TECHNICAL NOTE ON THE CALCULATION OF MAXIMALLY–LOCALIZED WANNIER FUNCTIONS WITHIN THE FLAPW + LO FORMALISM

We give in the following the formula used in our original 2002 implementation[1] of the maximally–localized Wannier functions (MLWF) method of Marzari and Vanderbilt[2] within the full–potential linearized–augmented–plane–wave (FLAPW) framework. This approach has been used during past years for various applications.[3–5] The FLAPW code which was basic to this implementation had been developed initially by Jansen and Freeman.[6]

1. Basic ingredients of the localization functional

Given the Bloch orbitals $\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\exp(i\,\mathbf{k}\cdot\mathbf{r})$, we determine their periodical part $|u_{n\mathbf{k}}\rangle$ on a regular mesh of $\mathbf{k}$–points, and use finite differences to evaluate required derivatives. For any given $\mathbf{k}$–point, we have a star $\mathbf{b}$ of points that are first–neighbors. We define $M_{mn}^{(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}}|u_{n,\mathbf{k}+\mathbf{b}}\rangle$ as the matrix elements between Bloch orbitals at neighboring $\mathbf{k}$–points. The $M_{mn}^{(\mathbf{k},\mathbf{b})}$ is a central quantity in the formalism,[2] since we can express all the contributions to the localization functional using the connection made by Blount,[7] together with the finite–difference evaluations of the gradients.

The Bloch wavefunctions are expanded in terms of a set of LAPW + LO basis functions $\phi_{j\mathbf{k}}(\mathbf{r})$:

$$\begin{aligned}\psi_{n\mathbf{k}}(\mathbf{r}) &= \sum_j z_{n\mathbf{k},j}\,\phi_{\mathbf{k},j}(\mathbf{r}) \\ &= \begin{cases} \Omega^{-1/2}\sum_j z_{n\mathbf{k},j}\exp[i(\mathbf{k}+\mathbf{G}_j)\cdot\mathbf{r}] & \mathbf{r}\in I; \\ \sum_L i^l\,[A_L^\alpha(n\mathbf{k})u_l(r_\alpha)+B_L^\alpha(n\mathbf{k})\dot{u}_l(r_\alpha)+C_L^\alpha(n\mathbf{k})u_l^{(2)}(r_\alpha)]Y_L(\widehat{r}_\alpha) & |\mathbf{r}-\boldsymbol{\tau}_{\boldsymbol{\alpha}}|\le R_\alpha, \end{cases}\end{aligned}$$

with

$$\begin{aligned} A_L^\alpha(n\mathbf{k}) &= \sum_j z_{n\mathbf{k},j}\widetilde{A}_L^\alpha(\mathbf{k}+\mathbf{G}_j)+\sum_{j_0} z_{n\mathbf{k},j_0}\widetilde{A}_{L_0}^\alpha(\mathbf{k}+\mathbf{G}_{j_0})\,\delta_{LL_0}, \\ B_L^\alpha(n\mathbf{k}) &= \sum_j z_{n\mathbf{k},j}\widetilde{B}_L^\alpha(\mathbf{k}+\mathbf{G}_j)+\sum_{j_0} z_{n\mathbf{k},j_0}\widetilde{B}_{L_0}^\alpha(\mathbf{k}+\mathbf{G}_{j_0})\,\delta_{LL_0}, \\ C_L^\alpha(n\mathbf{k}) &= \sum_{j_0} z_{n\mathbf{k},j_0}\widetilde{C}_{L_0}^\alpha(\mathbf{k}+\mathbf{G}_{j_0})\,\delta_{LL_0}. \end{aligned} \tag{1}$$

