Two points of view to look at symmetry

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Abstract. The concept of symmetry equivalence and its deep connection with localization in the general sense is here opposed to the more familiar idea of symmetry as invariance, widely adopted in quantum mechanics. It is shown that symmetry equivalences together with localization allow to devise efficient ways for the computation and storage of calculated constants in ab initio calculations. On the other hand, symmetry invariance, through the theory of linear representations, is extremely useful to perform efficient basis set transformations in variational algorithms. A combination of both strategies appears to be ideal in the context of the quantum chemistry of extended systems.

1. Introduction
To approximate the solutions of the stationary Schrödinger equation by means of algebraic techniques, it is customary to exploit the linear variational theorem and restrict the search of the stationary points of the energy functional into a subspace of the full Hilbert space: the so-called Model Space. The strategy involves the choice of suitable basis sets that not only must be able to accurately represent the states one is interested in, but also to allow neglecting of a significant amount of calculated constants and variables of the original equation giving rise to a substantial saving in computational cost.

A very common practice with historical roots in quantum mechanics has been to adopt symmetry adapted basis sets to this scope. They are characterized by the fact that their components are chosen so as to span the irreducible representations (irrep) of the Symmetry Group of the Hamiltonian. The use of such basis sets increases the efficiency of the calculations in particular when the Hamiltonian can be approximated by independent-particle operators, particularly in Mean Field-SCF procedures.

In the solid state context a clamorous success has been obtained by the Kohn-Sham approximation in plane-wave basis sets. [1–3] Plane-waves are bases of the Translational Group irreps (the so-called Bloch functions), and they can therefore be straightforwardly employed to represent the one-electron solutions of perfect crystalline one-electron Hamiltonians. Despite the remarkable efficiency of these methods, they present several shortcomings that restrict their general applicability. [4, 5] In this line we can mention: semi-empirical character of the functionals, need of pseudo-potentials even for light atoms like H, spurious self-interaction effects connected essentially to the local character of the exchange functionals and lack in the description of weak forces, among other inadequacies of Hohenberg-Kohn-Sham theory. [4]

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In going beyond the independent particle approximation, a good choice is to adopt a many-electron basis set of antisymmetrized products of one-electron wave-functions (Slater determinants). This is the foundation of the Configuration Interaction (CI) family of methods. One of the main difficulties in their implementation is the quite large scaling of the computational complexity, being $O(N^p)$, where $N$ is the number of electrons and the power, $p > 5$, increases with the accuracy level of the approximation considered. Symmetry adaption of the many-electron basis set, including spin adaption, provides a remarkable gain in efficiency, but not enough to revert the “scaling wall” that appears in extended systems. This becomes critical for perfect crystals, with an infinite number of electrons and integrals to be computed.

An alternative choice has been revealed useful so as to increase the efficiency of CI methods for extended systems. In it, Slater determinants are constructed in terms of basis sets constituted by spatially localized one-electron functions. It has been shown [6–9] that such a choice allows the efficient truncation of large series depending on one- and two-electron integrals, thanks to their quite fast decay in going to terms that involve more and more distant centers. The scaling of CI methods like Möller-Plesset or Coupled Cluster, drastically decreases reaching an effective computational linear-scaling behaviour. This remarkable feature makes possible to employ high-level methods for large systems with negligible loss in accuracy due to truncations. This is the basis of the so-called Local Correlation methods.[9]

In addition, localized basis functions allow a sound correspondence between one-electron functions and physico-chemical objects such as core or lone pair electrons and bonds. Accordingly, they resemble Heitler-London Valence Bond orbitals, permitting the performance and implementation of efficient Multi-Configurational variational approaches. [10, 11]

As currently assumed, it is not possible in general to build sets of orthonormal orbitals that simultaneously display both, spatial localization and symmetry adaption to the irreps, bringing about a kind of mix of the previously described strategies. This will be discussed in detail and supported from the fundamental point of view in what follows. Nonetheless, it is to be remarked that the usual adaption to the bases of the irreps is not the only way to exploit symmetry in quantum chemistry methods, [12] and there are other choices that lead to interesting implementations in which symmetry and localization appear combined.

