A note on the symmetry properties of Löwdin's orthogonalization schemes*

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Abstract

We point out that the well-known symmetry properties of the symmetrically and canonically orthogonalized vectors hold only under certain conditions on the overlapping vectors. In particular, the matrix of the transformation induced by the symmetry operator must be unitary. This requirement is not fulfilled if Cartesian d or f functions are used in the basis set. If such functions are present, canonically orthogonalized orbitals do not transform according to representations of the molecular point group; nor do Löwdin orthogonalized vectors preserve symmetry relation of the original vectors.

Keywords: canonical orthogonalization, symmetric orthogonalization, Slater–Koster theorem

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* Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday

INTRODUCTION

In quantum chemistry, one often deals with non-orthogonal vectors which may be orthogonalized for convenience. Among the infinitely many possible orthogonalization procedures, we list only four, which all have their own significances.

1. The Gram–Schmidt orthogonalization is a successive procedure. This is the method of choice if one does not want to alter a subspace obtained in the previous step; e.g., in the case of orthogonalizing valence functions to the cores.
2. Mayer's orthogonalization[1, 2] leaves only the first vector invariant, but it applies an explicit (non-successive) transformation to get a set of orthogonal vectors.
3. The canonical orthogonalization procedure[3] transforms the vectors with the eigenvectors of the overlap matrix $\mathbf{S}$. The orthogonal MOs belonging to the same overlap eigenvalue form representations of the symmetry group of the system.
4. Symmetric orthogonalization[4] transforms the vectors by the $\mathbf{S}^{-1/2}$ matrix. This procedure is usually called Löwdin orthogonalization, although the canonical procedure 3 was also discussed extensively by him. The symetric orthogonalization possesses two remarkable features: the Löwdin vectors
   a) are least distorted from the original ones in the least-squares sense;
   b) bear the same symmetry as the original ones. This statement is known also as the Slater–Koster theorem[5], and it is the reason for which this scheme is often called 'symmetric' orthogonalization.

In this note, we will revisit symmetry properties of the latter two procedures using atomic orbitals (AOs) as primary nonorthogonal vectors. We will point out that these are valid only if certain conditions are fulfilled by these AOs. In particular, we show that redundant Cartesian (i.e., $6d$, $10f$, etc.) sets do not qualify.

This is not the first caveat in the literature concerning the use of Cartesian functions together with Löwdin orthogonalization. In a recent letter[6], Mayer called attention to the fact that the so-called Löwdin charges (populations of Löwdin orthogonalized AOs) are rotation-invariant only if no Cartesian d AOs are included in the basis set. This problem can be cured by orthogonalizing $6d$ or $10f$ functions prior to use, as proposed by Davidson[7, 8]. This problem was revisited and further clarified in Ref. [9].

In this note, we sketch the essence of the problem of symmetry properties from the quantum chemical point of view. More detailed and more strict mathematical formulation will be published elsewhere.

SYMMETRY PROPERTIES OF ORTHOGONALIZED VECTORS

Let the functions φ_i form an overlapping set with metric $S_{ik} = \langle\varphi_i|\varphi_k\rangle$. The symmetrically (Löwdin) orthogonalized vectors are

$$\psi_k^{\mathrm{L}} = \sum_i (\mathbf{S}^{-1/2})_{ik}\varphi_i, \tag{1}$$

while the canonically orthogonalized and normalized vectors result from a transformation by the S-eigenvectors:

$$\psi_k^c = \frac{1}{\sqrt{\sigma_k}}\sum_i U_{ik}\varphi_i, \tag{2}$$

with

$$\sum_i S_{ji}U_{ik} = \sigma_k U_{jk}. \tag{3}$$

In the appendix of their seminal paper, Slater and Koster[5] proved the following theorem: Let $\hat{T}$ be a symmetry operator of the system. Then, the transformation properties of symmetrically orthogonalized vectors (1) are the same as those of the original nonorthogonal set, i.e. the matrices representing $\hat{T}$ in both sets are identical. This orthogonalization thus preserves the symmetry of the basis.

Symmetry properties of canonically orthogonalized vectors (2) were treated by Löwdin[10]. He concluded that these orbitals are eigenvectors of the symmetry operations of the molecular point group.

We do not repeat the proofs here, just mention that the derivation of both properties exploit the fact that the matrix representing the transformation in the original, nonorthogonal basis is unitary. Although symmetry operations as *operators* are, of course, unitary, for the *matrices* representing them in a nonorthogonal set this is not necessarily true. This is easily seen by representing the operator relation

$$\hat{T}\hat{T}^\dagger = \hat{I} \tag{4}$$

in an overlapping basis to yield

$$\sum_{jk} T_{ij}(\mathbf{S}^{-1})_{jk}T^\dagger_{kl} = S_{il}, \tag{5}$$

where $T_{ij} = \langle \varphi_i | \hat{T}\varphi_j \rangle$. Rewriting (5) to the form