In these formulas, $u_l(r_\alpha)\equiv u_l(r_\alpha,E_l^{(1)})$ and $\dot{u}_l(r_\alpha)\equiv \dot{u}_l(r_\alpha,E_l^{(1)})$ are the radial solutions of the scalar-relativistic Schrödinger equation inside the muffin-tin spheres and their energy derivatives, both evaluated at energy $E_l^{(1)}$. The extra radial function $u_l^{(2)}(r_\alpha)\equiv u_l(r_\alpha,E_l^{(2)})$ is added[8] to the $u_l(r_\alpha)$ and $\dot{u}_l(r_\alpha)$ for certain $l=l_0$ values (*e.g.* those corresponding to semi–core states, with energy parameters $E_l^{(2)}$ chosen accordingly, or when an enlargment of the standard basis is required in order to increase its variational freedom). The subset of additional reciprocal lattice vectors $\mathbf{G}_{j_0}$ associated with the local orbitals is written $\{\mathbf{G}_{j_0}\}$. Note that the relevant set of reciprocal lattice vectors $\{\mathbf{G}_j\}$ required for all expansions in the interstitial region does not include the $\{\mathbf{G}_{j_0}\}$ subset. Ω is the unit cell volume, R_α and $\boldsymbol{\tau}_{\boldsymbol{\alpha}}$ are the MT radius and position of atom α, $\mathbf{r}_\alpha=\mathbf{r}-\boldsymbol{\tau}_{\boldsymbol{\alpha}}$, and $L=\{l,m\}$ is a collective angular momentum index.

The $\widetilde{A}_L^\alpha(\mathbf{k}+\mathbf{G}_j)$ and $\widetilde{B}_L^\alpha(\mathbf{k}+\mathbf{G}_j)$ coefficients are determined by imposing the continuity of each LAPW basis function and of its radial derivatives at the muffin-tin boundaries. Similarly, the

extra $\widetilde{A}^{\alpha}_{L_0}(\mathbf{k}+\mathbf{G}_{j_0})$, $\widetilde{B}^{\alpha}_{L_0}(\mathbf{k}+\mathbf{G}_{j_0})$, and $\widetilde{C}^{\alpha}_{L_0}(\mathbf{k}+\mathbf{G}_{j_0})$ coefficients are determined by imposing that the local orbital basis functions and their radial derivatives go to zero at the muffin–tin boundaries.
The set $\{\mathbf{G}_j\}$ of reciprocal lattice vectors is determined by the condition $|\mathbf{k}+\mathbf{G}_j| \leq k_{\max}$.
We consider first the interstitial contribution to the overlap matrix elements. We have

$$u_{n\mathbf{k}}(\mathbf{r}) = \Omega^{-1/2} \sum_j z_{n\mathbf{k}}(\mathbf{G}_j) \exp(i\, \mathbf{G}_j{\cdot}\mathbf{r}),$$

giving

$$\begin{aligned} M^{(\mathbf{k},\mathbf{b})}_{mn}\Big|_I &= \langle u_{m\mathbf{k}} | u_{n,\mathbf{k}+\mathbf{b}} \rangle_I = \int_\Omega u^*_{m\mathbf{k}}(\mathbf{r}) u_{n,\mathbf{k}+\mathbf{b}}(\mathbf{r}) U(\mathbf{r}) d\mathbf{r} \\ &= \sum_{ij} z^*_{m\mathbf{k}}(\mathbf{G}_i)\, U(\mathbf{G}_i - \mathbf{G}_j)\, z_{n,\mathbf{k}+\mathbf{b}}(\mathbf{G}_j), \end{aligned} \tag{2}$$

where $U(\mathbf{G}_i - \mathbf{G}_j)$ is the Fourier transform of the step function $U(\mathbf{r})$. This expression is efficiently evaluated numerically, using Fast Fourier Transforms (FFT). We examine now the spheres contributions.
From the Bloch wavefunction inside the sphere α, we get

$$u^{\alpha}_{n\mathbf{k}}(\mathbf{r}) = \exp\left[-i\, \mathbf{k}{\cdot}(\boldsymbol{\tau}_{\boldsymbol{\alpha}} + \mathbf{r}_\alpha)\right] \psi^{\alpha}_{n\mathbf{k}}(\mathbf{r}),$$

leading to

$$\langle u_{m\mathbf{k}} | u_{n,\mathbf{k}+\mathbf{b}} \rangle_{S_\alpha} = \exp\left(-i\, \mathbf{b}{\cdot}\boldsymbol{\tau}_{\boldsymbol{\alpha}}\right) \int_{S_\alpha} \psi^{\alpha *}_{m\mathbf{k}}(\mathbf{r}_\alpha)\, \psi^{\alpha}_{n,\mathbf{k}+\mathbf{b}}(\mathbf{r}_\alpha) \exp\left(-i\, \mathbf{b}{\cdot}\mathbf{r}_\alpha\right) d\mathbf{r}_\alpha.$$

