Nonlocal Pseudopotential

12/13/99

— The angular-dependent pseudopotential, $V^{PP}_{ion,\ell}(r)$, when the z-valence electron problem is solved, reproduces the all-electron valence eigenstate for $r \geq r_{c\ell}$. "The core is a black box from which the valence wave functions emanate with some logarithmic derivative", and the pseudopotential yields that logarithmic derivative.

Rydberg

— Note that all $V^{PP}_{ion,\ell}(r) \longrightarrow -2Z/r$ for $r \to \infty$

— Ionic pseudopotential operator

$$V^{PP}_{ion}(r) = V^{PP}_{ion,local}(r) + \sum_{\ell,m} |\ell m\rangle \Delta V_\ell(r) \langle \ell m| \qquad (1)$$

where $V^{PP}_{ion,local}(r)$ is the local potential,

$$\Delta V_\ell(r) = V^{PP}_{ion,\ell}(r) - V^{PP}_{ion,local}(r) \qquad (2)$$

is the seminonlocal potential, and $|\ell m\rangle$ is the spherical harmonics:

$$|\ell m\rangle\langle \ell m| f(\theta,\varphi)\rangle \equiv Y_{\ell m}(\theta,\varphi) \int d\cos\theta' d\varphi' \, Y^*_{\ell m}(\theta',\varphi') f(\theta',\varphi') \qquad (3)$$

One of the $V^{PP}_{ion,\ell}(r)$, such as the P ($\ell=1$) potential, is used as the local potential

- Note that for $r \geq r_c \equiv \max\{r_{cl}\}$, all $V^{PP}_{ion,l}(r) = V^{PP}_{scr,l}(r) - V^{PP}_H(r) - V^{PP}_{xc}(r) = V^{AE}(r) - V^{PP}_H(r) - V^{PP}_{xc}(r)$, i.e., they are all identical!

$\therefore$ $V_{nonlocal,l}(r) = 0$ for $r \geq r_c \equiv \max\{r_{cl}\}$ (4)

Operation Count for Evaluating Nonlocal Pseudopotentials

12/14/99

Problem

Calculate

$$\hat{V}_{NL}|\psi\rangle = \sum_{lm} |lm\rangle \Delta V_l(r) \langle lm|\psi\rangle \quad (1)$$

where

$$\begin{cases} |\psi\rangle = \sum_{\mathbb{G}} a_{\mathbb{k}+\mathbb{G}} \exp[i(\mathbb{k}+\mathbb{G})\cdot\mathbb{r}] & (2) \\ a_{\mathbb{k}+\mathbb{G}} = \frac{1}{\Omega}\int_\Omega d\mathbb{r}\, \underbrace{u(\mathbb{r})}_{\psi(\mathbb{r})e^{-i\mathbb{k}\cdot\mathbb{r}},\ \text{periodic}} e^{-i\mathbb{G}\cdot\mathbb{r}} = \frac{1}{\Omega}\int_\Omega d\mathbb{r}\, \psi(\mathbb{r}) \exp[-i(\mathbb{k}+\mathbb{G})\cdot\mathbb{r}] & (3) \end{cases}$$

In the momentum space,

$$\hat{V}_{NL}|\psi\rangle = \sum_{\mathbb{G}} (\hat{V}_{NL}\psi)_{\mathbb{k}+\mathbb{G}} \exp[i(\mathbb{k}+\mathbb{G})\cdot\mathbb{r}] \quad (4)$$

$$(\hat{V}_{NL}\psi)_{\mathbb{k}+\mathbb{G}} = \frac{1}{\Omega}\int d\mathbb{r}\, \hat{V}_{NL}|\psi\rangle \exp[-i(\mathbb{k}+\mathbb{G})\cdot\mathbb{r}] \quad (5)$$

$$= \sum_{lm}\frac{1}{\Omega}\int d\mathbb{r} \exp[-i(\mathbb{k}+\mathbb{G})\cdot\mathbb{r}]\, Y_{lm}(\theta,\varphi)\Delta V_l(r)\, \underbrace{\langle lm|\psi\rangle}_{\int d\cos\theta' d\varphi'\, Y^*_{lm}(\theta',\varphi') \sum_{\mathbb{G}'} a_{\mathbb{k}+\mathbb{G}'} e^{i(\mathbb{k}+\mathbb{G}')\cdot\mathbb{r}'}}$$

$$\therefore (\hat{V}_{NL}\psi)_{\mathbb{k}+\mathbb{G}} = \sum_{\mathbb{G}'} \hat{V}^{NL}_{\mathbb{G}\mathbb{G}'} a_{\mathbb{k}+\mathbb{G}'} \quad (6)$$

