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Löwdin population analysis is not rotationally invariant

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Abstract

It is discussed that the Löwdin atomic populations (atomic populations computed in a Löwdin-orthogonalized basis) are invariant only under unitary transformations of the basis orbitals centered on the same atom, but not under the general rotational-hybridizational transformations as are the Mulliken populations. As a consequence, if basis sets containing 6 d-orbitals (or 10 f-orbitals, etc.) are used, then the Löwdin populations do not possess correct rotational invariance and equivalent atoms may be assigned different populations. Therefore, usual Löwdin populations are not appropriate tools of analysis if such basis sets are used. No such difficulty arises in the version proposed by Davidson, in which the basis orbitals belonging to the individual atoms are pre-orthogonalized; it, however, gives quite different results than the conventional scheme.

1. Introduction

Probably Pople [1] was the first who stressed the importance of the requirement of rotational invariance, i.e., that the results of a quantum chemical calculation should not depend on the orientation of the molecule with respect to the external coordinate frame. Most recently I have observed that the Löwdin atomic populations (the atomic populations computed in a Löwdin-orthogonalized basis [2,3]) which are used both as interpretative tools and as input data for some solvational etc. calculations, do not always fulfill this basic requirement. It has been found that in some cases the results of Löwdin population analysis exhibit a rotational dependence and predict non-equal populations for equivalent atoms, if the latter are oriented in different manner with respect to the Cartesian axes. Such an unexpected behaviour occurs if the basis set used contains the 6 Cartesian d-orbitals, as it is standard in the popular 6-31G* and 6-31G** basis sets, while no invariance problem appears if one uses the 5 'pure' d-orbitals. Contrary to this, Mulliken-populations are always invariant (for and explicit proof see the textbook [3]), and no invariance problem occurs either if the basis orbitals on the individual atoms are pre-orthogonalized, as used by Clark and Davidson [4]; this later scheme, however, gives quite different results than the conventional one (e.g. [5]).

The aim of the present note is to discuss briefly this situation and to call the attention that the usual Löwdin populations are lacking any physical meaning and do not represent appropriate tools of analysis if basis sets with 6 d-orbitals (or 10 f-orbitals, etc.) are used – although they are computed by different standard software systems without issuing any warnings. Obviously, the use of a quantity lacking correct rotational invariance cannot be admitted, even if the effect may be not too large.

Some simple numerical examples are presented in Table 1 and Fig. 1 (RHF level of theory). These calculations have been performed by a modified version of our program APOST [6] which processes the data in the 'formatted checkpoint file' generated by either of the 'GAUSSIAN' program series. The Löwdin population routine has been tested against several standard quantum chemical software packages; the numbers in Table 1 have also been cross-checked in a fully independent calculation performed by using GAUSSIAN-03 with the options 'Nosym' and 'iop(6/80 = 1)'.

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Table 1
Löwdin 'atomic populations' in the water molecule[a] calculated by using the 6-31G** basis set

Atom	Population
Symmetric arrangement[b]	
O	8.44351324
H_1	0.77824338
H_2	0.77824338
Non-symmetric arrangement[c]	
O	8.43688477
H_1	0.781971188
H_2	0.781144043

[a] R(OH) = 0.9437 Å, ∠HOH = 105.84°.
[b] Molecule in the *xy*-plane, the bisector of the HOH angle directed along the axis *x*.
[c] Molecule in the *xy*-plane, one of the OH bonds directed along the axis *x*.

