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REGULAR ARTICLE

A fundamental connection between symmetry and spatial localization properties of basis sets

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Abstract The problem of the compatibility between symmetry and localization properties of basis sets is addressed here. It is shown that both concepts are closely related from a fundamental point of view through the notion of *invariance extent*. This quantity is a functional that depends on the symmetry group and the basis set choices, and it is shown that all basis sets adapted in a general way to symmetry, i.e. induced from irreducible bases of the subgroups, are stationary points of it. In particular, the usual irreducible bases of the full group display a maximal invariance extent, while those symmetry-adapted basis sets that display a minimal value of this quantity feature in most cases the same symmetry properties as localized functions obtained by means of the Boys scheme. The most relevant conclusions are illustrated by means of simple molecular and periodic examples.

1 Introduction

It is generally assumed in the quantum chemistry community that symmetry-adapted basis sets of wave functions are necessarily delocalized objects. As a matter of fact, this is actually true just when the adaption yields a set that is constituted by bases of the irreducible representations (irreps) of the symmetry group of the system. Wigner's theorem ensures that the eigenfunctions of a totally symmetric operator can be always chosen to be symmetry adapted in that sense and for this reason this kind of basis sets has been widely employed to simplify the resolution of the Schrödinger equation for electronic structure problems. However, there is a wide variety of ways to generate orthonormal sets that display neat symmetry properties, distinct from the characteristic invariance of the irreducible sets. Most of these schemes do not exclude the resulting symmetry-adapted functions to simultaneously feature good spatial localization properties.

Most of the fundamental studies, focused on the localized character of wave functions that also display symmetry relationships, have been chiefly carried out in the context of solid-state physics. This is probably because the irreducible basis sets of the translational group (and eigenvectors of a one-electron periodic Hamiltonian), the Bloch functions, are evenly spread throughout the whole space due to the periodic infinite nature of the systems. Therefore, they lack the typical decay toward infinity of bounded states, a property that is always kept in the case of molecules.

The delocalized character often represents a drawback of the Bloch functions. For many solid-state applications, it appears to be better to consider one-electron localized states whose wave-functions additionally satisfy full consistency with the symmetry of the crystalline system.

This is the case with the pioneering work of Wannier [1], where a set of functions symmetry adapted to the translational symmetry, the so-called Wannier functions, is defined starting from the translationally invariant Bloch functions. It is shown that Wannier and Bloch functions

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Dedicated to the memory of Professor Jean-Pierre Daudey and published as part of the Daudey Memorial Issue.

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radically differ in the way they display symmetry properties: while the latter are invariant, the former feature equivalences to each other under translations. In his work, Wannier showed that such functions additionally envisage some kind of spatial localization (they are quadratically integrable in the coordinate space, which ensures a well-behaved decay in going towards infinity) making them suitable to represent isolated states in solids.

The characteristic equivalence properties of the Wannier functions have been placed into a general formal framework by the works of des Cloizeaux [2, 3]. The original Wannier's idea, based on translational symmetry, is extended to every space group making use of the theory of induced representations (indrep), i.e., considering basis sets of symmetry-adapted Wannier functions built up by applying the group operators to a few generating functions that are bases of the irreps of a point subgroup of the full space group.

A similar approach has been considered in a more recent study by von Boehm and Calais [4]. They propose a variational procedure that allows obtaining a set of localized symmetry-adapted Wannier functions that span the occupied space as a minimum of a functional that yields the total Hartree–Fock energy. More recently, works from Evarestov and Smirnov [5], Smirnov et al. [6] and Smirnov and Usvyat [7] have been devoted to the computation of well-localized symmetry-adapted Wannier functions, based on similar concepts as those proposed by des Cloizeaux. In this case, such functions are computed starting from the SCF-Hartree–Fock canonical Bloch functions.

Symmetry equivalences and spatial localization properties of basis sets have been also exploited so as to make feasible the computational implementation of ab initio wave function methods for crystalline solids. This is, for instance, the case with the accurate estimation of Coulomb and exchange series for the Periodic Hartree–Fock approach [8, 9] and the more recent development of the Local-MP2 method for periodic systems [10].

These precedents suggest that a deep theoretical connection between spatial localization and symmetry equivalence properties should somehow take place. Nonetheless, the issue of the existence of a general concept from which both properties can be derived, allowing to explain and predict possible compatibilities, still remains open.

In this study, we show that the concept of *invariance extent* might play such a theoretical role. This can be quantified by means of a functional, whose value depends on the choice of the orthonormal basis set that spans a given symmetry invariant subspace and it is shown that the usual bases of the the indreps (in accordance with the works of des Cloizeaux) are stationary points.

The present approach is completely general, as it concerns both finite and infinite systems, being based on the fundamental properties of group representations. In addition, it not only explains why the indrep basis sets are compatible with efficient spatial localization of the wave functions, but also predicts the symmetry properties of the localized solutions obtained, for instance, adopting the popular schemes proposed by Foster and Boys [11] or Pipek and Mezey [12]. This fact is illustrated by some simple molecular and periodic examples.

This study is dedicated to Jean-Pierre Dauday, excellent scientist and a better person, who made very important contributions to the investigation of the spatial localization properties of one-electron wave functions.

2 Theoretical framework

2.1 Symmetry-adapted basis sets in general

In accordance with previously mentioned literature [2, 3, 5], the construction of symmetry-adapted basis sets (SABS) suitable for general purposes in the study of the electronic structure of molecules and periodic systems is based on the Theory of Induced Representations. In the following, we shall briefly introduce the most relevant features concerning such a construction.

Let $\mathcal{G}$ be a group and $\mathcal{H}$ one of its subgroups; a left coset partition of the former by the latter is written as

$$\mathcal{G} = S_0\mathcal{H} \oplus S_1\mathcal{H} \oplus S_2\mathcal{H} \oplus \cdots \oplus S_P\mathcal{H}, \tag{1}$$

where $P = |\mathcal{G}|/|\mathcal{H}| - 1$ and it is intended that $S_0 = E$. Once chosen, the coset representatives $\{S_q\}$ in Eq. 1, any element $S \in \mathcal{G}$ has a unique decomposition $S = S_r\ R$ where $R \in \mathcal{H}$. On the other hand, let μ be an irrep of $\mathcal{H}$ and $\{|\mathcal{H}\mu, a\rangle\}_{a=1}^{n_\mu}$ a basis set for it. The application of a general $S \in \mathcal{G}$ to a given component of the basis vectors $|\mathcal{H}\mu, a\rangle$ gives as a result

$$\hat{S}|\mathcal{H}\mu, a\rangle = \hat{S}_r\hat{R}|\mathcal{H}\mu, a\rangle = \sum_{b=1}^{n_\mu} \hat{S}_r|\mathcal{H}\mu, b\rangle D_{ba}^{(\mu)}(R), \tag{2}$$

where $D_{ba}^{(\mu)}(R)$ are the matrix elements of $R \in \mathcal{H}$ for the irrep μ in the given basis set. The set generated by the application of all $S \in \mathcal{G}$ to all components of the basis set of μ spans an invariant subspace that is called the representation induced by μ of $\mathcal{H}$ in $\mathcal{G}$ or, symbolically, the $(\mathcal{H}\mu) \uparrow \mathcal{G}$ *indrep*. From Eq. 2 it turns out that a suitable basis set for the indrep is given by

$$\{\hat{S}_r|\mathcal{H}\mu, a\rangle \equiv |\mathcal{H}\mu, ar\rangle\}, \quad a = 1, \ldots, n_\mu, \quad r = 0, \ldots, P. \tag{3}$$

