbf{R}_I)\, \psi_m^{\alpha}(\mathbf{r}')\, P^{\alpha}(\mathbf{r}')\Big] \tag{1}$$

where $L = (l, \mu)$ collectively denotes angular momentum indices and

$$\xi_L^{I}(\mathbf{r}) = \frac{\Delta V_l^{I}(r)\, R_l^{I}(r)\, Y_{l\mu}(\hat{\mathbf{r}})}{\langle R_l^{I} | \Delta V_l^{I} | R_l^{I} \rangle^{1/2}} \tag{2}$$

is derived from the nonlocal pseudopotentials ΔV_l^{I} and pseudo-wavefunction R_l^{I} of ion I.

– Kohn-Sham equation

$$E_{DC} = \sum_{\alpha} T_S^{*}[\rho_0^{\alpha}(\mathbf{r})] + \int d\mathbf{r}\, \rho(\mathbf{r})\, v_{loc}(\mathbf{r}) + E_{NL}$$

$$+ \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})] \qquad (3)$$

where

$$\rho(\mathbf{r}) = \sum_{\alpha} \rho^{\alpha}(\mathbf{r}) \qquad (4)$$

$$\rho^{\alpha}(\mathbf{r}) = p^{\alpha}(\mathbf{r})\, \rho_0^{\alpha}(\mathbf{r}) \qquad (5)$$

$$\rho_0^{\alpha}(\mathbf{r}) = \sum_{m} f(\epsilon_m^{\alpha})\, |\psi_m^{\alpha}(\mathbf{r})|^2 \qquad (6)$$

and

$$T_S^{*}[\rho_0^{\alpha}(\mathbf{r})] = \sum_{m} f(\epsilon_m^{\alpha}) \int d\mathbf{r}\, p^{\alpha}(\mathbf{r})\, \psi_m^{\alpha *}(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_m^{\alpha}(\mathbf{r}) \qquad (7)$$

(Euler equation)

$$\frac{\delta E}{\delta \rho_0^{\alpha}(\mathbf{r})} = \underbrace{\frac{\delta T_S^{*}[\rho_0^{\alpha}(\mathbf{r})]}{\delta \rho_0^{\alpha}(\mathbf{r})}}_{\underbrace{\frac{d(p^{\alpha}(\mathbf{r})\rho_0^{\alpha}(\mathbf{r}))}{d\rho_0^{\alpha}(\mathbf{r})}}_{p^{\alpha}(\mathbf{r})} \frac{\delta T_S^{*}[\rho^{\alpha}]}{\delta \rho^{\alpha}(\mathbf{r})}} + \left[v_{loc}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \right] \times \underbrace{\frac{d}{d\rho_0^{\alpha}(\mathbf{r})} \sum_{\alpha'} p^{\alpha'}(\mathbf{r})\rho_0^{\alpha'}(\mathbf{r})}_{p^{\alpha}(\mathbf{r})}$$

$$+ \frac{\delta E_{NL}}{\delta \rho(\mathbf{r})} \times \underbrace{\frac{d}{d\rho_0^{\alpha}(\mathbf{r})} \sum_{\alpha'} p^{\alpha'}(\mathbf{r})\rho_0^{\alpha'}(\mathbf{r})}_{p^{\alpha}(\mathbf{r})}$$

$$= p^{\alpha}(\mathbf{r}) \left[\frac{\delta T_S^{*}}{\delta \rho^{\alpha}(\mathbf{r})} + v_{loc}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} + \frac{\delta E_{NL}}{\delta \rho(\mathbf{r})} \right] \qquad (8)$$

$$\underset{\sim\sim\sim}{\frac{\delta T_S^*}{\delta \rho^\alpha(\mathbf{r})}} + v_{loc}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} + \underset{\sim\sim\sim}{\frac{\delta E_{NL}}{\delta \rho(\mathbf{r})}} = 0 \qquad (9)$$

$\updownarrow$ equivalent

$$\begin{cases} \left[-\frac{1}{2}\nabla^2 + v_{loc}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} + \frac{\delta E_{NL}}{\delta \rho(\mathbf{r})}\right] \psi_m^\alpha(\mathbf{r}) = \epsilon_m^\alpha \psi_m^\alpha(\mathbf{r}) & (10) \\ \rho^\alpha(\mathbf{r}) = P^\alpha(\mathbf{r}) \sum_m f(\epsilon_m^\alpha) |\psi_m^\alpha(\mathbf{r})|^2 & (11) \end{cases}$$

(Operative definition of $\frac{\delta}{\delta \rho^\alpha(\mathbf{r})}$ & $\frac{\delta}{\delta \rho(\mathbf{r})}$ in Eq. (9))

$$\frac{\delta}{\delta[f(\epsilon_m^\alpha) P^\alpha(\mathbf{r}) \psi_m^{\alpha *}(\mathbf{r})]} \qquad (12)$$

