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REGULAR ARTICLE

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Symmetry-adapted localized Wannier functions suitable for periodic local correlation methods

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Abstract A scheme for the a posteriori symmetrization of a set of localized Wannier functions is presented and illustrated with some examples. The method has been implemented in the periodic code CRYSTAL using the LCAO approach and it is shown that they can be useful in the computational implementation of periodic local correlation methods. The resulting functions feature very accurate symmetry correspondences without a significant loss of the original localization properties.

1 Introduction

Since their initial formulation [1] Wannier functions (WF) have been employed in several theoretical formulations of the electronic structure of solids. They provide a picture alternative to that obtained from the much more commonly used Bloch Functions (BF), as both are suitable to span the same translationally invariant subspaces of the Hilbert space as, for instance, occupied or virtual manifolds, bands of energy states, etc. Nevertheless, at variance with BFs, which behave as waves propagating across the infinite crystal, WFs are quadratically integrable in real space, and display therefore a spatially localized character, which makes them very attractive for many computational applications.

In a recent work [2], it has been shown that WFs can be used in a straightforward extension to periodic systems of the so-called local correlation (LC) methods [3–5], initially developed for efficient many-body calculations of the electronic structure of large molecules. LC techniques use basis sets of highly localized orbitals to span the Hartree–Fock (HF) manifolds, the most common choice being the use of an orthonormal set for the occupied, and of a redundant set of projected atomic orbitals (AO) for the virtual manifolds. Based on the fact that dynamic electron-correlation effects decay as r^{-6}, only a small portion of the whole set of bi-electronic integrals are numerically significant with such a localized basis set, and computational schemes which scale linearly with the size of the system can be devised [6].

Localized WFs (LWF), as provided by the CRYSTAL code [7], are a good choice to form the basis sets for the occupied manifold in periodic LC techniques. This is because they can be very efficiently localized [8], are orthonormal and form sets of translationally equivalent objects. The latter property gives rise to translational equivalences within any set of tensors computed in terms of these like, for instance, the mono- and bi-electronic integrals.

In the same line, additional computational savings can be obtained if other equivalences within the set of LWFs and of projected AOs are exploited, as is the case of point symmetry. As the symmetry properties of AOs in periodic systems and the corresponding tensors have been described in detail in a previous work [9], we will focus our attention on LWF symmetry.

While a clear connection has been shown previously to exist between localization and some symmetry properties of the LWFs [10–13], this strongly depends on the localization criterion considered. For computational purposes, the optimal criterion would be one that minimizes the number of *irreducible* LWFs, from which all the others can be obtained by application of the point group operators, while preserving their locality features, as far as possible.

A suitable basis set of symmetry-adapted localized WFs (SALWF) can be generally characterized as follows. SALWFs are partitioned into subsets (f) belonging to a class b, each transforming into itself under the operators of a point subgroup G_f of the full point group, while the operations

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of the associated left- or right-cosets transform subset f into another equivalent one in the same class.

The choice is generally not unique and two possible cases may be mentioned:

(i) The subsets are chosen so as to minimize the order of G_f;
(ii) G_f is chosen so that the representation of its elements in the SALWF basis set is maximally factorized according to the irreducible representations (IRREP) of G_f.

Functions optimally localized under a given criterion may feature both properties (as is the case when a regular representation is possible), any one of them, or none of them. This is for instance what occurs with $\sigma-\pi$ vs "banana" representation of double bonds: Edminston–Ruedenberg [14] and Pipek-Mezey [15] localizations give orbitals belonging to one-dimensional IRREPs of the bond symmetry group, according to case (ii), while Boys [16] criterion gives the "banana" orbitals which are invariant under a point group of lower order, i.e. case (i). Another mentionable case occurs when in an ionic crystal, like MgO supercell, the valence electron pairs related to the anions are localized according to the Boys criterion [8,17]. In that situation, the localization criterion is just compatible with an sp^3 hybridization but, as the point symmetry of the atom is cubic and not tetrahedral, the set of orbitals is constrained to form a reducible representation of O_h with no privileged orientation. The LWFs fall into a situation not described by the previously mentioned cases. A similar behavior is displayed by "banana" orbitals in triple bonds, or core electrons in a variety of highly symmetric crystals.

For the scope of numerical applications, even in those cases where localization gives rise to definite symmetry properties, accurate symmetry equivalences are only reached under strong numerical conditions in the localization algorithm. This can be in several cases very computationally demanding, and a more efficient short-cut to obtain accurate symmetry equivalences together with a good localization character is therefore desirable.

Due to the previously mentioned difficulties of an a priori prediction of what kind of symmetry behavior will be compatible with good localization properties under efficient criteria, in the present work we adopt an a posteriori strategy based on a "chemical" analysis of the problem, which is made easier by the fact that WFs are expressed as a linear combination of AOs; it represents a compromise between the two criteria previously mentioned. Starting from a set of localized WFs, the main steps of the present scheme are: (1) recognize if classes of symmetry-related single-WF subsets already exist; (2) classify the remaining WFs, if possible, into atomic or bond WFs, according to indices introduced in previous works [17–19]; (3) using the previous information recognize the subsets, the invariant subgroups G_f and the IRREPs to which they belong; (4) generate, and orthonormalize the new SALWFs. The computational scheme is fully automatic in the sense that it does not require any external input parameter.