Illustrative examples of these alternative strategies in the exploitation of symmetry are some of the quantum chemistry methods for crystalline systems such as those implemented in the CRYSTAL [13, 14] and CRYSCOR [15] codes. It is worth noting that, while exploitation of symmetry is optional for Local Correlation methods of finite systems, in the extension to crystals it is mandatory, even at the lowest symmetry level envisaged by a crystal which is just periodicity. Indeed, crystals display in general very rich symmetry features (with both translational and point operators), full exploitation of them gives rise to significant improvements in efficiency for most of the methods. [15, 16]

The aim of the present paper is to discuss the compatibility between Localization and Symmetry in their most general sense and from the formal point of view. It is shown that both are very basic concepts that have a deep connection in our (human and computational) languages. Two different ways to understand symmetry are here discriminated, that involve either invariance or equivalence. Concerning the latter, it turns out that the concept of localization appears to be naturally derived from it.

All these considerations open the possibility to devise general and systematical ways to construct Symmetry Adapted/Localized sets (not only basis sets) and to deal with them in variational procedures, which does give rise to several applications in the quantum chemistry of materials. Most of the ideas here presented are indebted to previous works, from which I would like to particularly mention those from Dovesi et al. [13, 17] and Evarestov-Smirnov. [12, 18]
2. Symmetry invariance and its relevance in quantum mechanics

From the pioneering applications of Symmetry Group theory in quantum mechanics to nowadays, the main point of interest in the field was the theory of linear representations that provides a quite easy way to obtain, through the so-called Wigner’s theorem, relevant information on the solutions of the Schrödinger equation without the need of explicitly solving the eigenvalue problem. Obviously, such an information has been also employed in several cases to allow a simplified way to obtain the solutions themselves.

The theory is based on the concept of representation that involves a homomorphism between a given group of automorphisms (operators) within a given vector space, $V$, and the abstract group $G$. From this point of view, it is said that $V$ features symmetry if it is invariant under the operations of the corresponding group representation, $\Gamma$, of $G$. In the same way, a general operator in $V$ will be considered symmetric if it is invariant under the operations of the tensorial squared representation of $\Gamma$, $\Gamma \otimes \Gamma^*$, or, in other words, if it commutes with all the operators of the representation $\Gamma$.

Irreducibility may be considered as a generalization of the eigenvector problem. While the latter consists in finding all one-dimensional subspaces that remain invariant under a given operator, the problem of finding the irreps of a group is to determine the lowest dimension subspaces that are simultaneously kept invariant by all operators of $G$. Under this light, irreducibility appears as a kind of “maximal” invariance of the subspaces under the symmetry operators. The power of the Wigner’s theorem resides in that it ensures that the eigenvectors of a given operator must also be basis of the irrep subspaces of its symmetry group.

According to the previous analysis, one can devise a formal scheme to define in an abstract manner the notion of symmetry as invariance. The following features are required:

(i) A set of objects: $O = \{o\}$
(ii) A set of transformations $T = \{t\}$ between those objects, so as:

$$t(o) = o', \quad o, o' \in O,$$

where $t : O \leftrightarrow O$, is any automorphism in $O$. The transformations must form a group with composition law $t \ast s(o) = t(s(o))$, $t, s \in T$. It is worth noting that the last condition is automatically fulfilled if $O$ forms a vector space.

(iii) The subgroup of the transformations $t$ that leave invariant a given object $o$, is said to be its Symmetry Group, $G_o = (\{t, t(o) = o\}, \ast)$.

It arises that symmetry invariance is necessarily associated to the concept of transformation, in the same way as the state at rest appears associated to the feasibility of motion.

Transformations in the most general sense, are closely connected to the processing in computational algorithms. In particular, most of algorithms used in quantum-chemistry start from a given guess and evolve iteratively by successive transformations towards the best approximation to the solution (an optimum in variational approaches). The knowledge of the invariant properties of a system allows to simplify the resolution of the problem, as only the allowed degrees of freedom are selectively transformed during the iterative procedure.