Applying Eq. (12) to (1),

$$\frac{E_{NL}}{\rho(\mathbf{r})} \psi_m^\alpha(\mathbf{r}) = \sum_I \sum_L \frac{1}{2} \Big[\xi_L^I(\mathbf{r}-\mathbf{R}_I) \int d\mathbf{r}' \xi_L^{I*}(\mathbf{r}'-\mathbf{R}_I) \psi_m^\alpha(\mathbf{r}') + \underbrace{\xi_L^{I*}(\mathbf{r}-\mathbf{R}_I) \int d\mathbf{r}' \psi_m^{\alpha *}(\mathbf{r}') \xi_L^I(\mathbf{r}'-\mathbf{R}_I)}_{?} \Big] \qquad (13)$$

— Density-matrix formulation

$$\rho(\mathbf{r},\mathbf{r}') = \sum_{\alpha} \rho^{\alpha}(\mathbf{r},\mathbf{r}') \qquad (14)$$

$$\rho^{\alpha}(\mathbf{r},\mathbf{r}') = \sum_{m} \frac{\overbrace{\psi_m^{\alpha *}(\mathbf{r})\, \rho^{\alpha}(\mathbf{r})\, f(\epsilon_m^{\alpha})}\, \psi_m^{\alpha}(\mathbf{r}') + \psi_m^{\alpha *}(\mathbf{r})\, \overbrace{f(\epsilon_m^{\alpha})\, \rho^{\alpha}(\mathbf{r}')\, \psi_m^{\alpha}(\mathbf{r}')}}{2} \qquad (15)$$

(Rule)
Variation is taken to $\psi_m^{\alpha}(\mathbf{r})$ that is coupled to $\rho^{\alpha}(\mathbf{r})$.

- Hellmann-Feynman force

$$\mathbb{F}_I = -\frac{\partial}{\partial \mathbb{R}_I}\left\{ \int d\mathbb{r}\,\rho(\mathbb{r})\, v_{loc}^{I}(\mathbb{r}-\mathbb{R}_I) \sim \text{local} \right.$$

$$+ E_{NL} \sim \text{nonlocal}$$

$$\left. + \sum_{I<J} \frac{Z_I Z_J}{|\mathbb{R}_I - \mathbb{R}_J|} \right\} \sim \text{ion-ion} \qquad (16)$$

(Local force)

$$\mathbb{F}_I^{loc} = \int d\mathbb{r}\,\rho(\mathbb{r}) \frac{\partial(|\mathbb{r}-\mathbb{R}_I|)}{\partial(\mathbb{r}-\mathbb{R}_I)} \left.\frac{dv_{loc}^{I}}{dr}\right|_{r=|\mathbb{r}-\mathbb{R}_I|}$$

$$= \int d\mathbb{r}\,\rho(\mathbb{r})\, \widehat{\mathbb{r}-\mathbb{R}_I} \left.\frac{dv_{loc}^{I}}{dr}\right|_{r=|\mathbb{r}-\mathbb{R}_I|} \qquad (17)$$

↳ see flocal() & refloc() of Fuyuki

(Ion-ion force)

$$\mathbb{F}_I^{ion} = \sum_{J(\neq I)} Z_I Z_J \frac{\mathbb{r}_I - \mathbb{r}_J}{|\mathbb{r}_I - \mathbb{r}_J|^3} \qquad (18)$$

↳ Ewald

(Nonlocal force)

$$
\begin{aligned}
\mathbb{F}_I^{NL} = \sum_{\alpha}\sum_{m} f(\epsilon_m^{\alpha}) \sum_{L} \times \frac{1}{2} \Bigg\{ \\
& \int d\mathbf{r}\, P^{\alpha}(\mathbf{r})\, \psi_m^{\alpha *}(\mathbf{r}) \frac{\partial \xi_L^{I}(\mathbf{r}-\mathbf{R}_I)}{\partial(\mathbf{r}-\mathbf{R}_I)} \int d\mathbf{r}'\, \xi_L^{I*}(\mathbf{r}'-\mathbf{R}_I)\, \psi_m^{\alpha}(\mathbf{r}') \\
& + \int d\mathbf{r}\, P^{\alpha}(\mathbf{r})\, \psi_m^{\alpha *}(\mathbf{r})\, \xi_L^{I}(\mathbf{r}-\mathbf{R}_I) \int d\mathbf{r}' \frac{\partial \xi_L^{I*}(\mathbf{r}'-\mathbf{R}_I)}{\partial(\mathbf{r}'-\mathbf{R}_I)}\, \psi_m^{\alpha}(\mathbf{r}') \\
& + \int d\mathbf{r}\, \psi_m^{\alpha *}(\mathbf{r}) \frac{\partial \xi_L^{I}(\mathbf{r}-\mathbf{R}_I)}{\partial(\mathbf{r}-\mathbf{R}_I)} \int d\mathbf{r}'\, \xi_L^{I*}(\mathbf{r}'-\mathbf{R}_I)\, \psi_m^{\alpha}(\mathbf{r}')\, P^{\alpha}(\mathbf{r}') \\
& + \int d\mathbf{r}\, \psi_m^{\alpha *}(\mathbf{r})\, \xi_L^{I}(\mathbf{r}-\mathbf{R}_I) \int d\mathbf{r}' \frac{\partial \xi_L^{I*}(\mathbf{r}'-\mathbf{R}_I)}{\partial(\mathbf{r}'-\mathbf{R}_I)}\, \psi_m^{\alpha}(\mathbf{r}')\, P^{\alpha}(\mathbf{r}') \Bigg\} \qquad (18)
\end{aligned}
$$

c.c.

c.c.