The effectiveness of the procedure is demonstrated by examples, with reference to four test cases: the CH_3Cl molecule [with C_{3v} symmetry], linear poly-carbon chain $\cdots{\equiv}C{-}C{\equiv}C{-}\cdots$ [treated with $P\,4/m\,2/a\,2/a$ symmetry], lithium bromide with the rocksalt structure $[O_h^5(Fm3m)]$, and crystalline silicon $[O_h^7(Fd3m)]$.

2 Algorithms

The general LWF in cell $\mathcal{G}$, $\phi_{i\mathcal{G}}$, $[i=(1,\ldots,n)]$, is expressed as follows as a linear combination of AOs $\chi_{\alpha\mathcal{M}}$ [2, 8]:

$$\phi_{i\mathcal{G}}(\mathbf{r})=\phi_{i\,0}(\mathbf{r}-\mathbf{R}_{\mathcal{G}})\equiv|\,i\mathcal{G}\,\rangle$$
$$\phi_{i\,0}(\mathbf{r})\equiv|\,i\,0\,\rangle\;=\;\sum_{\alpha,\mathcal{M}} l^{\mathcal{M}}_{\alpha;i}\;\chi_{\alpha\mathcal{M}}(\mathbf{r}) \tag{1}$$

here $\mathbf{R}_{\mathcal{G}}$ is the lattice vector in which the LWF is centered and 0 identifies the reference zero cell. These LWFs have been obtained using a Boys-like scheme [16] modified for periodic systems [8]. Our aim is to transform the n LWFs, $\phi_{i\,0}$, as provided by the localization routine, into an equivalent set of n SALWFs, $\Phi_{[p,f,b]\,0}(\mathbf{r})\equiv|\,[p,f,b]\,0\,\rangle$. As is implicit in their symbolization, each SALWF in the reference cell is characterized by three indices corresponding to different levels of organization as anticipated in the Sect. 1. For the sake of clarity, they will be called "petal" (p), "flower" (f), and "bunch" (b), respectively, with $p\in f\subseteq b$. Each bunch contains $n_f(b)$ flowers, the symmetry equivalent subsets, each comprising $n_p(b)$ "petals" (the SALWFs belonging to that subset). Since this classification is unique, we must have:

$$n\;=\;\sum_b n_p(b)\times n_f(b) \tag{2}$$

Let us denote as $\widehat{V}^S_{\mathcal{N}}\;=\;\{\widehat{S}\mid\mathbf{R}_{\mathcal{N}}+\mathbf{t}_S\}$ the general symmetry operator of the space symmetry group G of the system, and T the subgroup of the pure translations $\widehat{V}^E_{\mathcal{N}}\;=\;\{\widehat{E}\mid\mathbf{R}_{\mathcal{N}}\}$. Each flower f is invariant under a subgroup $G_f\subset G$, and a set of symmetry operators, H_f, (not in general a subgroup of G) can be defined which contains one and only one representative of each left-coset of G obtained upon resolution with respect to the semidirect product between G_f and T. Accordingly, the SALWFs have to fulfill the following properties:

$$\begin{aligned}&\langle\,[p,f,b]\,\mathcal{M}|\,[p',f',b']\,\mathcal{M}'\,\rangle\\&\quad=\delta_{pp'}\,\delta_{ff'}\,\delta_{bb'}\,\delta_{\mathcal{M}\mathcal{M}'}\quad\text{orthonormality}\\&\widehat{V}^S_0\;|\,[p,f,b]\,0\,\rangle\\&\quad=\textstyle\sum_{p'}W^R_{pp'}(f,b)\,|\,[p',f^Q,b]\mathcal{G}^Q(f,b)\,\rangle\quad\text{transformation}\end{aligned} \tag{3}$$

where R and Q refer to operators belonging to G_f and H_f, respectively, that satisfy $\widehat{V}^S_0\;=\;\widehat{V}^Q_0\widehat{V}^R_0$; $W^R_{pp'}(f,b)$ are the matrix elements of R in the basis of the petals of f; f^Q is the flower obtained by applying Q on the petals of f, and $\mathcal{G}^Q(f,b)$ is the resulting translation with respect to the reference cell.

The correspondence with the notation introduced in Ref. [2] (where exploitation of point group symmetry in periodic

LC calculations is discussed) is as follows:

$$\begin{array}{llcl} |[p,f,b]\,\mathcal{M}\,\rangle & \text{(SAWF or petal)} & \longleftrightarrow & \mathbf{i}_{\lambda p,\,\mathcal{M}} \\ |[\{p\},f,b]\,\mathcal{M}\,\rangle & \text{(flower)}, n_p(b) & \longleftrightarrow & \mathbf{S}^{\ell}_{\Lambda,\mathcal{M}} \\ & & & \text{(shell)}, n(\ell) \\ |[\{\{p\},f\},b]\,\mathcal{M}\,\rangle & \text{(bunch)}, n_f(b) & \longleftrightarrow & \aleph_{\Lambda} \\ & & & \text{(set of shells)}, \\ & & & \text{(not given)} \\ & \mathbf{W}^R(f,b);\, \mathcal{G}^Q(f,b);\, f^Q & \longleftrightarrow & \mathbf{W}^{\ell}_V;\, \mathcal{G}^{\Lambda}_V\, \Lambda_V\,. \end{array} \tag{4}$$

Due to Eq. (3), the information that characterizes a representative flower per bunch determines the properties of all flowers in the same bunch. Therefore, the number of symmetry unique SALWFs is given by

$$n_{\text{ind}} \;=\; \sum_b n_p(b) \tag{5}$$

Comparison between Eqs. (2) and (5) shows that the larger the number of flowers per bunch and the smaller the number of their petals, exploitation of symmetry is more efficient.

