I. MATRIX ELEMENTS OF $\mathbf{v}^{\rm nl}_{nm}(\mathbf{k})$ AND $\boldsymbol{\mathcal{V}}^{{\rm nl},\ell}_{nm}(\mathbf{k})$

From Eq. (??), we have that

$$\begin{aligned}\mathbf{v}^{\rm nl}_{nm}(\mathbf{k}) = \langle n\mathbf{k}|\hat{\mathbf{v}}^{\rm nl}|m\mathbf{k}'\rangle &= \frac{i}{\hbar}\langle n\mathbf{k}|[\hat{V}^{\rm nl},\hat{\mathbf{r}}]|m\mathbf{k}'\rangle \\ &= \frac{i}{\hbar}\int d\mathbf{r}d\mathbf{r}'\langle n\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|[\hat{V}^{\rm nl},\hat{\mathbf{r}}]|\mathbf{r}'\rangle\langle\mathbf{r}'|m\mathbf{k}'\rangle \\ &= \frac{i}{\hbar}\delta(\mathbf{k}-\mathbf{k}')\int d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\langle\mathbf{r}|[\hat{V}^{\rm nl},\hat{\mathbf{r}}]|\mathbf{r}'\rangle\psi_{m\mathbf{k}'}(\mathbf{r}'),\end{aligned} \tag{1}$$

where due to the fact that the integrand is periodic in real space, $\mathbf{k}=\mathbf{k}'$ where $\mathbf{k}$ is restricted to the Brillouin Zone. Now,

$$\begin{aligned}\langle\mathbf{r}|[\hat{V}^{\rm nl},\hat{\mathbf{r}}]|\mathbf{r}'\rangle &= \langle\mathbf{r}|\hat{V}^{\rm nl}\hat{\mathbf{r}}-\hat{\mathbf{r}}\hat{V}^{\rm nl}|\mathbf{r}'\rangle = \langle\mathbf{r}|\hat{V}^{\rm nl}\hat{\mathbf{r}}|\mathbf{r}'\rangle - \langle\mathbf{r}|\hat{\mathbf{r}}\hat{V}^{\rm nl}|\mathbf{r}'\rangle \\ &= \langle\mathbf{r}|\hat{V}^{\rm nl}\mathbf{r}'|\mathbf{r}'\rangle - \langle\mathbf{r}|\mathbf{r}\hat{V}^{\rm nl}|\mathbf{r}'\rangle = \langle\mathbf{r}|\hat{V}^{\rm nl}|\mathbf{r}'\rangle\big(\mathbf{r}'-\mathbf{r}\big) = V^{\rm nl}(\mathbf{r},\mathbf{r}')\big(\mathbf{r}'-\mathbf{r}\big),\end{aligned} \tag{2}$$

where we use $\hat{r}\langle\mathbf{r}| = r\langle\mathbf{r}|$, $\langle\mathbf{r}'|\hat{r} = \langle\mathbf{r}|r'$, and $V^{\rm nl}(\mathbf{r},\mathbf{r}') = \langle\mathbf{r}|\hat{V}^{\rm nl}|\mathbf{r}'\rangle$ (Eq. (??)). Also, we have the following identity which will be used shortly,

$$\begin{aligned}(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})\frac{1}{\Omega}\int e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\rm nl}(\mathbf{r},\mathbf{r}')e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}' &= -i\frac{1}{\Omega}\int e^{-i\mathbf{K}\cdot\mathbf{r}}\left(\mathbf{r}V^{\rm nl}(\mathbf{r},\mathbf{r}')-V^{\rm nl}(\mathbf{r},\mathbf{r}')\mathbf{r}'\right)e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}' \\ (\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})\langle\mathbf{K}|V^{\rm nl}|\mathbf{K}'\rangle &= \frac{i}{\Omega}\int e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\rm nl}(\mathbf{r},\mathbf{r}')\big(\mathbf{r}'-\mathbf{r}\big)e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}',\end{aligned} \tag{3}$$

where Ω is the volume of the unit cell, and we defined

$$V^{\rm nl}(\mathbf{K},\mathbf{K}') \equiv \langle\mathbf{K}|V^{\rm nl}|\mathbf{K}'\rangle = \frac{1}{\Omega}\int e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\rm nl}(\mathbf{r},\mathbf{r}')e^{i\mathbf{K}'\cdot\mathbf{r}'}\,d\mathbf{r}d\mathbf{r}', \tag{4}$$