2. Invariant and non-invariant situations

As it is well known, the central step in performing Löwdin-orthogonalization is the diagonalization of the overlap matrix $\mathbf{S}$ by a unitary matrix $\mathbf{V}$

$$\mathbf{V}^{\dagger}\mathbf{S}\mathbf{V} = \mathbf{\Lambda}, \tag{1}$$

where matrix $\mathbf{\Lambda}$ is diagonal, with the diagonal elements $\lambda_\mu > 0$. The basis orbitals and the orbital coefficients transform to the Löwdin-orthogonalized basis by matrices $\mathbf{S}^{-1/2}$ and $\mathbf{S}^{1/2}$, respectively, which can be obtained as:

$$\begin{aligned} \mathbf{S}^{-1/2} &= \mathbf{V}\mathbf{K}\mathbf{V}^{\dagger}, \\ \mathbf{S}^{1/2} &= \mathbf{V}\mathbf{L}\mathbf{V}^{\dagger}, \end{aligned} \tag{2}$$

where $\mathbf{K} = \mathbf{\Lambda}^{-1/2}$ and $\mathbf{L} = \mathbf{\Lambda}^{1/2}$ are diagonal matrices with $\lambda_\mu^{-1/2}$ and $\lambda_\mu^{1/2}$ in their diagonal positions, respectively.

In the Löwdin basis the overlap matrix is a unit matrix, thus the orbital populations are expressed by the respective diagonal matrix elements $D^L_{\mu\mu}$. As the orbital coefficients transform by matrix $\mathbf{S}^{1/2}$, the density matrix in the Löwdin basis is $\mathbf{D}^L = \mathbf{S}^{1/2}\mathbf{D}\mathbf{S}^{1/2}$, thus the Löwdin population on atom A is given by

$$Q^L_A = \sum_{\mu\in A} (\mathbf{S}^{1/2}\mathbf{D}\mathbf{S}^{1/2})_{\mu\mu}, \tag{3}$$

where symbol $\mu \in A$ indicates the orbitals belonging to atom A. Accordingly, the resulting 'atomic charge' of atom A will be equal to $Z_A - Q^L_A$, where Z_A is the nuclear charge.

Now we shall show that the Löwdin populations are invariant under every *unitary* transformations of orbitals belonging to the same atom. To see this, let us consider the most general such transformation; it can be described by a block-diagonal unitary matrix

$$\mathbf{Z} = \begin{pmatrix} \mathbf{Z}^1 & \mathbf{0} & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \mathbf{Z}^2 & \mathbf{0} & \dots & \mathbf{0} \\ \vdots & \vdots & \vdots & & \vdots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \dots & \mathbf{Z}^M \end{pmatrix}, \tag{4}$$

where every $\mathbf{Z}^K$ is unitary and describes transformation of the orbitals belonging to atom K. (M is the number of the atoms in the system.) Using matrix $\mathbf{Z}$, the transformation of the whole basis of dimension m can compactly be defined as