In order to individualize or to generate the SALWFs, the following four-step procedure, already outlined in Sect. 1 is adopted.

2.1 Classification of the LWFs

A check is first performed if any one of the original LWFs, $|\,j\,0\,\rangle$, can be classified as a SALWF. All point operators $\widehat{V}_0^S$ are in turn applied to $|\,j\,0\,\rangle$; if in all cases the following condition is satisfied,

$$\widehat{V}_0^S\;|\,j\,0\,\rangle \;\approx\; \pm|\,j^Q\,\mathcal{G}^Q\,\rangle \quad , \tag{6}$$

according to Eq. (3), it can be said that the set of all partners $\{\,|\,j^S\,0\,\rangle\,\}$ form a bunch of "single petal" flowers with transformation matrix $W = \pm 1$.[1] In our experience, this favorable case is encountered whenever a covalent σ bond is formed between two atoms. An example is given by the four valence LWFs of diamond, localized along the C–C bond axes, which transform into one another (apart, possibly, from a translation vector) upon application of the $\widehat{V}_0^S$ operators. This kind of LWFs can also appear in circumstances other than the σ bonds. We can mention the π orbitals in double bounds or polarized lone-pairs as in the case of the O atoms in α-quartz.

In a second step, the residual LWFs are grouped in subsets according to their chemical characteristics. The electron density of LWF $|\,i\,0\,\rangle$ is partitioned into atomic populations $Q^i_{A\mathcal{M}}$, assigned to the different atoms A sitting in cell $\mathcal{M}$, according to the Mulliken analysis:

$$Q^i_{A\mathcal{M}} = \sum_{\alpha\in A}\sum_{\beta,\mathcal{N}} l^{\mathcal{M}}_{\alpha;i}\; l^{\mathcal{N}}_{\beta;i}\langle\, \chi_{\alpha\mathcal{M}}\,|\,\chi_{\beta\mathcal{N}}\,\rangle \times \left(\sum_{A,\mathcal{M}} Q^i_{A\mathcal{M}} = 1\right), \tag{7}$$

With this information, one can pre-classify $|\,i\,0\,\rangle$ in one of the following categories:

- Atomic LWF: an atom $A\mathcal{M}$ exists for which $Q^i_{A\mathcal{M}} \geq 0.9$. This category includes "core" LWFs, but also LWFs associated with valence AOs in anions of very ionic systems. "Lone-pair" or "hydrogen-bond" LWFs may also enter this category.
- Bond LWF: two near-by atoms $A\mathcal{M}$, $B\mathcal{N}$ exist such that $Q^i_{A\mathcal{M}} + Q^i_{B\mathcal{N}} \geq 0.9$, and the ratio $Q^i_{A\mathcal{M}}/Q^i_{B\mathcal{N}}$ is comprised between 1, for pure covalent situations, and about 1/4, that, with some dependence on the basis set choice, is the value for highly ionic systems like MgO, LiCl, etc.
- Atypical LWF: $|\,i\,0\,\rangle$ does not enter the previous categories.

A criterion based on a Mulliken analysis is adopted again to subdivide atomic LWFs associated to the same irreducible atom A into shell-subsets (without loss of generality, we will assume A to be in the 0 cell). If the AOs of A are grouped in m_A shells: $s,\ s',\ s'',\ldots,\ p,\ p',\ldots,\ sp,\ldots,\ d,\ldots,$ the population Q^i_{A0} is first partitioned into its λ shell components:

$$Q^i_{A0} = \sum_{\lambda\in A}^{m_A} q^i_\lambda$$

A "shell profile" $\mathbf{q}^i_A \equiv (q^i_1;\, q^i_2;\ldots;\, q^i_{m_A})$ can then be defined (see Table 1). LWFs with an equivalent shell profile, $\mathbf{q}^i_A \approx \mathbf{q}^j_A$, that is for which:

$$\sum_{\lambda\in A}^{m_A} |\; q^i_\lambda - q^j_\lambda\; | \;\leq t_\lambda = 8\times 10^{-2}\ , \tag{8}$$

are assigned to the same shell-subset. This classification, based on an empirical choice of the t_λ threshold, has proved itself sufficiently general and robust.[2]

As concerns bond LWFs, those that belong to the irreducible $A0 - B\mathcal{M}$ bonds, but have not been already classified as single bonds according to Eq. (6), are considered in this step. They are the representatives of double and triple bonds, and will be assigned to the $(A0 - B\mathcal{M})$-subset.

All the atypical LWFs, if any, are finally collected into a separate subset, which will constitute a single flower bunch, and is not further elaborated.