Developing the "overlap charge densities", we have

$$\psi^{\alpha *}_{m\mathbf{k}}(\mathbf{r}_\alpha)\, \psi^{\alpha}_{n,\mathbf{k}+\mathbf{b}}(\mathbf{r}_\alpha) = \sum_{L_1,L_2} i^{l_2-l_1}\, Y^*_{L_1}\, Y_{L_2} \sum_{\kappa_1,\kappa_2} \mathcal{A}^{\alpha\kappa_1\,*}_{L_1}(m,\mathbf{k}) \mathcal{A}^{\alpha\kappa_2}_{L_2}(n,\mathbf{k}+\mathbf{b})\, v^{\kappa_1}_{l_1}(r_\alpha)\, v^{\kappa_2}_{l_2}(r_\alpha).$$

Here, both indices κ_1 and κ_2 take the values 1, 2, and 3, and $(\mathcal{A}^{\kappa_i},\ v^{\kappa_i})$ refer to $(A,\ u)$, $(B,\ \dot{u})$, and $(C,\ u^{(2)})$ for $\kappa_i = 1$, 2, and 3 respectively. Together with the usual Rayleigh expansion of a plane wave

$$\exp(i\, \mathbf{k}{\cdot}\mathbf{r}_\alpha) = 4\pi \sum_L i^l\, Y^*_L(\widehat{k})\, Y_L(\widehat{r}_\alpha)\, j_l\,(k\, r_\alpha),$$

we obtain

$$\begin{aligned} M^{(\mathbf{k},\mathbf{b})}_{mn}\Big|_{S_\alpha} &= \langle u_{m\mathbf{k}} | u_{n,\mathbf{k}+\mathbf{b}} \rangle_{S_\alpha} = 4\pi\ \exp\left(-i\, \mathbf{b}{\cdot}\boldsymbol{\tau}_{\boldsymbol{\alpha}}\right) \sum_{L,L_1,L_2} (-1)^l\, Y^*_L\,(\widehat{b}) \int_0^{R_\alpha} r^2_\alpha dr_\alpha j_l\,(b\, r_\alpha) \\ &\quad \times i^{l_2-l_1+l}\, C^{L_1}_{L_2\, L} \sum_{\kappa_1,\kappa_2} \mathcal{A}^{\alpha\kappa_1\,*}_{L_1}(m,\mathbf{k})\, \mathcal{A}^{\alpha\kappa_2}_{L_2}(n,\mathbf{k}+\mathbf{b})\, v^{\kappa_1}_{l_1}(r_\alpha)\, v^{\kappa_2}_{l_2}(r_\alpha), \end{aligned} \tag{3}$$

where the Gaunt coefficients $C^{L_1}_{L_2\, L}$ are defined by

$$C^{L_1}_{L_2\, L} = \int Y^*_{L_1} Y_L Y_{L_2}\, d\widehat{r}.$$

Practically, the 9 radial integrals (for each atom type, l_1, l_2, and l values) corresponding to the products $u_{l_1} u_{l_2}$, $u_{l_1} \dot{u}_{l_2}$, $\dot{u}_{l_1} u_{l_2}$, $\dot{u}_{l_1} \dot{u}_{l_2}$, $u_{l_1} u_{l_2}^{(2)}$, $u_{l_1}^{(2)} u_{l_2}$, $\dot{u}_{l_1} u_{l_2}^{(2)}$, $u_{l_1}^{(2)} \dot{u}_{l_2}$, and $u_{l_1}^{(2)} u_{l_2}^{(2)}$, which are written symbolically

$$\int_0^{R_\alpha} r_\alpha^2 dr_\alpha \, j_l \, (b \, r_\alpha) \, v_{l_1}^{\kappa_1}(r_\alpha) \, v_{l_2}^{\kappa_2}(r_\alpha),$$