Any invariant space Σ can be decomposed as a direct sum of indreps and the union of the corresponding basis sets is also a basis set of Σ. With the addition of the orthonormality condition, this is what hereafter will be referred to as an SABS, $\{|\mathcal{H}_p\mu i, ar\rangle\}$. Five indexes are employed to label each component of the set, with μ, a and r having the same meaning as in Eq. 3, while $\mathcal{H}_p$, and i labeling the subgroup that induces the given indrep and the time indrep $(\mathcal{H}_p\mu) \uparrow \mathcal{G}$ appears in the Σ decomposition, respectively. At variance with the usual decomposition into irreps of the full group, the decomposition into indreps is not unique, but in what follows it will be shown that there is a straightforward criterion that allows us to know a priori the choice that allows the set to display optimal spatial localization properties.

The SABSs display invariance under the elements of the inducing subgroup $\mathcal{H}_p$ and equivalences to each other under the left-coset representatives S_r. On the other hand, it is worthwhile noting that the usual bases of the irreps of $\mathcal{G}$ widely adopted in quantum mechanics are just the special case in which $\mathcal{H}_p = \mathcal{G}$. In the same line, the SABSs obtained by considering the other improper subgroup $\mathcal{H}_p = \mathcal{C}_1 \equiv \{E\}$ contained into every symmetry group brings about a purely equivalent basis set of the regular representation.

Interestingly, as just one row of an irrep of $\mathcal{H}_p$ is required to generate the whole irreducible basis set by means of the shift projectors, then a single vector is sufficient to generate the full SABS of an indrep. In other words, all the information of the SABS of a given indrep is provided by the knowledge of a single generating vector.

As far as we know, this is the most general definition of SABS proposed in the context of the electronic structure studies.

2.2 Spatial localization from the symmetry viewpoint and its connection with invariance

Let $\mathcal{G}$ be a group that has a realization constituted by those transformations in R^3 that leave invariant the distance between any two points. This definition includes any operation that mixes proper or improper rotations with translations in real space. Accordingly, it is possible to perform a partition of the space into a maximal number N of asymmetric regions $\{\rho_p\}_{p=1}^{N}$ (with $N \leq |\mathcal{G}|$) such that one of them could generate the whole set by applying symmetry transformations $\mathbf{S}\rho_p = \rho_{p'}$, $S \in \mathcal{G}$ and $\mathbf{S} \in R^3 \times R^3$ denotes the matrix form of S.

Another realization of $\mathcal{G}$ connected with the previous one is constituted by transformations of functions $f : R^3 \rightarrow C$. If $S \in \mathcal{G}$ then $\hat{S}f(\mathbf{r}) = f(\mathbf{S}^{-1}\mathbf{r})$. Exploiting the equivalence properties imposed by $\mathcal{G}$ on $\{\rho_p\}$, it is possible to define a *spatial localization* of those functions by devising some kind of assignation of them to the asymmetric regions ρ_p. The assignation must satisfy the condition of being consistent with the symmetry equivalences between the asymmetric regions and may not necessarily be discrete, as it is the partition performed on R^3. A straightforward way to do this is by associating a number $\alpha(f, \rho_p) \in [0, 1]$ to each function f in each asymmetric region ρ_p, fulfilling the consistency condition: $\alpha(f, \rho_p) = \alpha(\hat{S}f, \mathbf{S}\rho_p), \forall S \in \mathcal{G}$.

A suitable assignation can be for the instance given by the normalized integration of the function distribution into a given asymmetric region ρ_p,

$$\alpha(f, \rho_p) = \frac{\int_{\rho_p} \mathrm{d}\mathbf{r} f(\mathbf{r})^* f(\mathbf{r})}{\int_{R^3} \mathrm{d}\mathbf{r} f(\mathbf{r})^* f(\mathbf{r})}; \tag{4}$$

therefore, one can say that, for a given f, the ρ_p with maximum α is the place where the function is mainly localized. The degree of localization can be also computed by considering different functionals that quantify the spread of the distribution of the quantity α along the set of regions $\{\rho_p\}$.

Independent of the way chosen to make the assignation $\alpha(f,\rho_p)$, it turns out that if f is invariant under all operations of $\mathcal{G}$, the consistency condition forces that $\alpha(f, \rho_s) = \alpha(f, \rho_r), \forall \rho_s, \rho_r$, as always there is an operation $T \in \mathcal{G}$ so that $\mathbf{T}\rho_s = \rho_r$ due to the equivalence properties initially imposed on the partition $\{\rho_p\}$. Accordingly, we shall say that the function is delocalized as it is not possible to assign it to any particular region.

A general conclusion arises that symmetry invariance acts as a constraint imposed on a given function that forces it to be spatially delocalized. This is apparent when considering a function that belongs to the totally symmetric irrep of any symmetry group. Hence, it must be in all cases delocalized in space, as for instance:

- in periodic systems, the asymmetric regions are the unit cells and a totally symmetric function under the translational group (Bloch function belonging to $\mathbf{k} = \mathbf{0}$ in reciprocal space) is evenly distributed over the whole space;
- in any point group, the asymmetric regions are angularly delimited in space, and the argument provided in the previous item is also valid here, considering angular localization.

Actually, any function that is basis of a one-dimensional irrep has maximal invariance imposed and is constrained to be fully delocalized.

In those cases where the group allows a partition in $|\mathcal{G}|$ asymmetric regions, the purely equivalent SABS of the regular representation (Sect. 2.1) may satisfy a full localization, as the only operation that keeps the component vectors invariant is trivially the identity. This means that the symmetry properties of such a basis set (all elements can be generated from a single one by the action of the group operations) allow full spatial localization, as invariance is minimally imposed.

The comparison between such extreme situations permits us to guess that a function belonging to a general representation will display maximal localization to the extent allowed by the invariance imposed by the symmetry group on it. In what follows, we define a quantity, the *invariance extent*, which can be taken as an index of the "amount of invariance" imposed on any vector by a given symmetry group. While the various definitions of spatial localization depend on whether the group has, or does not have, spatial realizations, the invariance extent is much more general and its definition only requires the existence of linear representations for $\mathcal{G}$.

As a matter of fact, according to the general concept that a "formal localization" is always present when symmetry equivalences are established in a set [13], it is not actually necessary to consider only functions defined in the coordinate space R^3 in order to find the symmetry properties of localized basis sets. It is sufficient to look at general reference sets, $A = \{q_i\}$, into which full symmetry equivalences have been defined, $S\ q_i = q_j$, and to establish an assignation $\alpha(|v\rangle, q_i) \in [0,1]$ between vectors $|v\rangle$ of a given representation and the elements of the set. Each q_i here plays the role of a generalized "place" to which the vectors are to be assigned. The only constraint imposed on the assignation is that consistency of the symmetry properties between the group representation and the reference set has to be satisfied, $\alpha(\hat{S}|v\rangle, Sq_i) = \alpha(|v\rangle, q_i)$.