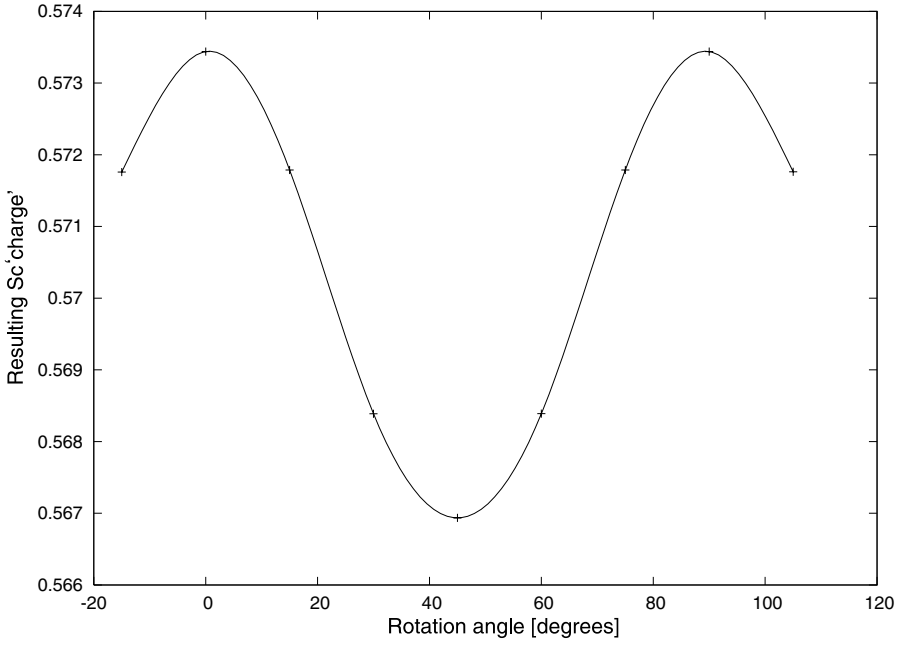

Fig. 1. The resulting 6-31G* Löwdin 'atomic charge' on the Sc atom in the ScF molecule rotated in the *xy* plane ($R_{ScF} = 1.950661$ Å).

$$\chi'_\mu = \sum_{\nu=1}^{m} Z_{\nu\mu}\chi_\nu, \quad \mu = 1,2,\ldots,m. \tag{5}$$

It follows from the general rules (e.g. [3]) that the overlap and density matrices **S** and **D**, respectively, transform as

$$\mathbf{S}' = \mathbf{Z}^\dagger\mathbf{S}\mathbf{Z}, \tag{6}$$

and

$$\mathbf{D}' = \mathbf{Z}^{-1}\mathbf{D}\mathbf{Z}^{-1\dagger} = \mathbf{Z}^\dagger\mathbf{D}\mathbf{Z}, \tag{7}$$

where we utilized that matrix **Z** is unitary ($\mathbf{Z}^{-1} = \mathbf{Z}^\dagger$).

One may insert two unit matrices $\mathbf{1} = \mathbf{Z}\mathbf{Z}^\dagger$ into Eq. (1) and get by using (6)

$$\mathbf{V}^\dagger\mathbf{Z}\mathbf{Z}^\dagger\mathbf{S}\mathbf{Z}\mathbf{Z}^\dagger\mathbf{V} = \mathbf{V}^\dagger\mathbf{Z}\mathbf{S}'\mathbf{Z}^\dagger\mathbf{V} = \mathbf{\Lambda}, \tag{8}$$

which means that after the unitary transformation **Z** of the basis orbitals the unitary matrix $\mathbf{V}'$ diagonalizing the transformed overlap matrix $\mathbf{S}'$ is

$$\mathbf{V}' = \mathbf{Z}^\dagger\mathbf{V}, \tag{9}$$

while the eigenvalue matrix $\mathbf{\Lambda}$ remains invariant. Obviously the same holds for matrix **L**, too. Therefore matrix $\mathbf{S}^{1/2}$ transforms as

$$\mathbf{S}'^{1/2} = \mathbf{V}'\mathbf{L}\mathbf{V}'^\dagger = \mathbf{Z}^\dagger\mathbf{V}\mathbf{L}\mathbf{V}^\dagger\mathbf{Z} = \mathbf{Z}^\dagger\mathbf{S}^{1/2}\mathbf{Z}. \tag{10}$$

By substituting (7) and (10) into (3) and using $\mathbf{Z}\mathbf{Z}^\dagger = \mathbf{1}$, one easily gets for the value of the Löwdin population after the unitary transformation

$$\begin{aligned} Q_A^{L'} &= \sum_{\mu\in A}(\mathbf{Z}^\dagger\mathbf{S}^{1/2}\mathbf{D}\mathbf{S}^{1/2}\mathbf{Z})_{\mu\mu}, \\ &= \sum_{\mu\in A}\sum_{\rho,\tau=1}^{m}(\mathbf{Z}^\dagger)_{\mu\rho}(\mathbf{S}^{1/2}\mathbf{D}\mathbf{S}^{1/2})_{\rho\tau}\mathbf{Z}_{\tau\mu}. \end{aligned} \tag{11}$$