are evaluated first. Inside the α, l_1, l_2, and l loops, the quantities

$$i^{l_2 - l_1 + l} \, C_{L_2 \, L}^{L_1} \, \mathcal{A}_{L_1}^{\alpha\kappa_1 \, *}(m, \mathbf{k}) \, \mathcal{A}_{L_2}^{\alpha\kappa_2}(n, \mathbf{k} + \mathbf{b})$$

are then evaluated. Because of the general condition on the Gaunt coefficients $C_{L_2 \, L}^{L_1}$, which vanish unless $l_1 + l_2 + l$ is an even integer, $l_2 - l_1 + l$ has also to be even, and $i^{l_2 - l_1 + l} = (-1)^{(l_2 - l_1 + l)/2}$ in the above equation.

The actual organization of the matrix elements $M_{mn}^{(\mathbf{k},\mathbf{b})}$ evaluation is now described.

First, the regular $N_1 \times N_2 \times N_3$ mesh of `num_kpts` points belonging to the Brillouin zone (BZ) is built using the following schematic algorithm

$i_{\mathbf{k}} = 0$
`do` $i = 1, \; N_1$
 `do` $j = 1, \; N_2$
  `do` $k = 1, \; N_3$
   $i_{\mathbf{k}} = i_{\mathbf{k}} + 1$
   $\mathbf{k}\,(i_{\mathbf{k}}) = (i-1)/N_1 \; \mathbf{a}_1^* + (j-1)/N_2 \; \mathbf{a}_2^* + (k-1)/N_3 \; \mathbf{a}_3^*$
  `end do`
 `end do`
`end do`
`num_kpts` $= i_{\mathbf{k}}$

where $\mathbf{a}_\alpha^*$ are the primitive vectors of the reciprocal lattice. For each $\mathbf{k}$–point of this list, the star of `nntot` first–neighbors ($\mathbf{k} + \mathbf{b} + \mathbf{G}_{\mathbf{k}+\mathbf{b}}$) is constructed, where $\mathbf{G}_{\mathbf{k}+\mathbf{b}}$ is the reciprocal lattice vector such that $\mathbf{k} + \mathbf{b}$ belongs to the first BZ. Indexes $i_{\mathbf{k}+\mathbf{b}}$ of these star elements with respect to the original $\mathbf{k}$–points list are available from the file `seedname.nnkp`, obtained in a preliminary run of the program `wannier90`. The matrix elements $M_{mn}^{(\mathbf{k},\mathbf{b})}$ can be finally evaluated.

The resulting information is written in a file `seedname.mmn`, whose first line is a user comment, and the second line the 3 integers: `num_bands`, `num_kpts`, `nntot`. It is followed by `num_kpts`×`nntot` blocks of data organized in sets whose structure is indicated below.

`do` $i_{\mathbf{k}} = 1,$ `num_kpts`
 `do` $i_{\mathbf{b}} = 1,$ `nntot`

$i_{\mathbf{k}}$ $\quad$ $i_{\mathbf{k}+\mathbf{b}}$ $\quad$ $(\mathbf{G}_{\mathbf{k}+\mathbf{b}})_1$ $\quad$ $(\mathbf{G}_{\mathbf{k}+\mathbf{b}})_2$ $\quad$ $(\mathbf{G}_{\mathbf{k}+\mathbf{b}})_3$

  `do` $n = 1,$ `num_bands`
   `do` $m = 1,$ `num_bands`

$\Re\,[M_{mn}^{(\mathbf{k},\mathbf{b})}]$ $\quad$ $\Im\,[M_{mn}^{(\mathbf{k},\mathbf{b})}]$
$\cdots$ $\quad$ $\cdots$

```
   end do
  end do
 end do
end do
```

2. Initial guess of Wannier functions

We consider a trial Wannier orbital $g_n^{(l_c)}(\mathbf{r}_\alpha)$, centered into an atomic sphere α, and restricted to it, consisting of a Gaussian function, modulated by a linear combination of spherical harmonics with a fixed $l = l_c$ value, and $-l_c \leq m_c \leq l_c$

$$g_n^{(l_c)}(\mathbf{r}_\alpha) = g(r_\alpha) \sum_{m_c} c^n_{l_c m_c} Y_{l_c m_c}(\widehat{r}_\alpha).$$