where $V^{\rm nl}(\mathbf{K}',\mathbf{K}) = V^{{\rm nl}*}(\mathbf{K},\mathbf{K}')$, since $V^{\rm nl}(\mathbf{r}',\mathbf{r}) = V^{{\rm nl}*}(\mathbf{r},\mathbf{r}')$ due to the fact that $\hat{V}^{\rm nl}$ is a hermitian operator. Using the plane wave expansion

$$\langle\mathbf{r}|n\mathbf{k}\rangle = \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{G}}A_{n\mathbf{k}}(\mathbf{G})e^{i\mathbf{K}\cdot\mathbf{r}}, \tag{5}$$

with $\mathbf{K}=\mathbf{k}+\mathbf{G}$, we obtain from Eq. (1) and Eq. (3), that

$$\begin{aligned}\mathbf{v}^{\rm nl}_{nm}(\mathbf{k}) &= \frac{i}{\hbar}\delta(\mathbf{k}-\mathbf{k}')\sum_{\mathbf{G},\mathbf{G}'}A^*_{n\mathbf{k}}(\mathbf{G})A_{m\mathbf{k}'}(\mathbf{G}')\frac{1}{\Omega}\int d\mathbf{r}d\mathbf{r}'e^{-i\mathbf{K}\cdot\mathbf{r}}\langle\mathbf{r}|[\hat{V}^{\rm nl},\hat{\mathbf{r}}]|\mathbf{r}'\rangle e^{i\mathbf{K}'\cdot\mathbf{r}'} \\ &= \frac{1}{\hbar}\delta(\mathbf{k}-\mathbf{k}')\sum_{\mathbf{G},\mathbf{G}'}A^*_{n\mathbf{k}}(\mathbf{G})A_{m\mathbf{k}'}(\mathbf{G}')\frac{i}{\Omega}\int d\mathbf{r}d\mathbf{r}'e^{-i\mathbf{K}\cdot\mathbf{r}}V^{\rm nl}(\mathbf{r},\mathbf{r}')\big(\mathbf{r}'-\mathbf{r}\big)e^{i\mathbf{K}'\cdot\mathbf{r}'} \\ &= \frac{1}{\hbar}\delta(\mathbf{k}-\mathbf{k}')\sum_{\mathbf{G},\mathbf{G}'}A^*_{n\mathbf{k}}(\mathbf{G})A_{m\mathbf{k}'}(\mathbf{G}')(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})V^{\rm nl}(\mathbf{K},\mathbf{K}').\end{aligned} \tag{6}$$

For fully separable pseudopotentials in the Kleinman-Bylander (KB) form,[1–3] the matrix elements $\langle\mathbf{K}|V^{\rm nl}|\mathbf{K}'\rangle = V^{\rm nl}(\mathbf{K},\mathbf{K}')$ can be readily calculated. [1] Indeed, the Fourier representation assumes the form,[3–5]

$$\begin{aligned}V^{\rm nl}_{\rm KB}(\mathbf{K},\mathbf{K}') &= \sum_s e^{i(\mathbf{K}-\mathbf{K}')\cdot\boldsymbol{\tau}_s}\sum_{l=0}^{l_s}\sum_{m=-l}^{l}E_l F^s_{lm}(\mathbf{K})F^{s*}_{lm}(\mathbf{K}') \\ &= \sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l}E_l f^s_{lm}(\mathbf{K})f^{s*}_{lm}(\mathbf{K}'),\end{aligned} \tag{7}$$

with $f^s_{lm}(\mathbf{K}) = e^{i\mathbf{K}\cdot\boldsymbol{\tau}_s}F^s_{lm}(\mathbf{K})$, and

$$F^s_{lm}(\mathbf{K}) = \int d\mathbf{r}\,e^{-i\mathbf{K}\cdot\mathbf{r}}\delta V^S_l(\mathbf{r})\Phi^{\rm ps}_{lm}(\mathbf{r}). \tag{8}$$