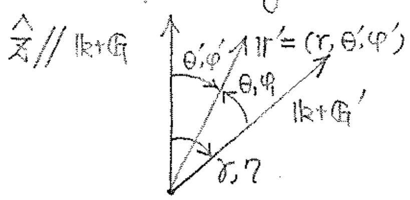
$$\hat{V}^{NL}_{\mathbb{G}\mathbb{G}'} = \sum_{lm}\frac{1}{\Omega}\int dr\, r^2 \Delta V_l(r) \int d\cos\theta d\varphi \exp[-i(\mathbb{k}+\mathbb{G})\cdot\underbrace{\mathbb{r}}_{(r,\theta,\varphi)}]\, Y_{lm}(\theta,\varphi)$$

$$\times \int d\cos\theta' d\varphi' \exp[i(\mathbb{k}+\mathbb{G}')\cdot\underbrace{\mathbb{r}'}_{(r,\theta',\varphi')}]\, Y^*_{lm}(\theta',\varphi') \quad (7)$$

We will measure angles with respect to $\mathbf{k}+\mathbf{G}$ as the z axis. Then,

$$\langle lm | \mathbf{k}+\mathbf{G}' \rangle = \int d\cos\theta' \, d\varphi' \, \exp\left[i(\mathbf{k}+\mathbf{G}')\cdot \overset{(r,\theta',\varphi')}{\mathbf{r}'} \right] Y^{*}_{lm}(\theta',\varphi') \qquad (8)$$

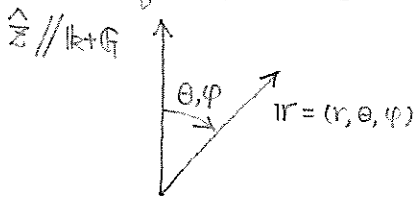
is a function of only r, the angular part of which is projected to $|lm\rangle$ with z pointing to $\mathbf{k}+\mathbf{G}$.



Similarly,

$$\langle \mathbf{k}+\mathbf{G} | lm \rangle = \int d\cos\theta \, d\varphi \, \exp\left[-i(\mathbf{k}+\mathbf{G})\cdot \overset{(r,\theta,\varphi)}{\mathbf{r}} \right] Y_{lm}(\theta,\varphi) \qquad (9)$$

is a function of only r, projected onto $|lm\rangle$.



With these notations,

$$\tilde{V}^{NL}_{\mathbf{G}\mathbf{G}'} = \sum_{lm} \frac{1}{\Omega} \int dr \, r^2 \, \Delta V_l(r) \, \langle \mathbf{k}+\mathbf{G} | lm \rangle \langle lm | \mathbf{k}+\mathbf{G}' \rangle \qquad (10)$$

Evaluation

We will use

$$\boxed{e^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^{l}(2l+1)\, j_{l}(kr)\, P_{l}(\cos\theta)} \qquad (11)$$

where $j_l(kr)$ is the spherical Bessel function, and an addition theorem

$$\boxed{P_{l}(\cos\gamma) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_{lm}(\theta',\varphi')\, Y^{*}_{lm}(\theta_1,\varphi_1)} \qquad (12)$$

(The asterisk may go on either spherical harmonics.)

$$\langle lm|\mathbf{k}+\mathbf{G}'\rangle = \int d\cos\theta'\, d\varphi'\, \exp\left[i|\mathbf{k}+\mathbf{G}|r'\cos\theta_1\right] Y^{*}_{lm}(\theta'\varphi')$$

$$= \sum_{l_1} i^{l_1}\cancel{(2l_1+1)}\, j_{l_1}(|\mathbf{k}+\mathbf{G}|r)\int d\cos\theta'\, d\varphi'\, \underbrace{P_{l_1}(\cos\theta_1)}_{\frac{\cancel{4\pi}}{\cancel{2l_1+1}}\sum_{m_1} Y^{*}_{l_1 m_1}(\gamma,\eta)\, Y_{l_1 m_1}(\theta',\varphi')\ \because (12)}\, Y^{*}_{lm}(\theta',\varphi') \quad \because (11)$$

$$= \sum_{l_1 m_1} 4\pi\, i^{l_1}\, j_{l_1}(|\mathbf{k}+\mathbf{G}|r)\, Y^{*}_{l_1 m_1}(\gamma,\eta)\underbrace{\int d\cos\theta'\, d\varphi'\, Y_{l_1 m_1}(\theta',\varphi')\, Y^{*}_{lm}(\theta',\varphi')}_{\delta_{l_1 l}\,\delta_{m_1 m}\ (\because \text{orthonormality})}$$

$$\therefore \langle lm|\mathbf{k}+\mathbf{G}'\rangle = 4\pi\, i^{l}\, j_{l}(|\mathbf{k}+\mathbf{G}|r)\, Y^{*}_{lm}(\gamma,\eta) \qquad (13)$$

$$\langle \mathbf{k}+\mathbf{G}|lm\rangle = \int d\cos\theta\, d\varphi\, \exp\left[-i|\mathbf{k}+\mathbf{G}|r\cos\theta\right] Y_{lm}(\theta,\varphi)$$

$$= \sum_{l_1} (-i)^{l_1}(2l_1+1)\, j_{l_1}(|\mathbf{k}+\mathbf{G}|r)\int d\cos\theta\, d\varphi\, P_{l_1}(\cos\theta)\, Y_{lm}(\theta,\varphi) \quad \because (11)$$