— Assymetric formulation

Divide-and-conquer approximation:

$\sum_\alpha \sum_m f(\epsilon_m^\alpha)\, p^\alpha(\mathbf{r}) \quad \times\ \forall\ \mathbf{r}$ function.

$$\boxed{E_{NL} = \sum_\alpha \sum_m f(\epsilon_m^\alpha) \sum_I \sum_L \int d\mathbf{r}\, p^\alpha(\mathbf{r})\, \psi_m^{\alpha *}(\mathbf{r})\, \xi_L^I(\mathbf{r}-\mathbf{R}_I) \int d\mathbf{r}'\, \xi_L^I(\mathbf{r}'-\mathbf{R}_I)\, \psi_m^\alpha(\mathbf{r}')} \tag{19}$$

where $L=(\ell,\mu)$ and

$$\xi_L^I(\mathbf{r}) = \frac{\Delta V_\ell^I(r)\, R_\ell^I(r)\, \bar{Y}_{\ell\mu}(\hat{\mathbf{r}})}{\langle R_\ell^I | \Delta V_\ell^I | R_\ell^I \rangle^{1/2}} \tag{20}$$

$$\begin{cases} \bar{Y}_{\ell|\mu|} = \frac{1}{\sqrt{2}}(Y_{\ell|\mu|} + Y_{\ell|\mu|}^*) = \sqrt{2}\,\mathrm{Re}\,Y_{\ell|\mu|} & \mu \neq 0 \\ \bar{Y}_{\ell-|\mu|} = \frac{1}{\sqrt{2}i}(Y_{\ell|\mu|} - Y_{\ell|\mu|}^*) = \sqrt{2}\,\mathrm{Im}\,Y_{\ell|\mu|} & \\ \bar{Y}_{\ell 0} = Y_{\ell 0} & \sim \text{real.} \end{cases} \tag{21}$$

$$\frac{\delta E_{NL}}{\delta \rho}\psi_m^\alpha(\mathbf{r}) = \sum_I \sum_L \xi_L^I(\mathbf{r}-\mathbf{R}_I) \int d\mathbf{r}'\, \xi_L^I(\mathbf{r}'-\mathbf{R}_I)\, \psi_m^\alpha(\mathbf{r}') \tag{22}$$

(Kohn-Sham equation)

$$\left[-\frac{1}{2}\nabla^2 + v_{loc}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}\right]\psi_m^\alpha(\mathbf{r})$$

$$+ \sum_I \sum_L \xi_L^I(\mathbf{r}-\mathbf{R}_I) \int d\mathbf{r}'\, \underbrace{\xi_L^I(\mathbf{r}'-\mathbf{R}_I)}_{\text{real (using Fuyuki's } \bar{Y}_{\ell\mu})}\, \psi_m^\alpha(\mathbf{r}') = \epsilon_m^\alpha \psi_m^\alpha(\mathbf{r}) \tag{23}$$

– Hellmann – Feynman force

(Local force)

$$\mathbb{F}_I^{loc} = \int d\mathbf{r}\, \rho(\mathbf{r})\, \widehat{\mathbf{r}-\mathbf{R}_I}\, \frac{dv_{loc}^I}{dr}\Big|_{r=|\mathbf{r}-\mathbf{R}_I|} \tag{24}$$

(Ion-ion force)

$$\mathbb{F}_I^{ion} = \sum_{J(\neq I)} Z_I Z_J \frac{\mathbf{r}_I - \mathbf{r}_J}{|\mathbf{r}_I - \mathbf{r}_J|^3} \tag{25}$$

(Nonlocal force)

$$\boxed{\begin{aligned}\mathbb{F}_I^{NL} = \sum_{\alpha}\sum_{m} f(\epsilon_m^\alpha) \sum_L \Bigg[&\int d\mathbf{r}\, P^\alpha(\mathbf{r})\, \psi_m^{\alpha *}(\mathbf{r}) \frac{\partial \xi_L^I(\mathbf{r}-\mathbf{R}_I)}{\partial(\mathbf{r}-\mathbf{R}_I)} \int d\mathbf{r}'\, \xi_L^I(\mathbf{r}'-\mathbf{R}_I)\, \psi_m^\alpha(\mathbf{r}') \\ &+ \int d\mathbf{r}\, P^\alpha(\mathbf{r})\, \psi_m^{\alpha *}(\mathbf{r})\, \xi_L^I(\mathbf{r}-\mathbf{R}_I) \int d\mathbf{r}' \frac{\partial \xi_L^I(\mathbf{r}'-\mathbf{R}_I)}{\partial(\mathbf{r}'-\mathbf{R}_I)} \psi_m^\alpha(\mathbf{r}') \Bigg]\end{aligned}} \tag{26}$$