An illustrative example is the use of basis sets adapted to the irreps of the symmetry group in the algebraic solution of the Schrödinger equation. Here the theory ensures that during transformations towards the variational energy minimum, only mixings between vectors belonging to the same irreps and rows are allowed. The algorithm can be accordingly factorized so as to deal independently within each of the small subspaces assigned to each irrep and row, with remarkable advantages from the computational point of view. This is substantially the role that plays the Bloch theorem in the Band theory of crystals.
3. Symmetry equivalence and its role in chemistry

In order to introduce the concept of symmetry equivalence let us consider the usual meaning of symmetry in the most basic chemical language: the molecular formulation. We shall consider the example of the methane molecule which is schematically represented in Fig. 1. The scheme in principle contains all the relevant information that a chemist needs to identify the molecule, \textit{i.e.} the atomic elements and the bonds. Atomic coordinates, for instance, do not introduce any relevant information to this respect, an aspect denoted in the scheme by its lack of “exact symmetry”. However, a kind of order is defined by the molecule connectivity: each atom, classified by elements, occupies a \textit{position} determined uniquely by the topological (vicinity) relationships with the others. Under such a manner to identify the methane molecule, the four H atoms can be said to be \textit{equivalent} irrespective of their precise position in space.

Starting from the previous illustrating example one can try to generalize it making a formal analysis of the symmetry equivalence, similar to that made for symmetry invariance in Sec. 3. What one essentially needs to find symmetry equivalences in a general system can be schematized as follows:

(i) A set of things: they may in general be called \textit{objects}, either mathematical constructs or real physical entities.

(ii) A set of places: this should be understood in a general way, in the sense that the same role would be played by a set of labels, pieces of computational memory, regions in space, etc. to be assigned to each thing. We impose the constraint that the number of different places should be the same as the number of things.

(iii) Each thing in each place: the assignation of a place to each thing may be called \textit{localization} or \textit{allocation}, depending on whether the context is physical or computational. In what follows the sets assigned in this way will be referred to as \textit{localized sets}.

(iv) Equivalent classes: A partition into equivalent classes is performed within each set, with the condition of keeping the assignation performed in item (iii), as it is schematized in Fig. 2.

(v) Generating operations: A set of operations that allow to generate any thing in its place from another thing belonging to the same equivalent class is defined. If each set forms a
group within each class, the abstract group of minimum dimension whose subgroups are isomorphic with them is called the Symmetry Group of the system.

One of the first issues that attract the attention is that the concept of localization appears to be intrinsic to the general notion of symmetry equivalence. This, obviously, by taking the term “localization” as the assignment of an abstract place to a given object [see item (iii)].

Equivalences have straightforward applications for computational purposes as they allow to decrease the algorithms complexity. This is because one can explicitly compute just one representative of each class, being the others generated by symmetry operations. An efficient localization would mean in this context to minimize the number of equivalence classes or, in other words, to maximize the equivalences between the objects.

On the other hand, the present way to systematize the concept of symmetry equivalent sets, allows to define a more general, but also more intuitive, kind of symmetry that we could call partial symmetry. The condition in item (v) would be slightly weakened by allowing to lose the strong requirement that generators do form a group within each class, but keeping the fact that all generators and their composition law must have correspondence with subsets of the Symmetry Group. Several physical systems display such characteristics, as for instance a real crystal in which, being a finite system, not all the infinite operators that belong to the space group are required as generators of the whole crystal.

Considering the previous concepts, disordered systems appear to be an extreme case of partial symmetry: they are constituted by one and only one representative of each class, forming a so-called asymmetric set. What is interesting in this point of view is that disorder can be merged into the general envisagement of symmetry equivalence. As a matter of fact, disordered systems are characterized by a set of “macroscopic” properties; accordingly, all systems that feature the same properties are equivalent. This is often exploited in Monte Carlo or Molecular Dynamics simulations, where the statistical properties of a class are taken from those of a single representative. While the explicit form of the generators that allow us to construct a full class of disordered systems from any representative is, by definition of disorder, unknown, it is possible to assume they form a group (or any subset of it) giving rise to symmetry equivalences between the disordered systems that belong to the same class. In accordance with the formal considerations concerning symmetry equivalences, a deep relationship between disorder and localization arises from this analysis that supports the usual intuitive assumptions to this respect.