Note

$$Y_{l0}(\theta,\varphi) = (-1)^{0}\sqrt{\frac{2l+1}{4\pi}\frac{(l-0)!}{(l+0)!}}\;\underbrace{P_l^{0}(\cos\theta)}_{(1-\cos^2\theta)^{0/2}\left(\frac{d}{dx}\right)^{0}P_l(\cos\theta)\,=\,P_l(\cos\theta)}\;e^{i0\varphi}$$

$$\therefore\; Y_{l,0}(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}}\,P_l(\cos\theta) \qquad (14)$$

$$\therefore\; \langle \mathbf{k}+\mathbf{G}|lm\rangle = \sum_{l_1}(-i)^{l_1}(2l_1+1)\,j_{l_1}(|\mathbf{k}+\mathbf{G}|r)\underbrace{\int d\cos\theta\, d\varphi\sqrt{\frac{4\pi}{2l_1+1}}\,Y_{l_1 0}(\theta,\varphi)\,Y_{lm}(\theta,\varphi)}_{\sqrt{\frac{4\pi}{2l_1+1}}\,\delta_{ll_1}\delta_{m0}}$$

$$\therefore\; \langle \mathbf{k}+\mathbf{G}|lm\rangle = (-i)^{l}\sqrt{4\pi(2l+1)}\;j_l(|\mathbf{k}+\mathbf{G}|r)\,\delta_{m0} \qquad (15)$$

Substituting Eqs. (13) and (15) in (10),

$$V_{\mathbf{G}\mathbf{G}'} = \sum_{l\cancel{m}}\frac{1}{\Omega}\int dr\,r^2\,\Delta V_l(r)\,\cancel{(-i)^{l}}\sqrt{\cancel{4\pi}(2l+1)}\;j_l(|\mathbf{k}+\mathbf{G}|r)\,\cancel{\delta_{m0}}$$
$$\times\, 4\pi\,\cancel{i^{l}}\,j_l(|\mathbf{k}+\mathbf{G}'|r)\,\underbrace{Y^{*}_{l\,m\to 0}(\gamma,\eta)}_{\sqrt{\frac{2l+1}{\cancel{4\pi}}}\,P_l(\cos\gamma)}$$

$$= \sum_{l}\frac{4\pi(2l+1)}{\Omega}\int dr\,r^2\;j_l(|\mathbf{k}+\mathbf{G}|r)\,\Delta V_l(r)\,j_l(|\mathbf{k}+\mathbf{G}'|r) \qquad (16)$$

In summary,

$$\boxed{\begin{aligned} V_{GG'} &= \sum_{lm} \frac{1}{\Omega} \int dr\, r^2 \langle \mathbf{k}+\mathbf{G} | lm \rangle \Delta V_l(r) \langle lm | \mathbf{k}+\mathbf{G}' \rangle && (17) \\ &= \sum_{l} \frac{4\pi(2l+1)}{\Omega} \int dr\, r^2 j_l(|\mathbf{k}+\mathbf{G}| r) \Delta V_l(r) j_l(|\mathbf{k}+\mathbf{G}'| r) && (18) \end{aligned}}$$

※ $j_l(kr) \to \frac{1}{kr} \sin(kr - \frac{n\pi}{2}) \propto \frac{1}{r}$ $(r \to \infty)$, however, the integration is finite range since $\Delta V_l(r) = 0$ for $r \geq \max\{r_{cl}\} \equiv r_c$.

— Operation count

$(V a)_{\mathbf{k}+\mathbf{G}} \leftarrow \emptyset$

for each ion I

for each plane wave $\mathbf{k}+\mathbf{G}$

$$(Va)_{\mathbf{k}+\mathbf{G}} \mathrel{+}= \sum_{\mathbf{G}'} \Big[\underbrace{\sum_l \frac{4\pi(2l+1)}{\Omega} \int_0^{r_c} dr\, r^2 j_l(|\mathbf{k}+\mathbf{G}| r) \Delta V_l(r) j_l(|\mathbf{k}+\mathbf{G}'| r)}_{\text{finite-range numerical integration}} \Big] a_{\mathbf{k}+\mathbf{G}'}$$

The operation count is

$O(N_I N_{PW}^2) \sim O(N_I^3)$!

where N_I is the number of ions, N_{PW} is the number of plane waves which should scale linearly with N_I.

※ (Semi) nonlocal potential is another source of $O(N^3)$ computation of DFT in addition to orthonormalization.