Here $\delta V_l^S(\mathbf{r})$ is the non-local contribution of the ionic pseudopotential centered at the atomic position $\boldsymbol{\tau}_s$ located in the unit cell, $\Phi^{\rm ps}_{lm}(\mathbf{r})$ is the pseudo-wavefunction of the corresponding atom, while E_l is the so called Kleinman-Bylander energy. Further details can be found in Ref. [5]. From Eq. (7) we find

$$
\begin{aligned}
(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})V^{\rm nl}_{\rm KB}(\mathbf{K},\mathbf{K}') &= \sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})f^s_{lm}(\mathbf{K})f^{s*}_{lm}(\mathbf{K}')\\
&= \sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l\left(\left[\nabla_{\mathbf{K}}f^s_{lm}(\mathbf{K})\right]f^{s*}_{lm}(\mathbf{K}')+f^s_{lm}(\mathbf{K})\left[\nabla_{\mathbf{K}'}f^{s*}_{lm}(\mathbf{K}')\right]\right), \qquad (9)
\end{aligned}
$$

and using this in Eq. (6) leads to

$$
\begin{aligned}
\mathbf{v}^{\rm nl}_{nm}(\mathbf{k}) &= \frac{1}{\hbar}\sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l\sum_{\mathbf{G}\mathbf{G}'}A^*_{n,\vec{k}}(\mathbf{G})A_{n',\vec{k}}(\mathbf{G}')\\
&\times\left(\nabla_{\mathbf{K}}f^s_{lm}(\mathbf{K})f^{s*}_{lm}(\mathbf{K}')+f^s_{lm}(\mathbf{K})\nabla_{\mathbf{K}'}f^{s*}_{lm}(\mathbf{K}')\right)\\
&= \frac{1}{\hbar}\sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l} E_l\left[\left(\sum_{\mathbf{G}}A^*_{n,\vec{k}}(\mathbf{G})\nabla_{\mathbf{K}}f^s_{lm}(\mathbf{K})\right)\left(\sum_{\mathbf{G}'}A_{n',\vec{k}}(\mathbf{G}')f^{s*}_{lm}(\mathbf{K}')\right)\right.\\
&+\left.\left(\sum_{\mathbf{G}}A^*_{n,\vec{k}}(\mathbf{G})f^s_{lm}(\mathbf{K})\right)\left(\sum_{\mathbf{G}'}A_{n',\vec{k}}(\mathbf{G}')\nabla_{\mathbf{K}'}f^{s*}_{lm}(\mathbf{K}')\right)\right], \qquad (10)
\end{aligned}
$$

where there are only single sums over $\mathbf{G}$. Above is implemented in the DP code.[6]

Indeed, in DP `calcolacommutatore.F90` above expansion coefficients are called $E_l f^s_{lm}(\mathbf{K})\to$ `fnlkslm` and $E_l\nabla_{\mathbf{K}}f^s_{lm}(\mathbf{K})\to$ `fnldkslm`, where `fnlkslm` is an array indexed by $\mathbf{k}+\mathbf{G}$, and `fnldkslm` is vector array indexed by $\mathbf{k}+\mathbf{G}$.

Now we derive $\boldsymbol{\mathcal{V}}^{\rm nl,\ell}_{nm}(\mathbf{k})$. First we prove that

$$
\sum_{\mathbf{G}}|\mathbf{k}+\mathbf{G}\rangle\langle\mathbf{k}+\mathbf{G}| = 1. \qquad (11)
$$

Proof:

$$
\langle n\mathbf{k}|1|n'\mathbf{k}\rangle = \delta_{nn'}, \qquad (12)
$$

take

$$
\begin{aligned}
\sum_{\mathbf{G}}\langle n\mathbf{k}||\mathbf{k}+\mathbf{G}\rangle\langle\mathbf{k}+\mathbf{G}||n'\mathbf{k}\rangle &= \int d\mathbf{r}d\mathbf{r}'\sum_{\mathbf{G}}\langle n\mathbf{k}||\mathbf{r}\rangle\langle\mathbf{r}||\mathbf{k}+\mathbf{G}\rangle\langle\mathbf{k}+\mathbf{G}||\mathbf{r}'\rangle\langle\mathbf{r}'||n'\mathbf{k}\rangle\\
&= \int d\mathbf{r}d\mathbf{r}'\sum_{\mathbf{G}}\psi^*_{n\mathbf{k}}(\mathbf{r})\frac{1}{\sqrt{\Omega}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}\frac{1}{\sqrt{\Omega}}e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}'}\psi_{m\mathbf{k}}(\mathbf{r}')\\
&= \int d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{k}}(\mathbf{r}')\frac{1}{V}\sum_{\mathbf{G}}e^{i(\mathbf{k}+\mathbf{G})\cdot(\mathbf{r}-\mathbf{r}')}\\
&= \int d\mathbf{r}d\mathbf{r}'\psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{k}}(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}') = \int d\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{k}}(\mathbf{r}) = \delta_{nn'}, \qquad (13)
\end{aligned}
$$

and thus Eq. (11) follows. `Q.E.D.` We used

$$
\langle\mathbf{r}|\mathbf{k}+\mathbf{G}\rangle = \frac{1}{\sqrt{\Omega}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \qquad (14)
$$