$$\mathbf{S}^{-1}\mathbf{T}\mathbf{S}^{-1}\mathbf{T}^\dagger = \mathbf{I} \tag{6}$$

convinces us that neither $\mathbf{T}$ nor $\mathbf{t} = \mathbf{S}^{-1}\mathbf{T}$ are unitary in general. However, if $\mathbf{T}$ and $\mathbf{S}$ (hence, $\mathbf{T}$ and $\mathbf{S}^{-1}$) commute, the last equation can be transformed to

$$(\mathbf{S}^{-1}\mathbf{T})\ (\mathbf{S}^{-1}\mathbf{T}^\dagger) = (\mathbf{S}^{-1}\mathbf{T})\ (\mathbf{T}\mathbf{S}^{-1})^\dagger = (\mathbf{S}^{-1}\mathbf{T})(\mathbf{S}^{-1}\mathbf{T})^\dagger \ = \ \mathbf{t}\mathbf{t}^\dagger = \mathbf{I}, \tag{7}$$

which shows that in this case $\mathbf{t} = \mathbf{S}^{-1}\mathbf{T}$, which actually performs the symmetry mapping in the non-orthogonal basis, is unitary.

We see that both Slater and Koster[5] and Löwdin[10] tacitly assumed that the representing matrix of the symmetry operation commutes with the overlap matrix. The question arises therefore whether this holds in all AO-basis sets. We will see that the answer is no.

Let us investigate the unitary nature of $\mathbf{t}$. There are important special cases when it is unitary even if $\mathbf{S} \neq \mathbf{I}$. As mentioned, $\mathbf{t}$ is the matrix which performs the mapping. In the simplest example we consider only s-type basis orbitals on each atomic center. The symmetry transformation maps an atom to another one, and it does the same to atomic s-orbitals. Hence $\mathbf{t}$ is a permutation matrix, and as such, it must be unitary. (Needless to say that we assume that symmetry-equivalent atoms have equivalent basis functions.)

A more complicated case is when p-type AOs enter the basis set, too. Let us consider real orbitals p_x, p_y, p_z. Then a particular p function is generally not mapped directly to another p function on the other atom, but into a linear combination of the three p's. The associated mapping matrix $\mathbf{t}$ is, therefore, no longer a simple permutation matrix. However, since the p subset on each atom is orthogonal, the local 3–by–3 transformation matrix is unitary. Therefore, *p orbitals do not destroy the unitary nature of* $\mathbf{t}$.

The above arguments also hold if orthogonal spherical d or f (etc.) functions enter the basis set. If, however, one uses Cartesian sets, the situation changes [6]: the symmetry transformation maps a d function into the linear combination of the non-orthogonal d subset of the target atom, thus the *mapping matrix t will no longer be unitary.* As a consequence, $\mathbf{T}$ and $\mathbf{S}$ do not commute and both Löwdin's orthogonalization schemes lose their symmetry properties mentioned in the Introduction – subsets of canonically orthogonalized vectors corresponding to the same overlap eigenvalue do not necessarily span representations, and, in addition, symmetrically orthogonalized vectors transform differently from the original ones.

EXAMPLES

We illustrate the above finding for the canonical orthogonalization on the example of the scandium(III) hydride molecule[11], ScH_3, which is the simplest possible molecule with valence electrons from d AOs. Its equilibrium structure is planar, exhibiting D_{3h} symmetry (Fig. 1). We applied the canonical orthogonalization procedure to a minimal Gaussian AO basis set consisting of a single s function on the hydrogens and a $4s3p1d$ set on atom Sc, using spherical or Cartesian d functions.

One selected canonically orthogonalized AO for the $5d$ and one for the $6d$ case are presented in Fig. 2. When using $5d$ functions matrix $\mathbf{S}$ reflects proper D_{3h} symmetry, hence there are degenerate overlap-eigenvalues, as the group is non-Abelian and $[\mathbf{T},\mathbf{S}]=\mathbf{0}$ for each symmetry operator $\hat{T}$ of the group. The lowest (in the order of $\mathbf{S}$-eigenvalues) nondegenerate canonically orthogonalized orbital of the $5d$ case, plotted in Fig. 2a, is totally symmetric, as one expects.

The corresponding AO from the $6d$ set is shown in Fig. 2b. Use of $6d$ orbitals induces $[\mathbf{T},\mathbf{S}]\neq\mathbf{0}$, eigenvalues of $\mathbf{S}$ are thus not necessarily degenerate (and, indeed, are not), reflecting loss of the symmetry of the matrix. The symmetry of canonically orthogonalized vectors is also destroyed: no traces of three-fold symmetry can be seen in Fig. 2b.