An interesting example arises when considering a reference set A constituted by the elements themselves of the symmetry group $\mathcal{G}$ and equivalences between elements are given through the well-known conjugacy relationship $\bar{R} = SRS^{-1}$. Equivalent elements, therefore, belong to the same conjugacy class and the assignation of any normalized vector $|v\rangle$ to $R \in \mathcal{G}$ as element of the reference set is given by $\alpha(|v\rangle, R) = \left|\langle v|\hat{R}|v\rangle\right|^2$. In what follows, we shall see that such a particular assignation is of great relevance in the present analysis.

2.3 The invariance extent

Formally, the degree of invariance of a normalized vector $|v\rangle$ belonging to a given representation of $\mathcal{G}$, namely Γ, with respect to the action of an operator $S \in \mathcal{G}$ can be given by the integral $|\langle v|\hat{S}|v\rangle|^2$. This quantity represents in terms of positive real numbers within the [0,1] range the extent the starting vector is recovered upon applying $\hat{S}$ on it, as

$$\hat{S}|v\rangle = |v\rangle\langle v|\hat{S}|v\rangle + |w\rangle, \quad \langle v|w\rangle = 0, \tag{5}$$

and is identical to the $\alpha(|v\rangle, S)$ defined above. For the group as a whole, one should sum the contributions from each operator, which gives rise to the following definition of *invariance extent* of a normalized vector $|v\rangle$ over $\mathcal{G}$,

$$I(\mathcal{G}, v) = \sum_{S\in\mathcal{G}} \left|\langle v|\hat{S}|v\rangle\right|^2. \tag{6}$$

The full meaning of $I(\mathcal{G}, v)$ arises by considering the particular case in which a normalized $|v\rangle$ is kept invariant by just a subset of the operations of $\mathcal{G}$. It turns out that a complete subset of operations under which a given vector is kept invariant must constitute a subgroup $\mathcal{H} \subseteq \mathcal{G}$ and therefore $|v\rangle$ will be the basis of a one-dimensional irrep μ of $\mathcal{H}$. Imposing the orthornormality, the set $\{\hat{S}_r|v\rangle\}$ has the same form as defined in Eq. 3 (SABS of indrep $(\mathcal{H}\mu) \uparrow \mathcal{G}$) and it is easy to verify that $I(\mathcal{G}, v) = |\mathcal{H}|$. This is because the only non-null terms of the sum in Eq. 6, those associated with $S \in \mathcal{H}$, are all unity. In other words, the invariance extent is the number of operators that leave $|v\rangle$ invariant.

If the vector belongs to the basis of an irrep μ of $\mathcal{H}$, of dimension n_μ, not necessarily 1, Eq. 6 applied to the generating vector $|v\rangle \equiv |\mathcal{H}\mu, a0\rangle$ reads

$$\begin{aligned} I(\mathcal{G}, v) &= \sum_{S\in\mathcal{G}} |\langle\mathcal{H}\mu, a0|\hat{S}|\mathcal{H}\mu, a0\rangle|^2 \\ &= \sum_{r=0}^{P}\sum_{R\in\mathcal{H}} |\langle\mathcal{H}\mu, a0|\hat{S}_r\hat{R}|\mathcal{H}\mu, a0\rangle|^2 \\ &= \sum_{R\in\mathcal{H}} \langle\mathcal{H}\mu, a0|\hat{R}|\mathcal{H}\mu, a0\rangle^* \langle\mathcal{H}\mu, a0|\hat{R}|\mathcal{H}\mu, a0\rangle \\ &= \frac{|\mathcal{H}|}{n_\mu}, \end{aligned} \tag{7}$$

where in the second equality the left-coset partition (Eq. 1) of $\mathcal{G}$ by $\mathcal{H}$ is exploited. In the third equality, all terms for $r \neq 0$ vanish because of the orthonormality of the SABS. In the fourth one, the first orthogonality theorem of the matrix elements of the irreps is exploited as

$$\langle\mathcal{H}\mu, a0|\hat{R}|\mathcal{H}\mu, a0\rangle = D_{aa}^{(\mu)}(R).$$

This result is in accordance with our initial interpretation of $I(\mathcal{G}, v)$, since if $|v\rangle$ belongs to a basis set of a multidimensional irrep, the invariance provided by operation $R \in \mathcal{H}$ is shared with the remaining rows of the irreducible basis set and its corresponding fraction would be $1/n_\mu$. By considering these particular cases, the invariance extent of $|v\rangle$ over $\mathcal{G}, I(\mathcal{G}, v)$, acquires a more precise meaning: it is *the effective number of those symmetry operators that impose invariance on a given vector*. In what follows, it will be assumed that this concept can be extended to any basis set of any representation of $\mathcal{G}$.

2.4 Global invariance extent of a basis set

The previous definition of the invariance extent of a vector, Eq. 6, is now generalized to the *global invariance extent* of a basis set, $\bar{I}(\mathcal{G}, \{v_i\}_{i=1}^L)$, defined as the average of the individual extents,

$$\bar{I}\left(\mathcal{G}, \{v_i\}_{i=1}^L\right) = \frac{1}{L}\sum_{i=1}^{L} I(\mathcal{G}, v_i). \tag{8}$$

According to the previous considerations, one expects that a maximally localized basis set $\{v_i^0\}$ should be minimally constrained by the invariance and therefore display a minimal value of $\bar{I}(\mathcal{G}, \{v_i^0\}_{i=1}^L)$.

The necessary condition for a point to be a minimum of a given functional is that its gradient must vanish at that point. The functional $\bar{I}(\mathcal{G}, \{v_i\})$ depends on unitary transformations of the basis set that can be written as

$$\hat{U}(\varepsilon_{jl}) = \exp\left[\frac{1}{2}\sum_{j<l}\varepsilon_{jl}\hat{E}_{jl}\right], \tag{9}$$

where the set of $\hat{E}_{jl} = |v_j\rangle\langle v_l| - |v_l\rangle\langle v_j|$ span the algebra of the generators of the unitary group and the $\{\varepsilon_{jl}\}_{j<l}$ are the variational parameters. The stationary condition is thus given by

$$\begin{aligned}\frac{\partial\bar{I}(\mathcal{G}, \{v_i\}_{i=1}^{L})}{\partial\varepsilon_{jl}} &= \frac{1}{L}\Re\sum_{i=1}^{L}\sum_{S\in\mathcal{G}}\langle v_i|[\hat{E}_{jl}, \hat{S}]|v_i\rangle\langle v_i|\hat{S}|v_i\rangle^{*}\\ &= \frac{1}{L}\Re\sum_{S\in\mathcal{G}}\left(\langle v_l|\hat{S}|v_j\rangle + \langle v_j|\hat{S}|v_l\rangle\right)\\ &\quad\times\left(\langle v_j|\hat{S}|v_j\rangle - \langle v_l|\hat{S}|v_l\rangle\right)^{*} = 0.\end{aligned} \tag{10}$$

Interestingly, it is shown in the Appendix that the SABSs provided in Sect. 2.1 are stationary points of the functional $\bar{I}$, i.e,. all the gradient elements of Eq. 10 do vanish simultaneously in that case.