4. Compatibility between invariance and equivalence

While the previous points of view cover the most general concept of symmetry, they appear to be complementary but not compatible as far as the formal languages concern. The incompatibility arises when one tries to quantify in some way the invariance-equivalence properties as a criterion to devise optimally symmetric sets. A set of objects that simultaneously displays maximum invariance (irreducible subspaces in vector spaces) and maximum equivalences (smallest asymmetric subsets in localized sets), can only appear in very particular situations, for instance in a normalized basis set of a one-dimensional space, but in general both optimal features are not compatible. This may be attributed to the fact that invariance and equivalence are logical constructs not derivable neither from each other, nor from a more general statement.

As a matter of fact, while invariance is based on the definition of a set of transformations as automorphisms in a vector space, equivalence involves a set of places (labels) to which the objects should be localized (assigned). Although a homomorphism between groups constituted

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2 In the Monte Carlo and Molecular Dynamics approaches, it is somehow assumed that the steps along the classical trajectories and the Markov processes, respectively, are good approximations to such generators if the system is in equilibrium.

3 The particularity of this case is that a transformation is the product by a unitary scalar, and there is only one “place” to assign the vector, therefore localizations and transformations become meaningless.
by either transformations or generators in symmetric sets can be always constructed, this must be done \textit{a posteriori}, after the definition of the transformation and generating rules. In other words, what we interpret as symmetry in reality, requires both concepts but there is no logical predecessor from which both could be deduced.

One can conceive a realization of the symmetry group that keeps somehow the notions of both invariance and equivalence. According to Cayley’s theorem, this can be represented as a group of permutations, which makes each equivalent class to also be invariant. Nonetheless, maximal invariance and equivalence requires the classes to be the smallest and the largest as possible, respectively, once more revealing their deep incompatibility.

As a matter of fact, there is a logical contradiction in the purpose to look transformations as permutations of localized objects. This is because when objects are changing place they cannot be formally localized, as they are no longer in any place. This is a problem whose ascendancy may be traced to the paradoxes from Zeno of Elea in the V-th c. BC, and it is also connected with Heisenberg’s uncertainty principle, as a sort of incompatibility between the precise simultaneous determination of motion (transformation) and position (assignation or localization).

Aside from these general theoretical implications, the present pure formal language analysis may help for analyzing and devising computational algorithms (essentially formal logic entities) in quantum chemistry. Accordingly, the previous considerations must be also reflected in the analysis of the performance of the various computational methods.

As concerns, for instance, the basis sets adopted to span the Model Space in the algebraic solution of the electronic Schrödinger Eq., they can be chosen to display both types of symmetry, as a basis set may span invariant subspaces and be labeled to bring about localized sets.

As equivalent classes in the basis set are invariant under the permutation realization of the symmetry group $G$, their components do span representations of $G$. Irreducibility will require smallest as possible representations but, at the same time, it is always possible to choose an irreducible basis set in which the different rows in each irrep are equivalent under the operations of a subgroup of $G$ forming an equivalence class. Nevertheless, the irreducibility condition makes the classes to be the smallest as possible, minimizing the equivalences.

On the other hand, if one chooses a maximally equivalent basis set, the associated requirement is to get the lowest number of generators or the largest equivalence classes. In case of chemical systems this may be done with basis functions that represent bonds, core or lone valence electrons, which are objects localized both in space and from the more abstract point of view discussed in Section 3. Obviously, the resulting representations are in general of large dimension and reducible, \textit{i.e.} they are minimal as concerns their invariance properties.