From Eq. (**??**), we would like to calculate

$$
\boldsymbol{\mathcal{V}}^{\rm nl,\ell}_{nm}(\mathbf{k}) = \frac{1}{2}\langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\rm nl}+\mathbf{v}^{\rm nl}C^\ell(z)|m\mathbf{k}\rangle. \qquad (15)
$$

We work out the first term in the r.h.s,

$$\begin{aligned}\langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\rm nl}|m\mathbf{k}\rangle &= \sum_{\mathbf{G}}\langle n\mathbf{k}|C^\ell(z)|\mathbf{k}+\mathbf{G}\rangle\langle\mathbf{k}+\mathbf{G}|\mathbf{v}^{\rm nl}|m\mathbf{k}\rangle\\
&= \sum_{\mathbf{G}}\int d\mathbf{r}\int d\mathbf{r}'\langle n\mathbf{k}||\mathbf{r}\rangle\langle\mathbf{r}|C^\ell(z)|\mathbf{r}'\rangle\langle\mathbf{r}'||\mathbf{k}+\mathbf{G}\rangle\\
&\times\int d\mathbf{r}''\int d\mathbf{r}'''\langle\mathbf{k}+\mathbf{G}||\mathbf{r}''\rangle\langle\mathbf{r}''|\mathbf{v}^{\rm nl}|\mathbf{r}'''\rangle\langle\mathbf{r}'''||m\mathbf{k}\rangle\\
&= \sum_{\mathbf{G}}\int d\mathbf{r}\int d\mathbf{r}'\langle n\mathbf{k}|\mathbf{r}\rangle C^\ell(z)\delta(\mathbf{r}-\mathbf{r}')\langle\mathbf{r}'|\mathbf{k}+\mathbf{G}\rangle\\
&\times\int d\mathbf{r}''\int d\mathbf{r}'''\langle\mathbf{k}+\mathbf{G}|\mathbf{r}''\rangle\langle\mathbf{r}''|\mathbf{v}^{\rm nl}|\mathbf{r}'''\rangle\langle\mathbf{r}'''|m\mathbf{k}\rangle\\
&= \sum_{\mathbf{G}}\int d\mathbf{r}\langle n\mathbf{k}|\mathbf{r}\rangle C^\ell(z)\langle\mathbf{r}|\mathbf{k}+\mathbf{G}\rangle\\
&\times\frac{i}{\hbar}\int d\mathbf{r}''\int d\mathbf{r}'''\langle\mathbf{k}+\mathbf{G}|\mathbf{r}''\rangle V^{\rm nl}(\mathbf{r}'',\mathbf{r}''')(\mathbf{r}'''-\mathbf{r}'')\langle\mathbf{r}'''|m\mathbf{k}\rangle,\end{aligned}\tag{16}$$

where we used Eq. (2) and (**??**). We use Eq. (5), (14) and (3) to obtain

$$\begin{aligned}\langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\rm nl}|m\mathbf{k}\rangle &= \sum_{\mathbf{G}}\sum_{\mathbf{G}'}A^*_{n\mathbf{k}}(\mathbf{G}')\frac{1}{\Omega}\int d\mathbf{r}e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}}C^\ell(z)e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}\\
&\times\sum_{\mathbf{G}''}A_{m\mathbf{k}}(\mathbf{G}'')\frac{i}{\hbar\Omega}\int d\mathbf{r}''\int d\mathbf{r}'''e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}''}V^{\rm nl}(\mathbf{r}'',\mathbf{r}''')(\mathbf{r}'''-\mathbf{r}'')e^{i(\mathbf{k}+\mathbf{G}'')\cdot\mathbf{r}'''}\\
&= \frac{1}{\hbar}\sum_{\mathbf{G}}\sum_{\mathbf{G}'}A^*_{n\mathbf{k}}(\mathbf{G}')\delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel}f_\ell(\mathbf{G}_\perp-\mathbf{G}'_\perp)\sum_{\mathbf{G}''}A_{m\mathbf{k}}(\mathbf{G}'')(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}''})V^{\rm nl}(\mathbf{K},\mathbf{K}''),\end{aligned}\tag{17}$$