In the general problem of finding the symmetry properties of localized basis sets for an arbitrary representation, Γ, one requires to find a decomposition in SABSs that gives rise to the minimal value of the global invariance extent (MGIE). In terms of SABSs, this can be easily calculated from Eqs. 6 to 8 as

$$\bar{I}(\mathcal{G}, \{\mathcal{H}_p\mu i, ar\}) = \frac{1}{L^{(\Gamma)}}\sum_{p=1}^{N_{sg}}\sum_{\mu=1}^{N_p}L^{(\mathcal{H}_p\mu)}\xi^{(\mathcal{H}_p\mu)}\frac{|\mathcal{H}_p|}{n_\mu}, \tag{11}$$

where the first and second sums in the rhs are restricted to the number $N_{s}g$ of subgroups involved in the decomposition and N_p of irreps of $\mathcal{H}_p$; the $\xi^{(\mathcal{H}_p\mu)}$ are the times the indrep $(\mathcal{H}_p\mu)\uparrow\mathcal{G}$ appears in the decomposition of Γ, $L^{(\mathcal{H}_p\mu)}$ and $L^{(\Gamma)} = \sum_{p=1}^{N_{sg}}\sum_{\mu}^{N_p}L^{(\mathcal{H}_p\mu)}\xi^{(\mathcal{H}_p\mu)}$ are the dimensions of the corresponding indreps and of Γ, respectively. As the indrep dimension is given by $L^{(\mathcal{H}_p\mu)} = |\mathcal{G}|\times n_\mu/|\mathcal{H}_p|$ (Eq. 3), Eq. 11 becomes

$$\bar{I}(\mathcal{G}, \{\mathcal{H}_p\mu i, ar\}) = \frac{1}{L^{(\Gamma)}}\sum_{p=1}^{N_{sg}}\sum_{\mu=1}^{N_p}|\mathcal{G}|\xi^{(\mathcal{H}_p\mu)} = \frac{|\mathcal{G}|}{L^{(\Gamma)}}N_I, \tag{12}$$

where $N_I = \sum_p\sum_\mu L^{(\mathcal{H}_p\mu)}\xi^{(\mathcal{H}_p\mu)}$ is the total number of indreps that participate in the decomposition of Γ. The minimum of the global invariance extent in terms of SABS is reached by a basis set, the components of which belong to a minimal number of indreps or, in other words, exhibit the minimal number of generators (as each generator has the necessary information to build up the full SABS of each indrep, see Sect. 2.2). These kind of basis sets will be referred to as *minimally invariant* SABS (MISABS).

3 Illustrating examples

The main results concerning the symmetry properties of localized orbitals, formally introduced in the previous sections, are illustrated by some simple examples, namely, two molecules (water and urea) and one periodic system (1D polyacetylene).

3.1 Structure and symmetry

Both water, H_2O, and urea, $CO(NH_2)_2$, exhibit the symmetry property of $\mathcal{C}_{2v}$ point group. The atomic structures of both molecules are depicted in Fig. 1a, b, respectively. The polyacetylene polymer, the structure of which is shown in Fig. 1c, envisages *P*2/*m* rod group symmetry, the corresponding point group of which $\mathcal{C}_{2h}$ is isomorphic with $\mathcal{C}_{2v}$. The character table of these point groups is reported in the first four rows of Table 1.

Their *proper* subgroups are three: $\mathcal{H}_1 = \{E, X\}$, $\mathcal{H}_2 = \{E, \sigma\}$ and $\mathcal{H}_3 = \{E, C_2\}$ (see Table 1 for the convention adopted in the notation of the symmetry elements). Furthermore the two *improper* subgroups are labeled as $\mathcal{H}_0 = \{E\}$ and $\mathcal{H}_4 \equiv \mathcal{C}_{2v}[\equiv \mathcal{C}_{2h}]$.

Each one of these five subgroups can be employed to perform a left-coset partition of the full point group $\mathcal{G} = (\mathcal{C}_{2v} \equiv \mathcal{C}_{2h})$ (Eq. 1); the sets of representative elements have been chosen to be $\{E, C_2, X, \sigma\}$, $\{E, X\}$ and $\{E\}$ for $\mathcal{G}/\mathcal{H}_0$, $\mathcal{G}/\mathcal{H}_3$ and $\mathcal{G}/\mathcal{H}_4$, respectively, and the same set $\{E, C_2\}$ for $\mathcal{G}/\mathcal{H}_2$ and $\mathcal{G}/\mathcal{H}_3$.

The total number of distinct indreps one can construct for this group is 11. The characters for the seven indreps obtained from the irreps of the three proper subgroups and $\mathcal{H}_0$ are documented in Table 1. The four indreps induced from $\mathcal{H}_4$ trivially coincide with the four irreps of $\mathcal{G}$. On inspection of Table 1, it is seen that the six indreps generated from the proper subgroups are all reducible and can be written as direct sums of two irreps of $\mathcal{G}$. The indrep $(\mathcal{H}_1\Gamma_1)\uparrow\mathcal{C}_{2v}$, for instance, is $A_1 \oplus B_1$; $(\mathcal{H}_2\Gamma_1)\uparrow\mathcal{C}_{2v} = A_1 \oplus B_2$ and so on. Indrep $(\mathcal{H}_0\Gamma_1)\uparrow\mathcal{G}$ is actually the regular representation of $\mathcal{G}$ into which all the irreps are once contained. For the sake of brevity, hereafter, we shall adopt the shorthand notation $(\mathcal{H}_p\Gamma_\mu)$ for $(\mathcal{H}_p\Gamma_\mu)\uparrow\mathcal{G}$.

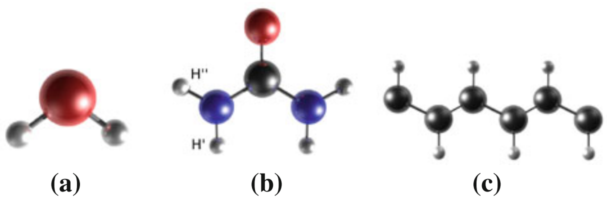


Fig. 1 Schematic representation of the structure of **a** the water molecule, **b** the urea molecule and **c** the polyacetylene polymer

Table 1 Character table of the point group of symmetry $\mathcal{G}(\mathcal{G} = C_{2v}[C_{2h}]$

$\mathcal{G}$	E	C_2	X	σ
$A_1[A_g]$	1	1	1	1
$A_2[A_u]$	1	1	−1	−1
$B_1[B_g]$	1	−1	1	−1
$B_2[B_u]$	1	−1	−1	1
$(\mathcal{H}_1\Gamma_1) \uparrow \mathcal{G}$	2	0	2	0
$(\mathcal{H}_1\Gamma_2) \uparrow \mathcal{G}$	2	0	−2	0
$(\mathcal{H}_2\Gamma_1) \uparrow \mathcal{G}$	2	0	0	2
$(\mathcal{H}_2\Gamma_2) \uparrow \mathcal{G}$	2	0	0	−2
$(\mathcal{H}_3\Gamma_1) \uparrow \mathcal{G}$	2	2	0	0
$(\mathcal{H}_3\Gamma_2) \uparrow \mathcal{G}$	2	−2	0	0
$(\mathcal{H}_0\Gamma_1) \uparrow \mathcal{G}$	4	0	0	0

For C_{2v}, $X = \sigma_{xz}$ and $\sigma = \sigma_{yz}$, while for C_{2h}, $X = i$ and $\sigma = \sigma_{xy}$. This table reports the four irreps of the group along with the corresponding seven indreps associated with the subgroups $\mathcal{H}_p, p = 0, \ldots, 3$. Γ_1 and Γ_2 label the two irreps of each of the subgroups $\mathcal{H}_p, p = 1, 2, 3$.