It is is harder to find such a pictorial example for the symmetric orthogonalization: preservation of the symmetry of the nonorthogonal set is most easily seen if the operator induces permutations between AOs, but then $[\mathbf{T},\mathbf{S}]=\mathbf{0}$ is ensured. We again turn to d orbitals and show that the matrix representation of the symmetry operator is not invariant with respect to Löwdin-orthogonalization if $6d$ sets are used. We will consider a free atom with a set of normalized (but certainly not orthogonal) Cartesian d functions (N_1 and N_2

are normalizing factors):

$$\begin{aligned}
\varphi_1 &= N_1 x^2\ \mathrm{e}^{-\alpha r^2} \\
\varphi_2 &= N_1 y^2\ \mathrm{e}^{-\alpha r^2} \\
\varphi_3 &= N_2 xy\ \mathrm{e}^{-\alpha r^2} \\
\varphi_4 &= N_2 xz\ \mathrm{e}^{-\alpha r^2} \\
\varphi_5 &= N_2 yz\ \mathrm{e}^{-\alpha r^2} \\
\varphi_6 &= N_1 z^2\ \mathrm{e}^{-\alpha r^2}
\end{aligned} \tag{8}$$

Rotation by an arbitrary angle α around the z axis is a symmetry operator of this system. As a result of a lengthy but simple calculation the matrix representing the operator in this set can be written as:

$$\mathbf{t}(\alpha) = \begin{pmatrix}
\frac{1+\cos(2\alpha)}{2} & \frac{1-\cos(2\alpha)}{2} & -\frac{\sqrt{3}}{2}\sin(2\alpha) & 0 & 0 & 0 \\
\frac{1-\cos(2\alpha)}{2} & \frac{1+\cos(2\alpha)}{2} & \frac{\sqrt{3}}{2}\sin(2\alpha) & 0 & 0 & 0 \\
\frac{1}{\sqrt{3}}\sin(2\alpha) & -\frac{1}{\sqrt{3}}\sin(2\alpha) & \cos(2\alpha) & 0 & 0 & 0 \\
0 & 0 & 0 & \cos(\alpha) & -\sin(\alpha) & 0 \\
0 & 0 & 0 & \sin(\alpha) & \cos(\alpha) & 0 \\
0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}. \tag{9}$$

This may be transformed into the basis of the respective Löwdin orthogonalized vectors, yielding

$$\mathbf{t}^{\mathrm{L}}(\alpha) = \begin{pmatrix}
\frac{1+\cos(2\alpha)}{2} & \frac{1-\cos(2\alpha)}{2} & -\frac{1}{\sqrt{2}}\sin(2\alpha) & 0 & 0 & 0 \\
\frac{1-\cos(2\alpha)}{2} & \frac{1+\cos(2\alpha)}{2} & \frac{1}{\sqrt{2}}\sin(2\alpha) & 0 & 0 & 0 \\
\frac{1}{\sqrt{2}}\sin(2\alpha) & -\frac{1}{\sqrt{2}}\sin(2\alpha) & \cos(2\alpha) & 0 & 0 & 0 \\
0 & 0 & 0 & \cos(\alpha) & -\sin(\alpha) & 0 \\
0 & 0 & 0 & \sin(\alpha) & \cos(\alpha) & 0 \\
0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}. \tag{10}$$

It is easy to see that the Slater–Koster theorem does not hold for arbitrary α: transformation matrices $\mathbf{t}$ and $\mathbf{t}^{\mathrm{L}}$ are different, as a consequence of $\mathbf{t}$ being non-unitary. Noteworthy, $\mathbf{t} = \mathbf{t}^{\mathrm{L}}$

if α is a multiple of $\pi/2$: these 'rotations' correspond to permuting and changing orientation of the Cartesian axes, which can again be described by a unitary matrix on this basis.

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Figure legends

Fig. 1

D_{3h} structure of scandium(III) hydride

Fig. 2

Contour plot of the third (in order of increasing $\mathbf{S}$ eigenvalue) canonically orthogonalized atomic orbital for ScH_3.

(a): minimal basis using $5d$ set

(b): minimal basis using $6d$ set

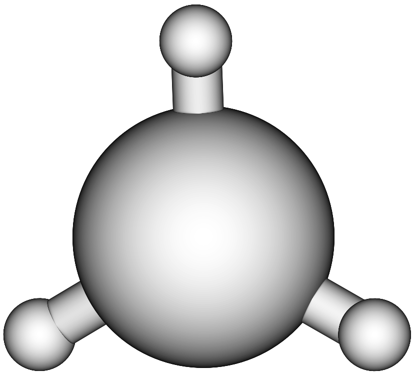

Fig. 1

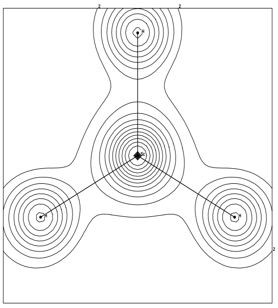

Fig. 2a

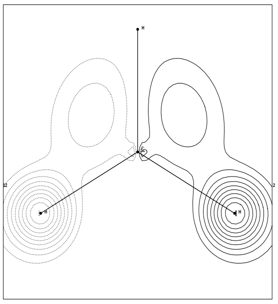

Fig. 2b