The situation is now as follows. Part of the LWFs have already been classified as SALWFs, either those that satisfy Eq. (6) that only require numerical refinement, or the subset including all the atypical ones. All others are grouped in subsets Σ, either of a "shell" or of a "bond" type, each one comprising n_Σ members.

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[1] Here and in the following the " $\approx$ " sign is used to indicate coincidence within a given tolerance. In the present instance, this is checked by calculating the overlap between the rotated LWF and the $|\,j^S\,\mathcal{G}^S\,\rangle$ one, which must not differ from unity more than a given tolerance, for instance 0.05. The re-adjustment of the SALWFs to make Eq. (3) accurately satisfied is described in what follows.

[2] This value has been tested in the following systems: Diamond, Silicon bulk, MgO, Ice(XI), LiBr ,LiF, LiCl, NaF, carbon polymer, CH3Cl, Urea and Methane.

Table 1 Classification of shell subsets associated to the bromine atom in LiBr, and subsequent transformation into SALWFs. The average shell charges q_λ for the different subsets Σ and their standard deviation (in parentheses) are in atomic units. The spatial spread $L = \langle (r - r_0)^2 \rangle$ is in bohr^2

		Shell profile of subset Σ										
Σ	n_Σ	q_s	$q_{(sp)}$	$q_{(sp)'}$	q_d	$q_{(sp)''}$	L	b	n_f	n_p	Symmetry	L
$1_{(sp)}$	4	−0.013(00)	1.052(00)	−0.038(00)	0.000(00)	0.000(00)	0.029	3	1	1	A_{1g} (s)	0.0384
								4	1	3	T_{1u} (x, y, z)	0.0353
$2_{(sp)'d}$	9	0.000(00)	−0.017(01)	0.470(30)	0.547(30)	0.003(03)	0.218	5	1	1	A_{1g} (s)	0.357
								6	1	3	T_{1u} (x, y, z)	0.373
								7	1	2	E_g (d_E)	0.328
								8	1	3	T_{2g} (d_T)	0.328
$3_{(sp)''}$	4	0.000(00)	0.000(00)	−0.004(30)	0.001(01)	0.980(00)	3.441	9	1	1	A_{1g} (s)	4.181
								10	1	3	T_{1u} (x, y, z)	4.489

2.2 Symmetry characterization of the LWFs

The next step consists in characterizing the Σ subsets from the point of view of their point symmetry invariances and to construct the corresponding IRREPs.

Bond and atomic LWFs are characterized by one and two atomic centers, respectively. Using this information, the subgroup G_f that leaves invariant the corresponding symmetry element (either a center or an axis in real space) is found. The set H_f containing the $n_f - 1$ representatives of the corresponding cosets [see Eq. (3)] is also kept in memory for further use. The IRREPs of G_f are found; for each of them (κ, say, of dimension l_κ), the representative matrices $\mathbf{D}^{(\kappa)}[R]$ are first constructed using the scheme detailed in Ref. [20] and then used to build up the idempotent projector operators $\hat{P}_1^{(\kappa)}$ for the first row and the shift operators $\hat{P}_{\mu,1}^{(\kappa)}$ for all other rows $\mu = 2, \ldots, l_\kappa$ of each IRREP.

2.3 Generation of the SALWFs

For each subset Σ with central or axial point symmetry given by subgroup G_f, the following procedure is now adopted:

- An iterative loop on the LWFs $\phi_{i\,0} \in \Sigma$ is performed:
  (a) By acting in turn with the $\{\hat{P}_1^{(\kappa)}\}$ operators, the first row component of κ is tentatively extracted from $\phi_{i\,0}$:
  $\hat{P}_1^{(\kappa)}\, \phi_{i\,0} = \phi_1^{(\kappa)}(i)$
  (b) In order for $\phi_1^{(\kappa)}(i)$ to be considered the first petal of the first flower of a new bunch, it has to satisfy two conditions: its norm must be larger than a given tolerance t_ϕ, and its independence from all previously obtained basis functions $\phi_1^K(i')$ $(i' < i)$ has been checked through a Gram-Schmidt procedure.
  (c) If both criteria are fulfilled, a new bunch b is defined and the following correspondences are established, after normalization of $\phi_1^{(\kappa)}(i)$:
  $$\mathbf{W}^b[R] = \mathbf{D}^{(\kappa)}[R], \ \big(\forall R \in G_f\big)$$
  $$n_p(b) = l_\kappa$$
  $$|[1,\ 1,\ b]\,0\,\rangle = |\phi_1^{(\kappa)}(1)\rangle$$
  (d) The other $n_p(b) - 1$ petals of the new flower are computed by means of the shift operators:
  $|[\mu,\ 1,\ b]\ 0\ \rangle = \hat{P}_{\mu,1}^{(\kappa)} |[1,\ 1,\ b]\ 0\ \rangle$
  (e) If the Σ subspace is completely spanned, that is if $\sum_{b \in \Sigma} n_p(b) = n_\Sigma$ we can exit the loop; otherwise, steps a to d are repeated on the subsequent $\phi_{j\,0} \in \Sigma$ until this condition is satisfied.
- In case of LWFs that already fulfill Eq. (6) and, therefore, have only need of numerical refinement, they are just projected onto the totally symmetric IRREP of G_f giving rise to a one-petal flower.
- The other $n_f - 1$ flowers of each bunch $b \in \Sigma$, and their corresponding petals, are found by using the symmetry operators $\hat{V}^Q \in H_f$ as follows:

$$\hat{V}^Q\ |[\mu,\ 1,\ b]\ 0\ \rangle = |[\mu,\ q,\ b]\ \mathcal{G}(q)\ \rangle \equiv |\,[p',\, f^Q, b]\mathcal{G}^Q(f, b)\ \rangle, \tag{9}$$

where in the last equality the equivalence with the notation used in Eq. (3) is given.