5. \textbf{Space symmetry adapted and localized strategies in solid state quantum chemistry}

As discussed in Sections 2 and 3 maximal symmetry invariant properties give rise to algorithms where transformations between consecutive points of iterative procedures are fast, while maximal equivalences between basis set components allow us to reduce the complexity of the algorithms. Although both optimal properties can not be achieved simultaneously for a given basis set, several strategies have been devised so as to try to exploit as possible symmetry properties in electronic structure calculations.

In the context of calculations on crystalline systems one of the most paradigmatic strategies to compute the electronic structure making a full use of symmetry is the one implemented in the \textsc{Crystal} code. \cite{14} To overcome the problem of the incompatibility between optimal equivalence and invariance, two basis set are considered warranting a significant efficiency in both integral calculation-storage and transformations along the SCF process. \cite{13} An Atomic Orbital (AO) basis set is employed for the calculation of the mono- and bi-electronic integrals, where their natural symmetry equivalences \cite{17} and localization properties are fully exploited so as to not
only make finite an, in principle, infinite problem, but also to bring about a quasi linearity in its computational complexity. As concerns the transformations between each SCF cycle, they are performed in terms of symmetry adapted crystalline orbitals (SACO). These functions form bases for the irreps of the full Space Group of the crystal allowing a very efficient diagonalization of the one-electron Hamiltonians (Fock or Kohn-Sham) so as to compute a basis for the occupied subspace at each cycle. [19, 20]

Both basis sets are in principle infinite and can be transformed to each other through well defined formulae that involve integrals and infinite series. In computational applications these formulae are made discrete and truncated, respectively, and involve finite dimensional basis sets. At variance with the infinite case, these finite basis sets do not span the same subspace due to different boundary conditions: AOs are quadratically integrable in the whole real space, while SACOs within the cyclic Born-von Karman space. Obviously, this incompatibility (derived from the more fundamental one described in Sec. 4) can be minimized by suitable computational conditions, though in some particular cases their choice may not be an easy task.

Another remarkable strategy to approach the electronic Schrödinger equation for crystals by exploiting both symmetry and localization is the one implemented in the recently reported CRYSCOR code. [15] The program is intended to estimate the electron-electron correlation effects so as to correct, up to second order of perturbation, the Hartree-Fock solution. In this case two basis sets are also considered, but at variance with the previously discussed approach, both sets are symmetry equivalent and spatially localized. To span the occupied subspace, a set of symmetrized Wannier Functions, localized starting from the set of SACOs that solve the Hartree-Fock equations and further symmetry adapted is chosen. [16, 22] The other set spans the virtual space and is not orthonormal but redundant. It is obtained from projection of a the set of AOs, a procedure that warrants to keep to a rather satisfactory extent, symmetry relationships and localization features of the original AO basis set.

A generalization to these approaches could be devised by defining basis sets that allow symmetry equivalences compatible with efficient spatial localization, together with the feasibility to perform efficient unitary transformations that keep their symmetry features. Basis sets of this kind can be generated by means of the theory of induced representations, [12] and can be extremely useful in quantum chemistry of materials, as in terms of them it would be possible to perform optimizations of functionals depending on the basis set, to which construction the exploitation of symmetry equivalences and localization is crucial.

Two examples of this usefulness can be here mentioned. First, a scheme of this kind would permit to obtain a set of localized symmetry adapted Wannier functions, as required in CRYSCOR, from a symmetric optimization of a suitable localization functional. This choice presents several advantages with respect to the a posteriori scheme, as it would improve both the computational efficiency, according to the previous discussion and the numerical accuracy in the symmetric and orthonormalization properties of the Wannier functions.

Another very interesting application of this general strategy for symmetry adaption and localization, would be to implement other variational procedures involving the total energy. One can mention, for instance, methods for the computation of optimal multi-reference wave functions for crystalline systems by minimizing a suitable energy functional, as it is the case in the Generalized Valence Bond or the Complete Active Space schemes, among others. This would open the possibility of implementing high level methods for crystalline solids, that allow to go beyond the Hohenberg-Kohn-Sham theory.

Work is in progress so as to rigorously define and implement these strategies, and will be the subject of forthcoming papers.
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