The coefficients $c^n_{l_c m_c}$ might correspond, *e.g.,* to the transformation of a spherical harmonic in a rotated coordinate system, as given generally below in terms of the Euler angles α, β and γ

$$Y_{lm}(\widehat{\mathbf{r}}') = \sum_{m'=-l}^{+l} Y_{lm'}(\widehat{\mathbf{r}})\, D^{(l)}_{m'm}\,(\alpha,\beta,\gamma),$$

and/or to those of the linear combination of spherical harmonics forming the hybrid orbitals of Table 3.2 in the User Guide. We found indeed that a very fast convergence can be achieved, starting from trial WF's displaying both the correct symmetry and the proper orientation with respect to the structure under consideration. We have

$$g(r_\alpha) = \exp\,[-(r_\alpha/\lambda)^2],$$

with λ chosen so that $g(r_\alpha)$ is zero outside the sphere α.
We suppose now that the Gaussian is centered in a sphere β, which is *not* necessarily coinciding with its atom basis representative α. This implies that $\mathbf{r}_\beta = \mathbf{r} - (\boldsymbol{\tau}_\alpha + \mathbf{R})$, where $\mathbf{R}$ is the direct lattice vectors combination, connecting the atom β with its representative α.
Using the notations of the previous subsection for the LAPW coefficients, a Bloch function representation inside the sphere β can be written symbolically

$$\psi_{m\mathbf{k}}(\mathbf{r})|_{S_\beta} = \exp\,(i\,\mathbf{k}\cdot\mathbf{R}) \sum_L i^l \sum_\kappa \mathcal{A}^{\alpha\kappa}_L(m,\mathbf{k})\, v^\kappa_l(r_\alpha)\, Y_L(\widehat{r}_\alpha).$$

This in turn leads to the following form of the matrix $A^{(\mathbf{k})}_{mn}$ of phases

$$\begin{aligned} A^{(\mathbf{k})}_{mn} &= \langle\psi_{m\mathbf{k}}|g_n\rangle = \langle\psi_{m\mathbf{k}}|g_n\rangle_{S_\beta} \\ &= \exp\,(-i\,\mathbf{k}\cdot\mathbf{R})\, i^{-l_c} \sum_{m_c} c^n_{l_c m_c} \sum_\kappa \mathcal{A}^{\alpha\kappa\,*}_{l_c m_c}(m,\mathbf{k}) \int_0^{R_\alpha} r_\alpha^2 dr_\alpha\, g(r_\alpha)\, v^\kappa_{l_c}(r_\alpha). \end{aligned} \qquad (4)$$

Use has been made of spherical harmonics orthonormality. The 3 below radial integrals (for the relevant atom type representative α and the l_c value), corresponding to u_{l_c}, $\dot{u}_{l_c}$, and $u^{(2)}_{l_c}$

$$\int_0^{R_\alpha} r_\alpha^2 dr_\alpha\, g(r_\alpha)\, v^\kappa_{l_c}(r_\alpha),$$

are evaluated separately.

As indicated in the Appendix D of Ref. (2), a symmetric orthonormalization is performed on $A_{mn}^{(\mathbf{k})}$ in a subsequent step, in order to get the basic unitary matrix $U_{mn}^{(\mathbf{k})}$, transforming the Bloch orbitals into Wannier functions.
Information regarding the "projection matrices" $A_{mn}^{(\mathbf{k})}$ is written in file `seedname.amn`, whose first line is a user comment, and the second line is the 3 integers: `num_bands`, `num_kpts`, `num_wann`. It is followed by `num_bands`×`num_wann`×`num_kpts` lines obtained as indicated below

```
do i_k = 1, num_kpts
 do m = 1, num_bands
  do n = 1, num_wann
```

m	n	$i_{\mathbf{k}}$	$\Re\,[A_{mn}^{(\mathbf{k})}]$	$\Im\,[A_{mn}^{(\mathbf{k})}]$
...	...	...	...	...

```
  end do
 end do
end do
```