2.4 Orthonormalization of the SALWFs

Finally, when all atomic and bond subsets have been symmetry adapted, they are orthonormalized. Orthonormalization is performed in two steps.

Using a given net in reciprocal space, the non-orthogonal functions generated in the previously described steps are transformed into BF, orthonormalized using a L'owdin scheme in each **k**-point of the net, and back-transformed into WF. This is accomplished using a straightforward modification of the wannierization scheme reported in Ref. [8].

At this step the resulting SALWFs are orthonormal just under Born–Von Karman cyclic conditions. If necessary, the functions can be corrected to satisfy accurate orthonormalization by integration over the whole real space. The correction is made by applying the first order approximation to the Löwdin transformation onto the whole set of SALWFs,

$$\left(S^{-1/2}\right)_{mn}^{\mathcal{G}} \approx T_{mn}^{\mathcal{G}} = \delta_{mn}\, \delta(\mathbf{R}_{\mathcal{G}} - \mathbf{R}_0) - \frac{1}{2}\Delta_{mn}^{\mathcal{G}}, \tag{10}$$

where $\Delta_{mn}^{\mathcal{G}} = S_{mn}^{\mathcal{G}} - \delta_{mn}\, \delta(\mathbf{R}_{\mathcal{G}} - \mathbf{R}_0)$ and $S_{mn}^{\mathcal{G}}$ is the overlap matrix in the non-orthogonal SALWF basis set. The expression is valid when $\Delta_{mn}^{\mathcal{G}}$ has components small enough, which is, in general, the case when the orthonormalization in reciprocal space has been performed using a suitably dense net.

3 Results and discussion

Let us now illustrate the performance of the method by considering the four test cases mentioned in Sect. 1. All HF calculations were performed using the CRYSTAL code [7], the adopted basis sets being as follows: standard STO3G for bromine, and a modified 6-21G for lithium [21]; standard Pople 6-21G* for silicon (*d* exponent 0.50); standard Pople 6-31G* for carbon (slightly modified for the polymer, where the *d* exponent is 1.1 instead of 0.8); 86-311G for chlorine [21]. The geometry was optimized in all cases with the above basis sets.

The case of lithium bromide lends itself to illustrating the second and third step of the strategy outlined in the previous section. Both LWFs associated with the 1*s* AOs of lithium and bromine have been preliminarily recognized as SALWFs, and classified as bunches 1 and 2, respectively. As expected, due to the very ionic character of the system, all other LWFs are associated with bromine. Table 1 shows their partition into Σ subsets owing to their shell profile. In particular, a subset containing nine LWFs is found, given by an *spd* hybridization of AOs of the third atomic shell; the LWFs are shown in Fig. 1. Following projection (the invariant G_{Br} subgroup is $\mathcal{O}^h$, which coincides with the point group of the crystal), the subset is split into four bunches of symmetry s, p, d_E and d_T respectively (see Fig. 2). The ionic bond between Br and Li is described by four LWFs, which are classified as an atomic set because most of the charge is localized on bromine (0.9707). Their symmetry adaptation yields again an s and a p bunch. Table 1 shows that in all cases the spatial spread, as defined in the caption of the table, is slightly worse for the SALWFs than for the original LWFs. As is apparent from a comparison of Figs. 1 and 2, this is due to the fact that the original LWFs of the subset are centered at different locations about bromine, while the resultant SALWFs must cover the same spatial region being centered in the Br core. However, their atomic character is well preserved (the ionic radius of Br^- is 3.71 Bohr), which is what matters in LC calculations.

The original bond LWFs in silicon already display very good symmetry properties upon the Boys-like localization [8], and are therefore pre-classified as a bunch of four single-petal flowers. In the final step, it is only required to refine them in order to reach sufficient accuracy for further numerical uses. In fact, the overlap between a bond LWF and a rotated one from the same bunch differs from unity by 2.7×10^{-3}; for the corresponding SALWFs, the difference is at least two orders of magnitude smaller. In principle, the same symmetry could be obtained starting from the four 2*sp* LWFs of the silicon core. However, these are classified as atomic functions and therefore, after projection according to the IRREPs of the corresponding invariant T_d group, they are split into a single-petal (A_1) and a three-petal (T_2) flower. Both belong to a two-flower bunch, due to the equivalence of the two silicon atoms in the crystal. It is worth noting that in this case there is practically no loss in localized character upon symmetrization.