3.2 MISABS and their localization properties

3.2.1 Water and urea

The present analysis is restricted to the valence subspaces $\Gamma^{(\mathrm{val})}$ that are reducible representations of $\mathcal{G}$. As both molecules display the same C_{2v} symmetry, the main difference between them from the group-theoretical viewpoint is the composition of $\Gamma^{(\mathrm{val})}$ in terms of irreps. According to Wigner's theorem, those irreps describe the symmetry properties of the canonical orbitals (CO).

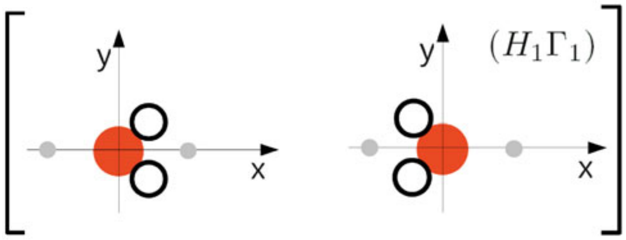
The aim here is to find in each case a SABS for $\Gamma^{(\mathrm{val})}$, compatible with maximal spatial localization, which is shown to be accomplished by adopting the MISABS introduced in Sect. 2.4.

In the case of water, four different solutions in terms of SABSs can be employed to fill $\Gamma^{(\mathrm{val})}$. Two of them are considered, together with the usual irrep decomposition (CO).

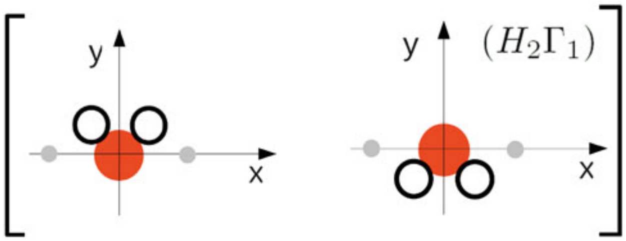
$$\begin{aligned}\Gamma^{(\mathrm{val})}_{\mathrm{H_2O}} &= 2A_1 \oplus B_1 \oplus B_2 && \text{(CO)}\\ &= (\mathcal{H}_1\Gamma_1) \oplus (\mathcal{H}_2\Gamma_1) && \text{(i)}\\ &= (\mathcal{H}_1\Gamma_1) \oplus (\mathcal{H}_4A_1) \oplus (\mathcal{H}_4B_2). && \text{(ii)}\end{aligned}$$

Solution (i) corresponds to the MISABS with $\bar{I} = 4/4 \times 2 = 2$, according to Eq. 12. The other solution, (ii), displays a larger $\bar{I} = 4/4 \times 3 = 3$ and is considered for comparison.

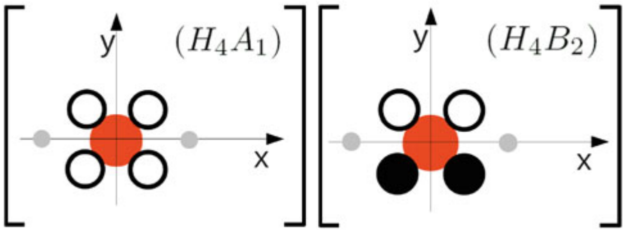
The symmetry properties of the basis functions that enter these two selected solutions are graphically schematized in Fig. 2. The water molecule is depicted along the xy plane. The big red and the two small gray circles represent the oxygen and the two hydrogen atoms (projected onto the plane of the paper), respectively. One must recall that the z direction corresponds to the principal axis of the C_{2v} group and that the three atoms lie on the xz plane now perpendicular to the paper.



(a) (i-ii) OH *bond* **(b)** (i-ii) OH *bond*



(c) (i) *lone pair* **(d)** (i) *lone pair*



(e) (ii) *lone pair* **(f)** (ii) *lone pair*

Fig. 2 Pictorial representation of the symmetry properties of the two selected solutions for water (i) (**a**–**d**) and (ii) (**a**, **b**, **e**, **f**) in terms of SABS. The two basis functions (**a**, **b**) proper of the $(\mathcal{H}_1\Gamma_1)$ indrep, the two basis functions (**c**, **d**) proper of the $(\mathcal{H}_2\Gamma_1)$ indrep, and the two basis functions proper of the two indreps $(\mathcal{H}_4A_1)$ (**e**) and $(\mathcal{H}_4B_2)$ (**f**) are reported

The symmetry features of these functions can be described by highlighting points in general positions of the space. Here, for instance, black circles have been adopted to label those points. The circles can be either empty or full, depending on their sign. Employing this convention, every possible action of any symmetry operation can be graphically identified permitting to schematically characterize each component of the SABS.

Concerning solution (i), the minimally invariant one, the two basis functions of indrep $(\mathcal{H}_1\Gamma_1)$ are invariant under σ_{xz} and can be generated from each other by applying the corresponding coset representative element: C_2. Accordingly, they are to be ascribed to the two OH *bond* orbitals. Analogously, the two basis functions of indrep $(\mathcal{H}_2\Gamma_1)$ are invariant under σ_{yz} and are symmetry related by C_2. This allows to associate them with the two *lone pair* of orbitals centered on the oxygen atom. On the other hand, solution (ii) is made up of three indreps; the first one is the same as in the previous solution, while the last two coincide with the A_1 and B_2 irreps of $\mathcal{C}_{2v}$.

In accordance with the formal analysis provided in Sect. 2, the explicit calculation of localized orbitals, using any scheme, brings about a basis set, the symmetry properties of which are those of solution (i), the MISABS of $\Gamma^{(\mathrm{val})}$. In addition, it is shown that such a solution has an apparent connection with the intuitive chemical analysis of the electronic structure based on the Lewis theory.