where

$$\frac{1}{\Omega}\int d\mathbf{r}\,C^\ell(z)e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} = \delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel}f_\ell(\mathbf{G}_\perp-\mathbf{G}'_\perp),\tag{18}$$

and

$$f_\ell(g) = \frac{1}{L}\int_{z_\ell-\Delta^b_\ell}^{z_\ell+\Delta^f_\ell}e^{igz}dz,\tag{19}$$

where $f^*(g) = f(-g)$. We define

$$\mathcal{F}^\ell_{n\mathbf{k}}(\mathbf{G}) = \sum_{\mathbf{G}'}A_{n\mathbf{k}}(\mathbf{G}')\delta_{\mathbf{G}_\parallel\mathbf{G}'_\parallel}f_\ell(\mathbf{G}'_\perp-\mathbf{G}_\perp),\tag{20}$$

and

$$\mathcal{H}_{n\mathbf{k}}(\mathbf{G}) = \sum_{\mathbf{G}'}A_{n\mathbf{k}}(\mathbf{G}')(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})V^{\rm nl}(\mathbf{K},\mathbf{K}'),\tag{21}$$

thus we can compactly write,

$$\langle n\mathbf{k}|C^\ell(z)\mathbf{v}^{\rm nl}|m\mathbf{k}\rangle = \frac{1}{\hbar}\sum_{\mathbf{G}}\mathcal{F}^{\ell*}_{n\mathbf{k}}(\mathbf{G})\mathcal{H}_{m\mathbf{k}}(\mathbf{G}).\tag{22}$$

Now, the second term of Eq. (15)

$$\begin{aligned}
\langle n\mathbf{k}|\mathbf{v}^{\rm nl}C^\ell(z)|m\mathbf{k}\rangle &= \sum_{\mathbf{G}}\langle n\mathbf{k}|\mathbf{v}^{\rm nl}|\mathbf{k}+\mathbf{G}\rangle\langle\mathbf{k}+\mathbf{G}|C^\ell(z)|m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}}\int d\mathbf{r}''\int d\mathbf{r}'''\langle n\mathbf{k}||\mathbf{r}''\rangle\langle\mathbf{r}''|\mathbf{v}^{\rm nl}|\mathbf{r}'''\rangle\langle\mathbf{r}'''||\mathbf{k}+\mathbf{G}\rangle \\
&\times\int d\mathbf{r}\int d\mathbf{r}'\langle\mathbf{k}+\mathbf{G}||\mathbf{r}\rangle\langle\mathbf{r}|C^\ell(z)|\mathbf{r}'\rangle\langle\mathbf{r}'||m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}}\frac{i}{\hbar}\int d\mathbf{r}''\int d\mathbf{r}'''\langle n\mathbf{k}|\mathbf{r}''\rangle V^{\rm nl}(\mathbf{r}'',\mathbf{r}''')(\mathbf{r}'''-\mathbf{r}'')\langle\mathbf{r}'''|\mathbf{k}+\mathbf{G}\rangle \\
&\times\int d\mathbf{r}\langle\mathbf{k}+\mathbf{G}|\mathbf{r}\rangle C^\ell(z)\langle\mathbf{r}|m\mathbf{k}\rangle \\
&= \sum_{\mathbf{G}}\sum_{\mathbf{G}'}A^*_{n\mathbf{k}}(\mathbf{G}')\frac{i}{\hbar\Omega}\int d\mathbf{r}''\int d\mathbf{r}'''e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}''}V^{\rm nl}(\mathbf{r}'',\mathbf{r}''')(\mathbf{r}'''-\mathbf{r}'')e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}'''} \\
&\times\sum_{\mathbf{G}''}A_{m\mathbf{k}}(\mathbf{G}'')\frac{1}{\Omega}\int d\mathbf{r}e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}C^\ell(z)e^{i(\mathbf{k}+\mathbf{G}'')\cdot\mathbf{r}} \\
&= \frac{1}{\hbar}\sum_{\mathbf{G}}\sum_{\mathbf{G}'}A^*_{n\mathbf{k}}(\mathbf{G}')(\nabla_{\mathbf{K}}+\nabla_{\mathbf{K}'})V^{\rm nl}(\mathbf{K}',\mathbf{K}) \\
&\times\sum_{\mathbf{G}''}A_{m\mathbf{k}}(\mathbf{G}'')\delta_{\mathbf{G}_\parallel\mathbf{G}''_\parallel}f_\ell(\mathbf{G}''_\perp-\mathbf{G}_\perp) \\
&= \frac{1}{\hbar}\sum_{\mathbf{G}}\mathcal{H}^*_{n\mathbf{k}}(\mathbf{G})\mathcal{F}^\ell_{m\mathbf{k}}(\mathbf{G}).
\end{aligned} \tag{23}$$