An indefinition concerning the symmetry properties, similar to that featured by the internal silicon 2*sp* shell in the previous example, occurs in the case of the triple bond in the Carbon polymer. The Boys-like scheme gives rise to three *banana*-type LWFs with arbitrary orientation. After symmetry adaptation this situation is resolved into two bunches of σ and π type symmetry, respectively. This splitting is well illustrated in the maps of Figs. 3 and 4. Again, symmetrization does not lead to significant changes of the overall localization properties of the set, as the small increase in the spatial spread of the π bonds is partly compensated by the simultaneous spatial contraction of the σ bond.

The $\mathrm{CH_3Cl}$ molecule provides indications similar to those obtained for LiBr. Of the 13 LWFs, 6 are preliminarily recognized as SALWFs, 3 of them constituting single-flower, single-petal bunches (the 1*s* functions on C and Cl, and the C–Cl bond), 3 associated in a three-flower, single-petal bunch (the C–H bonds). All other LWFs, corresponding to the atomic 2*sp* shell and to the three lone pairs, are recognized as atomic functions on Cl. As shown in Table 2, the two subsets are clearly recognized from their shell profile, and split in the C_{3v} environment in three and two bunches, respectively. Note in particular that the first subset contains two flowers of the same symmetry (A_1). On the whole, the number n_{ind} of independent SALWFs is 11, according to Eq. (5). In the present instance, the locality character is hardly affected by symmetrization.

It may be interesting to observe that the outcome of the procedure depends in this case on the Wannierization procedure. If a “full-Boys” procedure [to be presented in a forthcoming publication (C.M. Zicovich-Wilson, in preparation)] is adopted instead of the standard one, *all* LWFs are preliminarily recognizable as single-petal flowers, and n_{ind} is reduced to seven (four single-flower, three three-flower bunches), which is the best that can be achieved.

Finally, a comment is made on the numerical accuracy of the present procedure. From the the formal point of view, no loss in accuracy in LC calculations is to be expected when using SALWFs instead of the original LWFs, irrespective of the way they are classified by symmetry to generate the coset resolution required by the present method (Sect. 2.1). This is because, by construction, SALWFs span always the starting (occupied or valence) manifold. Nevertheless, very slight differences in the correlation energy may occur (at the sixth decimal figure in Hartree, as tested in several systems), mainly due to changes in the numerical approximations used for the estimation of mono- and bi-electronic integrals in the periodic LC scheme [2].

4 Conclusions and prospects

We have presented a method for generating, starting from a set of (generally non-symmetric) LWF, an equivalent set of orthonormal functions which are adapted not only to the

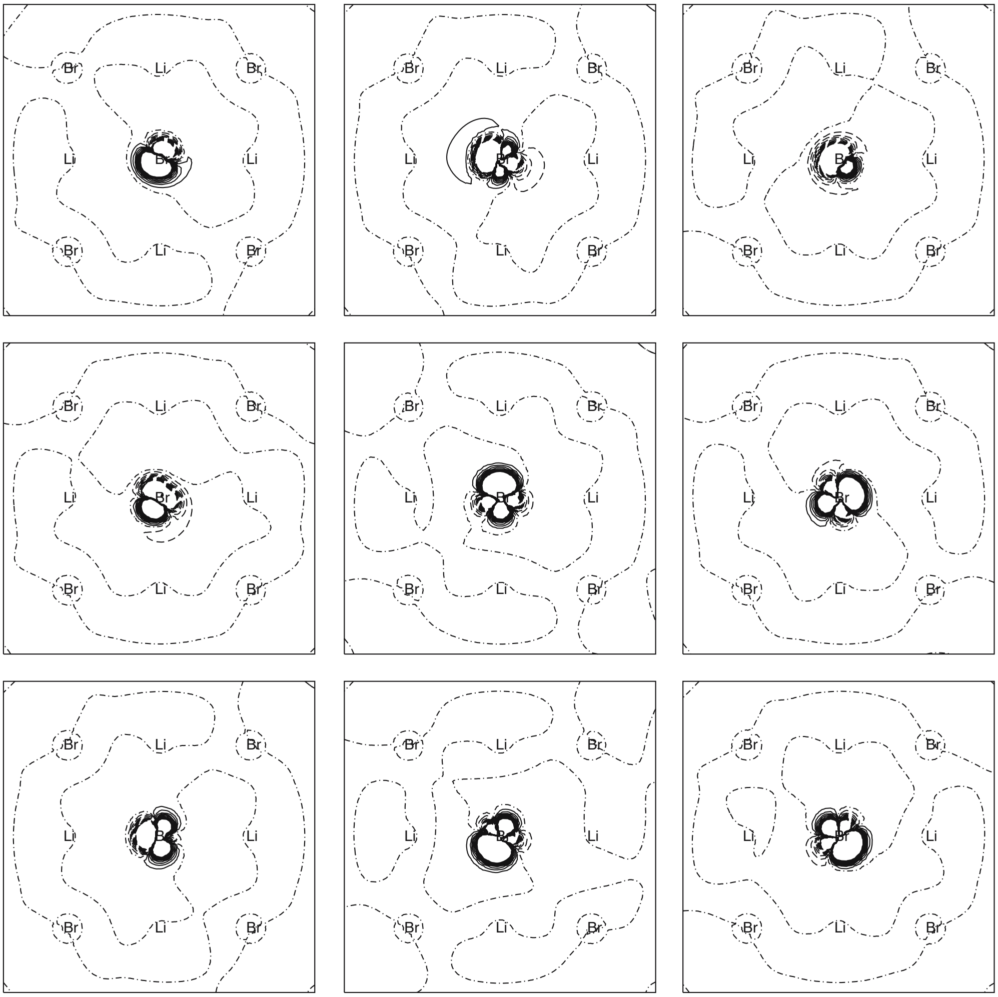

Fig. 1 Maps of the LWFs in the second Σ subset attributed to the bromine atom in lithium bromide, before the symmetrization (see Table 1). The maps are drawn in the y–z plane; iso-amplitude lines differ by 0.01 a.u.; positive, zero, and negative amplitudes are drawn with *continuous*, *dot-dash*, and *dashed lines*, respectively