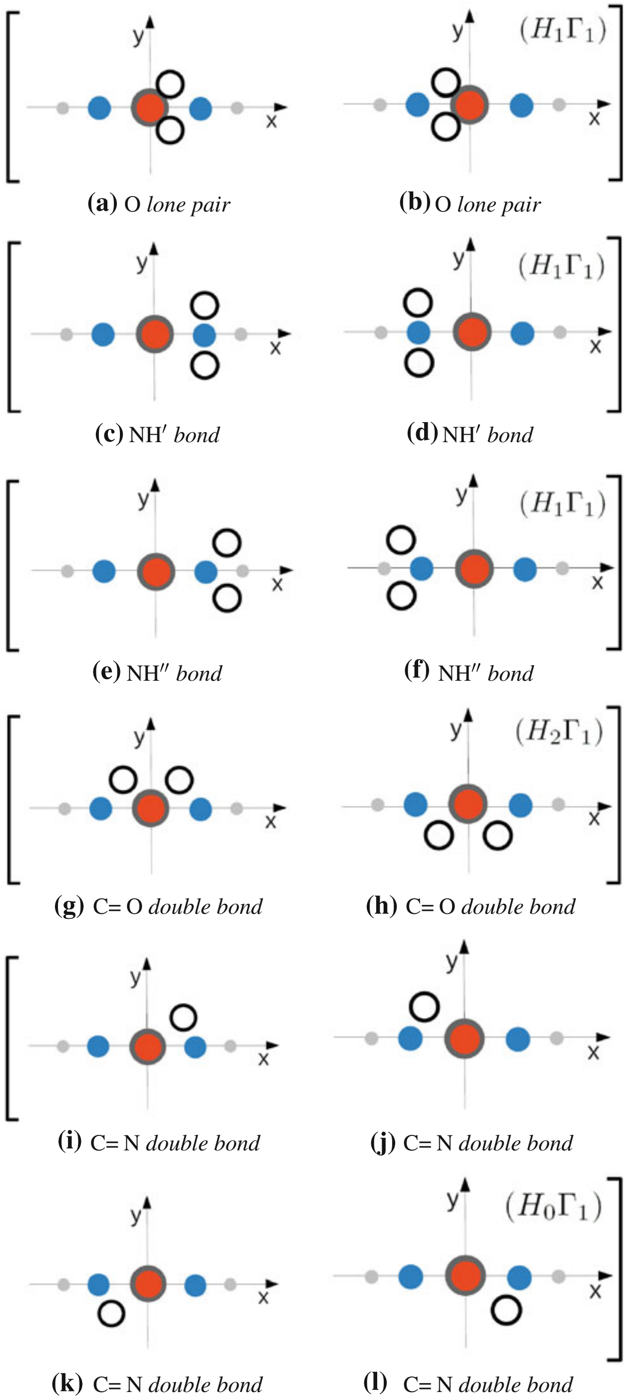
For the urea molecule, the possible solutions in terms of SABSs that span the valence subspace are 92. The MISABS, i.e., the one that displays minimal invariance according to functional $\bar{I}$ is denoted below as (i):

$$\begin{aligned}\Gamma^{(\mathrm{val})}_{\mathrm{CO(NH_2)_2}} &= 5A_1 \oplus A_2 \oplus 4B_1 \oplus 2B_2 && (\mathrm{CO})\\ &= 3(\mathcal{H}_1\Gamma_1) \oplus (\mathcal{H}_2\Gamma_1) \oplus (\mathcal{H}_0\Gamma_1). && (\mathrm{i})\end{aligned}$$

This solution, graphically represented in Fig. 3, consists of five indreps. Indrep $(\mathcal{H}_1\Gamma_1)$ appears three times. The corresponding basis functions are invariant under σ_{xz} and they are to be assigned to the two *lone pair* orbitals of the oxygen atom (Fig. 3a, b) and to the four NH covalent bonds (related by pairs) (Fig. 3c–f). Indrep $(\mathcal{H}_2\Gamma_1)$ appears once. Its basis functions are invariant under σ_{yz} and are to be ascribed to both partial C=O *banana* orbitals, according to the symmetry features shown in Fig. 3g, h. The last indrep considered in the solution is the four-dimensional *regular* representation, the $(\mathcal{H}_0\Gamma_1)$ indrep, whose basis functions, depicted in Fig. 3i–l, are trivially invariant under the identity. They can be transformed into each other by the four symmetry operators of $\mathcal{C}_{2v}$. The basis functions of this indrep cannot be easily assigned according to the Lewis theory, but one can ascribe them to a kind of partial C=N *banana* orbitals. According to Eq. 12 the global invariance extent of this solution is $\bar{I} = 4/12 \times 5 = 1.667$.

It has to be pointed out that the MISABS does not properly describe in this case the conjugate double bonds in the Lewis-like expected manner, as the occurrence of partial C=O and C=N double bonds should be invoked in order to chemically interpret the features of the SABS. However, the solution is fully compatible with the Foster–Boys scheme, as the corresponding localized orbitals display exactly the same symmetry features as predicted.

As it is well known, the localized orbitals obtained by means of the Pipek–Mezey scheme [12], for instance, provide a different kind of solution for the conjugate double bond system, as they are given in terms of σ–π orbitals instead of *the banana* ones.



(a) O *lone pair* **(b)** O *lone pair*

(c) NH′ *bond* **(d)** NH′ *bond*

(e) NH″ *bond* **(f)** NH″ *bond*

(g) C= O *double bond* **(h)** C= O *double bond*

(i) C= N *double bond* **(j)** C= N *double bond*

(k) C= N *double bond* **(l)** C= N *double bond*

Fig. 3 Urea molecule. Pictorial representation of the symmetry properties of the 12 basis functions grouped according to their indreps: **a–f**, **g**, **h** and **i–l** proper of the $(\mathcal{H}_1\Gamma_1), (\mathcal{H}_2\Gamma_1)$ and the *regular* indrep $(\mathcal{H}_0\Gamma_1)$, respectively, forming the MISABS of urea. The C and the O atoms are represented by the *concentric circles* in the center, N and H are depicted with the *blue* and the *small gray* ones. Only two H atoms are shown for the sake of clarity. The molecule is oriented perpendicularly to the paper plane

As a matter of fact, the subspace $(\mathcal{H}_2\Gamma_1) \oplus (\mathcal{H}_0\Gamma_1)$ exhibited by the MISABS appears resolved into

$$(\mathcal{H}_1\Gamma_1) \oplus (\mathcal{H}_1\Gamma_2) \oplus (\mathcal{H}_4A_1) \oplus (\mathcal{H}_4B_2)$$

in the Pipek–Mezey solution. This involves two σ_{CN}, two p_{N} (perpendicular to the molecule plane), one σ_{CO} and one π_{CO} orbital types, respectively. This is in better agreement with the chemical intuition than the Foster–Boys localized orbitals and the MISABS. However, the value of the global invariance extent for the Pipek–Mezey solution is larger than for solution (i), taking a value of $\bar{I} = 2.333$, which does indicate a lower degree of angular spatial localization.

3.2.2 Polyacetylene

While in molecules the task of filling the valence subspace with indreps is rather straightforward due to the finite nature of the systems, this is not the case for infinite periodic structures. In the latter $\Gamma^{(\mathrm{val})}$ has infinite dimension and there are an infinite number of irreps contained in it, which are assigned to the stars of **k**-points located inside the first Brillouin zone (FBZ).

In addition, we may find SABS induced from bases of irreps of finite and infinite subgroups, the former featuring only point operations, while in the latter the infinite number of additional operations display translational parts. In accordance with the discussion made in Sect. 2.2, a finite dimensional subspace of functions invariant under an infinite subgroup will necessarily be delocalized as they must be spread throughout an infinite number of spatial regions. Therefore, to construct SABS compatible with spatial localization for periodic systems, only point subgroups of the space symmetry group of the system are to be considered for induction. The resulting SABSs are actually the symmetry-adapted Wannier functions proposed by des Cloizeaux [2, 3], which form an infinte set of functions with finite subsets assigned to each of the unit cells of the lattice.