Therefore Eq. (15) is compactly given by

$$\boldsymbol{\mathcal{V}}^{\rm nl,\ell}_{nm}(\mathbf{k}) = \frac{1}{2\hbar}\sum_{\mathbf{G}}\left(\mathcal{F}^{\ell*}_{n\mathbf{k}}(\mathbf{G})\mathcal{H}_{m\mathbf{k}}(\mathbf{G})+\mathcal{H}^*_{n\mathbf{k}}(\mathbf{G})\mathcal{F}^\ell_{m\mathbf{k}}(\mathbf{G})\right). \tag{24}$$

For fully separable pseudopotentials in the Kleinman-Bylander (KB) form [1–3], we can use Eq. (9) and evaluate above expression, that we have implemented in the DP code [6]. Explicitly,

$$\begin{aligned}
\boldsymbol{\mathcal{V}}^{\rm nl,\ell}_{nm}(\mathbf{k}) &= \frac{1}{2\hbar}\sum_s\sum_{l=0}^{l_s}\sum_{m=-l}^{l}E_l \\
&\Bigg[\left(\sum_{\mathbf{G}''}\nabla_{\mathbf{G}''}f^s_{lm}(\mathbf{G}'')\sum_{\mathbf{G}}A^*_{n\mathbf{k}}(\mathbf{G})\delta_{\mathbf{G}_{||}\mathbf{G}''_{||}}f_\ell(G_z-G''_z)\right)\left(\sum_{\mathbf{G}'}A_{m\mathbf{k}}(\mathbf{G}')f^{s*}_{lm}(\mathbf{K}')\right) \\
&+\left(\sum_{\mathbf{G}''}f^s_{lm}(\mathbf{G}'')\sum_{\mathbf{G}}A^*_{n\mathbf{k}}(\mathbf{G})\delta_{\mathbf{G}_{||}\mathbf{G}''_{||}}f_\ell(G_z-G''_z)\right)\left(\sum_{\mathbf{G}'}A_{m\mathbf{k}}(\mathbf{G}')\nabla_{\mathbf{K}'}f^{s*}_{lm}(\mathbf{K}')\right) \\
&+\left(\sum_{\mathbf{G}}A^*_{n\mathbf{k}}(\mathbf{G})\nabla_{\mathbf{G}}f^s_{lm}(\mathbf{G})\right)\left(\sum_{\mathbf{G}''}f^{s*}_{lm}(\mathbf{G}'')\sum_{\mathbf{G}'}A_{m\mathbf{k}}(\mathbf{G}')\delta_{\mathbf{G}'_{||}\mathbf{G}''_{||}}f_\ell(G''_z-G'_z)\right) \\
&+\left(\sum_{\mathbf{G}}A^*_{n\mathbf{k}}(\mathbf{G})f^s_{lm}(\mathbf{G})\right)\left(\sum_{\mathbf{G}''}\nabla_{\mathbf{G}''}f^{s*}_{lm}(\mathbf{G}'')\sum_{\mathbf{G}'}A_{m\mathbf{k}}(\mathbf{G}')\delta_{\mathbf{G}'_{||}\mathbf{G}''_{||}}f_\ell(G''_z-G'_z)\right)\Bigg].
\end{aligned} \tag{25}$$

For a full slab calculation, equivalent to a bulk calculation, $C^\ell(z)=1$ and then $f_\ell(g)=\delta_{g0}$, and Eq. (25) reduces to Eq. (10).

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