Table 2 Classification of shell subsets associated to the chlorine atom in CH_3Cl, and subsequent transformation into SALWFs; conventions as in Table 1

		Shell profile of subset Σ										
Σ	n_Σ	q_s	$q_{(sp)}$	$q_{(sp)'}$	$q_{(sp)''}$	$q_{(sp)'''}$	L	b	n_f	n_p	Symmetry	L
$1_{(sp)}$	4	−0.005(00)	1.037(02)	−0.031(01)	0.001(01)	−0.001(00)	0.169	5	1	1	A_1	0.158
								6	1	1	A_1	0.165
								7	1	2	E	0.208
$2_{(sp)'(sp)'''(sp)'''}$	3	0.000(00)	0.031(00)	0.290(00)	0.603(00)	0.141(00)	3.124	8	1	1	A_1	2.769
								9	1	2	E	4.216

translational, but also to the point symmetry of the crystalline structure, while maintaining good locality features. They are called therefore SALWFs (symmetry adapted localized Wannier functions). At variance with other methods reported in the literature [10], the present one is largely based on a chemical analysis of the LWFs, which allows finding coset resolutions of the space group compatible with SALWFs of good locality properties suitable for periodic LC calculations. Despite the somewhat arbitrary character of this kind of analysis, the method performs very well with a variety of molecular and crystalline systems, as shown by the test cases analyzed.

Nevertheless, it is expected that in some particular situations where the chemical character of the LWFs cannot be unambiguously stated, the method can give rise to some slightly erratic behavior. This would be the case for instance when the nature of a given electron pair makes difficult to assess whether the associated LWF corresponds to a polarized covalent, or to an ionic (lone-pair) situation. This is not critical in single point calculations using LC methods, as just

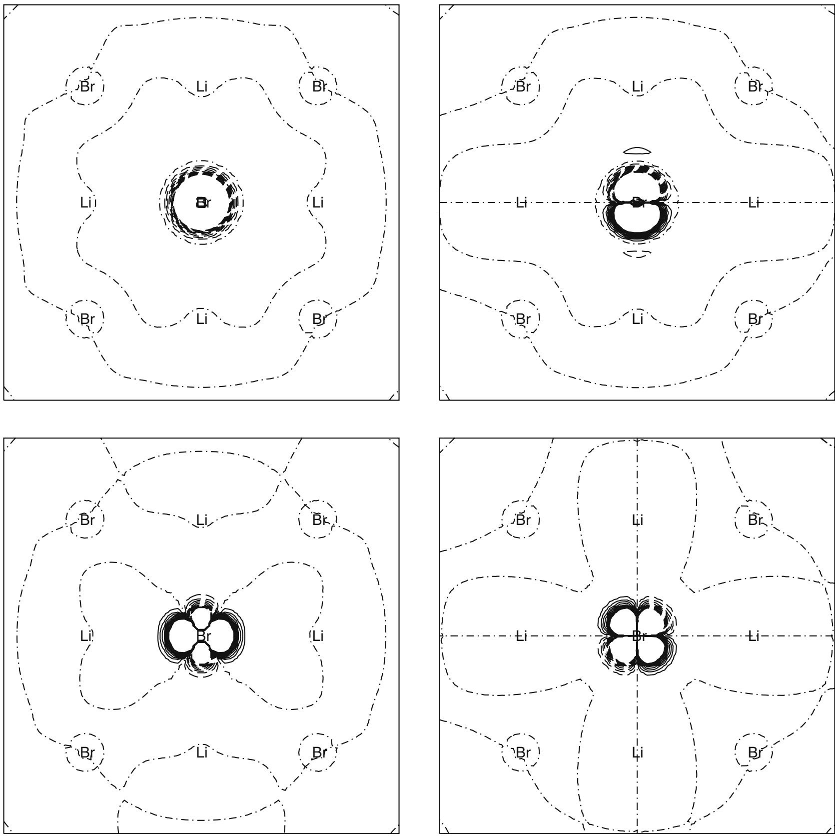

Fig. 2 SALWFs in lithium bromide obtained from symmetrization of those of Fig. 1 (see Table 1). Only one SALWF per symmetry species is drawn: A_{1g} (*top left*); T_{1u} (*top right*); E_g (*bottom left*); T_{2g} (*bottom right*); Conventions as in Fig. 1