Our purpose in this illustrating periodic example is to recognize the symmetry properties of one of such subsets of functions centered on the origin of the reference cell and on its borders with adjacent ones. Accordingly, it is sufficient to consider only those subspaces of $\Gamma^{(\mathrm{val})}$ associated with the irreps ascribed to the central point $\mathbf{k} = \mathbf{0}$ and to some of the special points at the border of the FBZ. In the case of 1D polyacetylene, the irreps of just two points, namely $k = 0$ and $k = 1/2$, have actually to be considered.

The irrep decomposition of $\Gamma^{(\mathrm{val})}$ in those points reads

$$\Gamma^{(\mathrm{val})}(k = 0) = 3A_g \oplus A_g \oplus B_u$$
$$\Gamma^{(\mathrm{val})}(k = 1/2) = 2A_g \oplus B_g \oplus 2B_u$$

where the irreps of the space group are labeled according to those of the corresponding little co-groups, which are the same in both cases, namely $\mathcal{C}_{2h}$.

The possible solutions in terms of SABS are four, from which the MISABS reads

$$\Gamma^{(\mathrm{val})}(h) = (\mathcal{H}_2\Gamma_1) \oplus (\mathcal{H}_3\Gamma_1) \oplus (\mathcal{H}_4A_g)$$

where the argument h runs over all cells of the lattice and indicates that equivalent SABSs appear assigned to each cell. Regarding the type of symmetry operations contained in each point subgroup of $\mathcal{C}_{2h}$, they are isomorphic with those provided in Table 1. Nonetheless, each of the $\mathcal{H}_p$ subgroups is in general centered on different Wyckoff positions of the lattice. With regard to the previous solution, $\mathcal{H}_2$ and $\mathcal{H}_4$ are centered on the origin, while $\mathcal{H}_3$ is on the cell borders, at the middle point of the C=C double bond.

The MISABS solution is graphically represented in Fig. 4, where the two cells ($h = 0$ [left],1[right]) of the polymer are reported and only the SABS associated with $h = 0$ is drawn. The two basis functions of indrep $(\mathcal{H}_2\Gamma_1)$, represented in Fig. 4a, b, are to be ascribed to the two CH σ orbitals and are symmetry related by C_2; the two basis functions of indrep $(\mathcal{H}_3\Gamma_1)$ (Fig. 4d, e) correspond to the two C=C *banana* orbitals and are symmetry related through σ_{xy}. The basis function of indrep $(\mathcal{H}_4A_g)$ is invariant under the whole set of operators of the group and is assigned to the CC *σ-bond*.

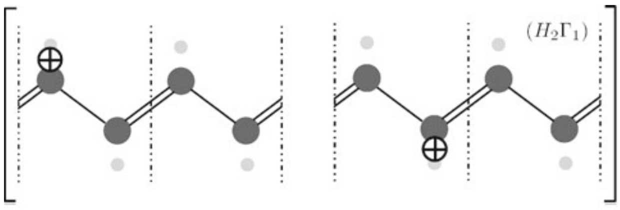
It is worth noting that also in this periodic example, the MISABS exhibits the same symmetry as the set of localized orbitals computed by means of the Wannier–Boys method, a periodic extension of the molecular Foster–Boys scheme implemented in the CRYSTAL code [14].

4 Discussion

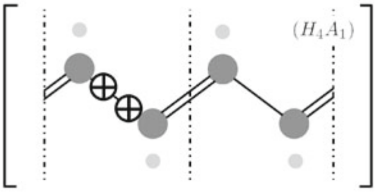
As far as it appears in the simple illustrating examples shown in Sect. 3, and also in other several cases that display much more involved symmetries [15], the MISABS usually coincides in its symmetry features with the set of localized orbitals obtained by the Foster–Boys scheme or its periodic extension, the Wannier–Boys one already mentioned above.

The observed exceptions concern the well-known cases of continuous degeneracy in which the localization method is unable to fix the orientation of some of the orbitals of the solution, because there are transformations of the localized basis sets that do not carry any change in the value of the functional [16].

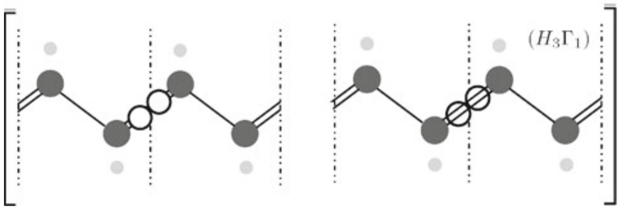
It is worth noting that the criterion of MGIE favors the solutions that display *banana* orbitals for multiple bonds instead of the more intuitive σ–π resolution. This is because the latter displays additional symmetry operations through which the orbitals are kept invariant. The same kind of solutions are in general obtained by means of the



(a) CH *bond* **(b)** CH *bond*



(c) CC *σ-bond*



(d) C= C *bond* **(e)** C= C *bond*

Fig. 4 Schematic representation of the symmetry features of the five functions, which constitute the MISABS for the polyacetylene polymer $[\Gamma^{(\mathrm{val})}(h = 0)]$. The *dark large* and *light small gray circles* represent the positions of the C and H atoms, respectively. The polymer lies on the *xy* plane; *empty black circles* highlight general points above or below this plane depending on whether they cover, or do not cover, the bond lines, respectively. *Crossed circles* highlight pairs of symmetry equivalent points that lie above and below the plane

Foster–Boys method, while other schemes such as the Pipek–Mezey one provides σ–π resolution, instead [12]. This is apparent in our example of urea where both, the Foster–Boys method and the criterion of MGIE, yields as the best spatially localized solution the one that envisages *banana* instead of σ–π orbitals.

The present work can, therefore, contribute to the old controversy concerning the tendency of the Boys method to resolve multiple bonds in terms of *banana* orbitals, which is frequently considered as a shortcoming. The criterion of MGIE is based on general concepts that involve the fundamental properties of group representations, and its agreement with the Foster–Boys localization criterion does indicate that the method derived from the latter is probably the soundest procedure to obtain spatially localized functions, at least from the formal point of view.

It is also to be highlighted that the MISABS, as they are made up of basis sets of a minimal number of indreps, can be also generated from a minimal number of functions by applying symmetry and shift operators (see Sect. 2.1). This is of paramount relevance for the use of localized SABSs in computational applications for the estimation of tensorial objects, as discussed in what follows. This is the case, for instance, of the one or bi-electronic integrals used in ab initio methods, or of the particle-hole excitations from a given reference Slater determinant.

The combined exploitation of localization and symmetry adaption allows us to design efficient computational strategies. On one hand, the maximal localization provides powerful criteria suitable to a priori determine the numerical relevance of the individual tensor components and select them up to a desired accuracy. On the other hand, the minimal number of generators provides symmetry relationships between the components of the tensors, making it necessary to explicitly compute a substantially reduced fraction of them. The practical importance of this kind of techniques in the context of ab initio wave function calculations of crystalline systems has been discussed in detail in previous works [8, 10, 15].

The formal analysis provided in this paper demonstrates that both strategies to perform the efficient computational management of tensorial objects rely on a single concept that is the criterion of the MGIE applied to SABS in the general definition provided in Sect. 2.1.