3. Projections of Wannier functions

It can be of interest to calculate the projection of any Wannier function sitting in the central cell $\mathbf{R} = \mathbf{0}$ onto some given "building blocks". We can write

$$|w_{n\mathbf{0}}\rangle = \sum_{l,\mathbf{R}} |w_{l\mathbf{R}}^{\rm bb}\rangle\langle w_{l\mathbf{R}}^{\rm bb}|w_{n\mathbf{0}}\rangle = \frac{\Omega}{(2\pi)^3}\int_{BZ} d\mathbf{k} \sum_m U_{mn}^{(\mathbf{k})}\,|\psi_{m\mathbf{k}}\rangle.$$

We have also

$$\langle w_{l\mathbf{R}}^{\rm bb}| = \frac{\Omega}{(2\pi)^3}\int_{BZ} d\mathbf{k}'\, e^{i\mathbf{k}'\cdot\mathbf{R}} \sum_j U_{jl}^{*{\rm bb}\,(\mathbf{k}')}\,\langle\psi_{j\mathbf{k}'}|,$$

so that

$$\begin{aligned}
\langle w_{l\mathbf{R}}^{\rm bb}|w_{n\mathbf{0}}\rangle &= \left[\frac{\Omega}{(2\pi)^3}\right]^2 \int\int d\mathbf{k}\, d\mathbf{k}'\, e^{i\mathbf{k}'\cdot\mathbf{R}} \sum_{j,m} U_{jl}^{*{\rm bb}\,(\mathbf{k}')}\, U_{mn}^{(\mathbf{k})}\,\langle\psi_{j\mathbf{k}'}|\psi_{m\mathbf{k}}\rangle \\
&= \frac{\Omega}{(2\pi)^3}\int_{BZ} d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{R}} \sum_m U_{ml}^{*{\rm bb}\,(\mathbf{k})}\, U_{mn}^{(\mathbf{k})} \\
&= \frac{1}{N}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} \sum_m U_{ml}^{*{\rm bb}\,(\mathbf{k})}\, U_{mn}^{(\mathbf{k})}, \qquad (5)
\end{aligned}$$

making use of $\langle\psi_{j\mathbf{k}'}|\psi_{m\mathbf{k}}\rangle = \delta_{jm}\,\delta_{\mathbf{k}'\mathbf{k}}$.

4. (l,m)–projections of Wannier functions

We want to calculate the (l,m)–projection inside the sphere S_β centered on site β of a Wannier function in the central cell at $\mathbf{R} = \mathbf{0}$, *i.e.* the quantity $\underset{lm}{\langle w_{n\mathbf{0}}|w_{n\mathbf{0}}\rangle_{S_\beta}}$. We have

$$|w_{n\mathbf{0}}\rangle = \frac{\Omega}{(2\pi)^3}\int_{BZ} d\mathbf{k} \sum_p U_{pn}^{(\mathbf{k})}\,|\psi_{p\mathbf{k}}\rangle = \frac{1}{N}\sum_{\mathbf{k}}\sum_p U_{pn}^{(\mathbf{k})}\,|\psi_{p\mathbf{k}}\rangle.$$

We can write

$$\langle w_{n\mathbf{0}}|w_{n\mathbf{0}}\rangle_{S_\beta} = \frac{1}{N^2}\sum_{\mathbf{k},\mathbf{k}'}\sum_{p,p'} U^{*(\mathbf{k}')}_{p'n} U^{(\mathbf{k})}_{pn}\ \langle\psi_{p'\mathbf{k}'}|\psi_{p\mathbf{k}}\rangle_{S_\beta}.$$