Now, by utilizing the fact that if $\mu \in A$ then $(\mathbf{Z}^\dagger)_{\mu\rho}$ and $\mathbf{Z}_{\tau\mu}$ differ from zero only if $\rho \in A$ and $\tau \in A$, respectively, Eq. (11) may be rewritten as

$$\begin{aligned} Q_A^{L'} &= \sum_{\mu,\rho,\tau\in A}\mathbf{Z}_{\tau\mu}(\mathbf{Z}^\dagger)_{\mu\rho}(\mathbf{S}^{1/2}\mathbf{D}\mathbf{S}^{1/2})_{\rho\tau} \\ &= \sum_{\rho\in A}(\mathbf{S}^{1/2}\mathbf{D}\mathbf{S}^{1/2})_{\rho\rho} = Q_A^L, \end{aligned} \tag{12}$$

which proves the invariance of the Löwdin populations under unitary transformations of the basis orbitals centered on the individual atoms.

In the case in which the transformation matrix **Z** is not unitary, the transformed overlap matrix is again described by relation (6); it is again Hermitian, but the transformation is not any more a similarity transformation and the eigenvalues of the overlap matrix become different [1]. As a consequence, the above considerations cannot be applied and the Löwdin populations are, in general, not invariant. This may be connected with the fact that the Löwdin populations are expressed via the matrix $\mathbf{S}^{1/2}$, which, in turn, is intimately related to the matrix **L** containing the square roots of the eigenvalues of the overlap matrix.

Another possible look on the problem is the following. Matrix $\mathbf{S}^{1/2}$ can be obtained by using the series expansion in terms of the powers of the off-diagonal part of the overlap matrix $\mathbf{s} = \mathbf{S} - \mathbf{1}$. The powers of **s** transform similarly to the matrix **S** if the transformation is unitary, because in that case one has

$$\begin{aligned} \mathbf{s}'^2 &= (\mathbf{S}' - \mathbf{1})^2 = \mathbf{Z}^\dagger\mathbf{S}\mathbf{Z}\mathbf{Z}^\dagger\mathbf{S}\mathbf{Z} - 2\mathbf{Z}^\dagger\mathbf{S}\mathbf{Z} + \mathbf{1} \\ &= \mathbf{Z}^\dagger(\mathbf{S} - \mathbf{1})^2\mathbf{Z} = \mathbf{Z}^\dagger\mathbf{s}^2\mathbf{Z}, \end{aligned} \tag{13}$$

and so on. Thus one can arrive to (10) in an independent manner. If, however, **Z** is not unitary, then (13) does not hold, thus (10) does not hold either.

Rotation of the molecule as a whole with respect to the external frame induces a unitary transformation between the basis orbitals if they are expressed by *pure spherical harmonics*, as is the case when the set of 5 d-orbitals is applied, but not when one uses 6 d-orbitals: the basis functions proportional to x^2, y^2 and z^2 are not orthogonal, and the transformation matrix connecting the basis orbitals before and after the rotation is not unitary. The situation is different if one performs a pre-orthogonalization of basis orbitals on each atom, as used by Clark and Davidson [4]: the transformation between two orthogonal basis sets spanning the same subspace is unitary, thus pre-orthogonalization ensures rotational invariance automatically. We plan to perform in the near future a systematic comparison of the two-variants of Löwdin population analysis (with and without pre-orthogonalization) in order to compare their performance.

3. Conclusion

The aim of this note is to call the attention to the fact that the use of atomic populations computed in a Löwdin-orthogonalized basis, often representing rather useful quantities, must be avoided if the basis used contains the 6 Cartesian d-orbitals as is the case of the standard 6-31G* and 6-31G** basis sets, because they are not rotationally invariant. (Apparently the problem is not actually realized by the scientific community.) It is demonstrated that the Löwdin populations are invariant under unitary transformations, but – contrary to the case of Mulliken populations – this invariance is absent in the case of a general rotation-hybridization transformation.

[1] If two Hermitian matrices have the same set of eigenvalues, then they are related to each other by a similarity transformation performed by a unitary matrix.

Acknowledgements

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