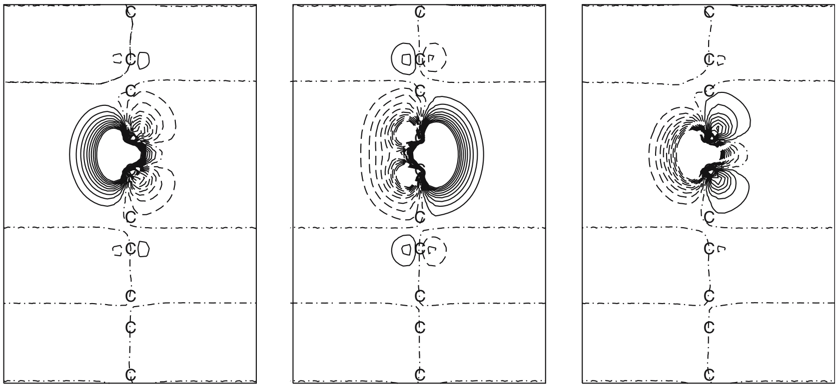

Fig. 3 LWFs associated with the triple bond of the carbon polymer before symmetrization; conventions as in Fig. 1

very small differences in the correlation energy are expected between different choices of SALWF (see discussion at the end of Sect. 3). However, when performing series of calculations, as in the case of geometry optimizations, undesirable discontinuities may appear. A way to overcome this problem is to perform the analysis once along the series and apply the same criteria of classification in all points, in a manner similar to that already used in the CRYSTAL code for the tolerances in the integral calculations [7]. It is worth noting that the method proposed in Ref. [10] is free of this kind of problems as the coset resolution is always based on site symmetries that should be kept along the optimization series, though in general this choice does not guarantee suitable locality properties in the resulting SALWFs.

SALWFs obtained by means of the present scheme appear ideally suited for use in LC calculations for periodic systems.

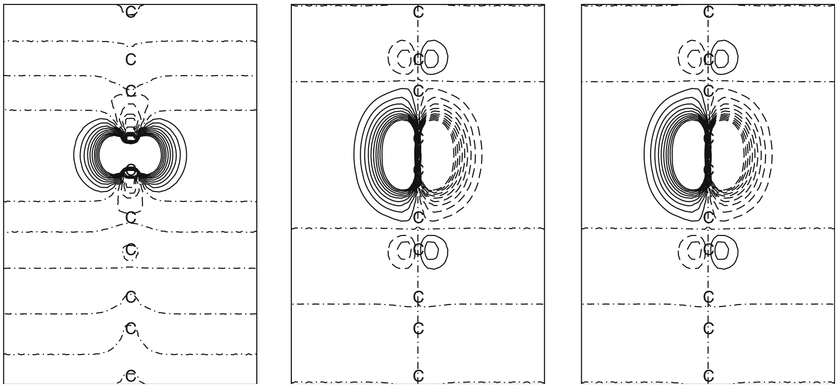

Fig. 4 SALWFs associated with the triple bond of the carbon polymer after symmetrization of those of Fig. 3; conventions as in Fig. 1

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References

1. Wannier GH (1937) Phys Rev 52:191
2. Pisani C, Busso M, Capecchi G, Casassa S, Dovesi R, Maschio L, Zicovich-Wilson CM, Schütz M (2005) J Chem Phys 122:094113
3. Saebø S, Pulay P (1987) J Chem Phys 86:914
4. Pulay P, Saebø S (1986) Theor Chim Acta 69:357
5. Pulay P (1983) Chem Phys Lett 100:151
6. Werner H-J, Knowles PJ, Lindh R, Schütz M et al. MOLPRO, a package of ab initio programs. (info at http://www.molpro.net)
7. Saunders VR, Dovesi R, Roetti C, Orlando R, Zicovich-Wilson CM, Harrison NM, Doll K, Civalleri B, Bush IJ, Ph. D'Arco, Llunell M (2003) CRYSTAL03 User's Manual, Università di Torino, Torino
8. Zicovich-Wilson CM, Dovesi R, Saunders VR (2001) J Chem Phys 115:9708
9. Dovesi R (1986) Int J Quantum Chem 29:1755
10. Smirnov VP, Evarestov RA, Usvyat DE (2002) Int J Quantum Chem 88:642
11. Cloizeaux JD (1964) Phys Rev A 135:685
12. Cloizeaux JD (1964) Phys Rev A 135:698
13. Kohn K (1959) Phys Rev 115:809
14. Edminston C, Ruedenberg K (1963) Rev Mod Phys 35:457
15. Pipek J, Mezey PG (1989) J Chem Phys 90:4916
16. Boys SF (1966) In: Löwdin P-O (ed) Quantum theory of atoms, molecules and the solid state. A tribute to John C. Slater. Academic, New York, p 253
17. Zicovich-Wilson CM, Bert A, Roetti C, Dovesi R, Saunders VR (2002) J Chem Phys 116:1120
18. Fernández-Catá G, Álvarez LJ, Dovesi R, Zicovich-Wilson CM (2004) J Phys Chem B 108:7316
19. Bert A, Llunell M, Dovesi R, Zicovich-Wilson CM (2003) PCCP 5:5319
20. Zicovich-Wilson CM, Dovesi R (1998) Int J Quantum Chem 67:299
21. Prencipe M, Zupan A, Dovesi R, Aprà E, Saunders VR (1995) Phys Rev B 51:3391