The braket on the right–hand side of this equation is not a product of Kronecker functions, because the direct space integration is performed on a portion of the full unit cell only.
We suppose now that the sphere at β is not necessarily coinciding with the one of its atom representative α. This implies for the atomic positions that $\boldsymbol{\tau}_\beta = \boldsymbol{\tau}_\alpha + \mathbf{R}_\beta$, where $\mathbf{R}_\beta$ is the direct lattice vectors combination connecting the atom at β with its representative at α. Using the notations of subsection 1 for the LAPW coefficients, a Bloch function representation inside the sphere S_β can be written symbolically

$$\psi_{p\mathbf{k}}(\mathbf{r})|_{S_\beta} = e^{i\mathbf{k}\cdot\mathbf{R}_\beta}\sum_{l,m} i^l \sum_{\kappa} \mathcal{A}^{\alpha\kappa}_{lm}(p,\mathbf{k})\ v^{\kappa}_l(r_\alpha)\ Y_{lm}(\widehat{r}_\alpha).$$

Using the orthogonality of spherical harmonics, we have

$$\begin{aligned}\langle\psi_{p'\mathbf{k}'}|\psi_{p\mathbf{k}}\rangle_{S_\beta} &= e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_\beta}\sum_{l,m}\sum_{\kappa_1,\kappa_2}\mathcal{A}^{\alpha\kappa_1\,*}_{lm}(p',\mathbf{k}')\mathcal{A}^{\alpha\kappa_2}_{lm}(p,\mathbf{k})\int_0^{R_\alpha} r_\alpha^2 dr_\alpha\ v^{\kappa_1}_l(r_\alpha)\ v^{\kappa_2}_l(r_\alpha)\\ &= \sum_{l,m}\{e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_\beta}\sum_{\kappa_1,\kappa_2}\mathcal{A}^{\alpha\kappa_1\,*}_{lm}(p',\mathbf{k}')\mathcal{A}^{\alpha\kappa_2}_{lm}(p,\mathbf{k})\ N_l^{\alpha\,\kappa_1,\kappa_2}\},\end{aligned}$$

where $N_l^{\alpha\,\kappa_1,\kappa_2}$ are the radial integrals

$$N_l^{\alpha\,\kappa_1,\kappa_2} = \int_0^{R_\alpha} r_\alpha^2 dr_\alpha\ v^{\kappa_1}_l(r_\alpha)\ v^{\kappa_2}_l(r_\alpha).$$

Because of the occurence of a (l,m)–summation in $\langle\psi_{p'\mathbf{k}'}|\psi_{p\mathbf{k}}\rangle_{S_\beta}$, we have the result

$$\langle w_{n\mathbf{0}}|w_{n\mathbf{0}}\rangle^{S_\beta}_{lm} = \frac{1}{N^2}\sum_{\mathbf{k},\mathbf{k}'} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_\beta}\sum_{p,p'} U^{*(\mathbf{k}')}_{p'n} U^{(\mathbf{k})}_{pn}\sum_{\kappa_1,\kappa_2}\mathcal{A}^{\alpha\kappa_1\,*}_{lm}(p',\mathbf{k}')\mathcal{A}^{\alpha\kappa_2}_{lm}(p,\mathbf{k})\ N_l^{\alpha\,\kappa_1,\kappa_2}.$$

The total charge associated with $|w_{n\mathbf{0}}\rangle$ in S_β is simply $\sum_{l,m}\langle w_{n\mathbf{0}}|w_{n\mathbf{0}}\rangle^{S_\beta}_{lm}$.

References

[1] M. Posternak, A. Baldereschi, S. Massidda, and N. Marzari, Phys. Rev. B **65**, 184422-1/11 (2002).

[2] N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997).

[3] G. Cangiani, A. Baldereschi, M. Posternak, and H. Krakauer, Phys. Rev. B **69**, 121101(R)–1/4 (2004).

[4] M. Posternak, A. Baldereschi, E.J. Walter, and H. Krakauer, Phys. Rev. B **74**, 125113–1/8 (2006).

[5] F. Lechermann, A. Georges, A. Poteryaev, S. Biermann, M. Posternak, A. Yamasaki, O.K. Andersen, Phys. Rev. B **74**, 125120–1/26 (2006).

[6] H.J.F. Jansen and A.J. Freeman, Phys. Rev. B **30**, 561 (1984).

[7] E.I. Blount, Solid State Physics **13**, 305 (1962).

[8] D. Singh, Phys. Rev. B **43**, 6388 (1991).

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