5 Concluding remarks

In this work, the issue of the compatibility between symmetry and spatial localization is addressed by considering the concept of invariance extent. It is shown that this is quantified through a functional that depends on the basis set choice and the symmetry group, and the SABS that yield the minimal value of the functional corresponds in most cases to the maximally localized orbitals obtained through the Foster–Boys scheme.

This provides a strong indication that this particular localization method is the most suitable one to obtain basis sets that combine spatial localization and symmetry properties appropriate for computational purposes.

Two drawbacks mainly arise for the efficient application of the Boys method to obtain localized SABS:

- small numerical inaccuracies in the symmetry relationships between the basis set components, usually originated by the approximate character of the functional optimization, which affect the accuracy of the total calculation, and
- the continuous degeneracy problem discussed in Sect. 4.

In addition, these drawbacks make difficult the efficient implementation of algorithms that allow the a posteriori detection of the symmetry relationships between the basis set components, required for the previously discussed computational applications.

However, the construction of localized SABS can be efficiently managed by imposing a priori the symmetry relationships characteristic of the MISABS from the beginning of the functional optimization using a constraining procedure. The theory developed in this study ensures the symmetry constraints to be fully compatible with maximal spatial localization. This strategy will be explored in forthcoming works.

Other points that deserve further investigation are the characterization of the SABS as stationary points of the global invariant extent and the unisity of the MISABS solution. With regard to the former, the question that arises is whether or not the SABS are local minima of the functional and whether they are unique or there are other stationary points that do not behave as SABS in the sense considered in this work.

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Appendix: Gradients of the functional $\bar{I}$ in terms of the SABS

Let us first consider unitary transformations inside the indrep spanned by the set $\{|\mathcal{H}\mu, ar\rangle\}$ given in Eq. 3; for the sake of simplicity the first indexes $\mathcal{H}$ and μ will be omitted. The gradient element that corresponds to generator $\hat{E}_{ag,bh}$ (Eq. 10) reads

$$\begin{aligned}\frac{\partial \bar{I}(\mathcal{G},\{|cf\rangle\})}{\partial \varepsilon_{ag;bh}} &= \frac{1}{L}\Re\sum_{S\in\mathcal{G}}\left(\langle bh|\hat{S}|ag\rangle + \langle ag|\hat{S}|bh\rangle\right)\\ &\quad\times\left(\langle ag|\hat{S}|ag\rangle - \langle bh|\hat{S}|bh\rangle\right)^*\\ &= \frac{1}{L}\Re\sum_{S\in\mathcal{G}}\langle bh|\hat{S}|ag\rangle\langle ag|\hat{S}|ag\rangle^*\\ &\quad-\frac{1}{L}\Re\sum_{S\in\mathcal{G}}\langle bh|\hat{S}|ag\rangle\langle bh|\hat{S}|bh\rangle^*\\ &\quad+\frac{1}{L}\Re\sum_{S\in\mathcal{G}}\langle ag|\hat{S}|bh\rangle\langle ag|\hat{S}|ag\rangle^*\\ &\quad-\frac{1}{L}\Re\sum_{S\in\mathcal{G}}\langle ag|\hat{S}|bh\rangle\langle bh|\hat{S}|bh\rangle^*.\end{aligned} \tag{13}$$

To determine whether or not the involved sums vanish, let us study the behavior of the constituent integrals. Considering Eq. 3, it arises that

$$\langle ag|\hat{S}|bh\rangle = \langle a0|\hat{S}_g^{-1}\hat{S}\hat{S}_h|b0\rangle, \tag{14}$$

which vanishes if $S_g^{-1}SS_h \notin \mathcal{H}$. This is because, in such a case $S_g^{-1}SS_h = S_rR(R\in\mathcal{H}, r\neq 0)$, in accordance with the left-coset partition (Eq. 1), and

$$\begin{aligned}\langle ag|\hat{S}_r\hat{R}|bh\rangle &= \sum_{b'=1}^{n_\mu}\langle a0|S_r|b'0\rangle D^{(\mu)}_{b'b}(R)\\ &= \sum_{b'=1}^{n_\mu}\langle a0|b'r\rangle D^{(\mu)}_{b'b}(R),\end{aligned} \tag{15}$$

where Eqs. 2 and 3 are used in the first and second equalities, respectively, and the last expression is null due to the orthonormality of the SABS.

It therefore appears that if $g\neq h$, the gradient vanishes as there is no choice for S that allows both factors in each term of Eq. 13 simultaneously not to vanish. Let us take as example the first sum. The previous analysis shows that the first and second factors will vanish in those terms in which $S_h^{-1}SS_g\notin\mathcal{H}$ and $S_g^{-1}SS_g\notin\mathcal{H}$, respectively. However, there is no S that satisfies both conditions if $g\neq h$, as otherwise it would mean that $SS_g\in S_h\mathcal{H}$ and $SS_h\in S_h\mathcal{H}$, contradicting the left-coset partition, and therefore the whole sum vanishes.

In the case $g=h$, Eq. 13 becomes

$$\begin{aligned}\frac{\partial \bar{I}(\mathcal{G},\{|cf\rangle\})}{\partial \varepsilon_{ag;bg}} &= \frac{1}{L}\Re\sum_{S\in\mathcal{H}^{[g]}}\langle bg|\hat{S}|ag\rangle\langle ag|\hat{S}|ag\rangle^*\\ &\quad-\frac{1}{L}\Re\sum_{S\in\mathcal{H}^{[g]}}\langle bg|\hat{S}|ag\rangle\langle bg|\hat{S}|bg\rangle^*\\ &\quad+\frac{1}{L}\Re\sum_{S\in\mathcal{H}^{[g]}}\langle ag|\hat{S}|bg\rangle\langle ag|\hat{S}|ag\rangle^*\\ &\quad-\frac{1}{L}\Re\sum_{S\in\mathcal{H}^{[g]}}\langle ag|\hat{S}|bg\rangle\langle bg|\hat{S}|bg\rangle^*,\end{aligned} \tag{16}$$

where the sums are restricted to $\mathcal{H}^{[g]} = S_g\mathcal{H}S_g^{-1}$, which is isomorphic with $\mathcal{H}$, as for the remainder of the $S\in\mathcal{G}$ the terms vanish according to Eq. 15. It appears that the set $\{|ag\rangle\}_{a=1}^{n_\mu}$ is a basis for the irrep μ of $\mathcal{H}^{[g]}$ and, therefore, each sum in Eq. 16 does vanish owing to the First Theorem of the Orthogonality of the irrep matrices, giving a null gradient component.

In case $|v_j\rangle$ and $|v_l\rangle$ in Eq. 10 belong to different indreps, it is easy to prove that the corresponding gradient component vanishes. This is because $\hat{S}|v_j\rangle$, $\forall S\in\mathcal{G}$ belong to the same indrep as $|v_j\rangle$ that is orthogonal by definition to the subspace that contains $|v_l\rangle$. This makes $\langle v_j|\hat{S}|v_l\rangle = \langle v_l|\hat{S}^{-1}|v_j\rangle^* = 0$, $\forall S\in\mathcal{G}$ with the subsequent vanishing of the whole sum in Eq. 10.

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