Löwdin Population Analysis With and Without Rotational Invariance

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ABSTRACT: Theoretical arguments and calculations are presented concerning atomic orbital-based population analyses, as well as the way they are affected by rigid rotation of the molecule. It was recently shown that the Löwdin distribution of atomic charges (atomic populations computed in a Löwdin-orthogonalized basis) is, in general, not rotationally invariant unless an initial atom-centered basis of pure spherical harmonics is used or the atomic orbitals on the same atom are pre-orthogonalized. In the present work, we compare the effect of linear transformations of the initial basis on charges within a series of organic, transition metal, and actinide compounds that have been computed in a basis containing either the Cartesian $6d$ and $10f$ orbitals or the pure spherical harmonics ($5d$, $7f$ components), respectively. Löwdin populations obtained without pre-orthogonalization are orientationally dependent when computed in the $6d$-, $10f$-component basis and the asymmetric distribution of the Löwdin atomic charges among symmetry-equivalent atoms is observed.   © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 106: 2065–2072, 2006

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Introduction

Population analysis is a tool used widely by chemists to rationalize molecular properties by determining the distribution of electrons in a molecule among each of its constituent atoms. The mathematical definitions of the properties of atoms in molecules cannot be deduced from the first principles of quantum mechanics, but require additional postulates, and are thus somewhat arbitrary. Popular orbital-based partitioning schemes include Mulliken [1–6] and Löwdin [7]. The former does not require an orthogonal basis, but as a consequence yields gross orbital populations that may have values less than zero or greater than two. In contrast, Löwdin analysis uses a transformation of all the atomic orbitals to an orthogonal basis that automatically restricts the number of electrons in each transformed atomic orbital to the correct range. Both methods lead to populations that are not unique in the complete basis set limit and can be quite unreasonable if diffuse basis functions lacking pronounced atomic character are present. Further, both methods require the use of atom-centered basis sets and are not defined for plane-wave or bond-centered bases. Despite these well-known limitations, the small atom-centered basis set size typically used to calculate organic molecules has led to a long history of successful applications of the Mulliken and Löwdin methods. Although less frequent, both Mulliken and Löwdin techniques have been applied to transition metal and actinide complexes, where larger basis sets sometimes yield quantities that are not chemically meaningful [8].

Recently, Mayer [9] has considered another fundamental aspect of Mulliken and Löwdin analysis, that 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) [10]. Mulliken populations can be shown to be invariant under any general linear transformation of the basis functions on one center among themselves [11]. The Löwdin method, on the other hand, is only strictly invariant under unitary transformation of atom-centered basis orbitals. As such, the Löwdin population analysis may exhibit rotational dependence and can predict nonequal populations for symmetry equivalent atoms in the conventional Cartesian Gaussian basis but will have no problem with a spherical harmonic basis. As an example, consider the 6-component Cartesian d orbitals wherein the basis functions x^2, y^2, and z^2 are not orthogonal, or the 10-component Cartesian f orbitals, which is found in the standard 6-31G* basis set. Although the original work of Löwdin was based on semi-empirical calculations where the one-center bases were orthonormal by assumption, the correct generalization of his scheme to a more general basis set has led to two different implementations.

Conventional Cartesian Gaussian atomic basis sets are defined relative to a fixed axis system. Rotation of the molecule within that axis system is equivalent to rotation of the axes in the reverse direction and hence generates a linear transformation of the basis set relative to an axis system fixed in the molecule. If a basis of spherical harmonics, or any orthonormal atomic basis, is used, it is well known that rotation of the axes will generate a unitary transformation of the basis. Davidson has made use of this by transforming all results to a basis in which the AOs belonging to the same atom have been orthogonalized before carrying out a Löwdin analysis (pre-orthogonalization) [12]. The second, more popular, implementation of Löwdin's method does not invoke pre-orthogonalization, and has been recently shown to lead to rotational variance in the cases of H_2O and ScF [9]. For the sake of clarity, the common implementation will be labeled Löwdin, while the pre-orthogonalized version will be designated as Davidson–Löwdin.

In the present study, we systematically compare the performance of Mulliken, Löwdin, and Davidson–Löwdin schemes for a series of organic, transition metal, and actinide compounds using either a 5d-, 7f- or 6d- 10f-component basis. For the latter, the conventional Löwdin populations exhibit a periodic dependence on the angle describing the rotation of the molecule as a whole and deviation from an equal distribution of Löwdin atomic charges for symmetry-equivalent atoms. This is completely meaningless from the physical point of view; of course no such erratic behavior is observed in either the Davidson–Löwdin or Mulliken methods.

Theory: Rotational Variance and Invariance in Population Analysis

The Mulliken population [2–6] on an atom A in a molecule is defined as

$$N_A^M = \sum_{k \in A} (\mathbf{PS})_{kk}, \qquad (1)$$

where k refers to the index of basis orbitals centered on atom A. In Eq. (1), $\mathbf{P}$ is the density matrix formed from the products of the expansion coefficients for the wave function

$$\mathbf{P} = \mathbf{P}^\alpha + \mathbf{P}^\beta \qquad (2)$$

with

$$\mathbf{P}^\sigma = \sum_{i=1}^{n\sigma} c_i^\sigma c_i^{\sigma\dagger}, \qquad (3)$$

where c_i^σ is the vector of the orbital coefficients of the ith occupied orbital of spin σ ($\sigma = \alpha$ or β) and n_σ is the number of the latter. The matrix $\mathbf{S}$ in Eq. (1) refers to the overlap matrix. Eq. (1) is not the only possibility for calculating populations, as it is a well-known property of matrices that, for three square matrices $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$,

$$\mathrm{tr}(\mathbf{ABC}) = \mathrm{tr}(\mathbf{BCA}) = \mathrm{tr}(\mathbf{CAB}). \qquad (4)$$

Therefore, taking the trace of $\mathbf{S}^\lambda \mathbf{P} \mathbf{S}^{\lambda-1}$ will give the same number, N, for any λ but different partial traces over the blocks corresponding to each atom. The only measurable physical quantity, the number of electrons, will be the same for an infinite number of schemes for determining electron populations on each atom. It was shown [7, 13] that the linear transformation $\mathbf{S}^{-1/2}$ produced the orthonormal basis set having maximum similarity in the least-squares sense to the original nonorthogonal basis. If the population on center A is chosen to be the population of these orthogonalized orbitals most like the original basis on A, the Löwdin population is obtained:

$$N_A^L = \sum_{k \in A} (\mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2})_{kk}. \qquad (5)$$

The atomic charges for each methodology can be written as

$$q_A^M = Z_A - N_A^M \qquad (6)$$

and

$$q_A^L = Z_A - N_A^L, \qquad (7)$$

respectively.

As shown by Mayer [9], the effect of a rotation upon the Löwdin populations can be understood by examining how the $\mathbf{S}$ and $\mathbf{P}$ matrices behave under such a transformation. The overlap and coefficient matrices transform under a rotation as:

$$\mathbf{S}' = \mathbf{Z}^\dagger \mathbf{S} \mathbf{Z} \qquad (8)$$

$$\mathbf{P}' = \mathbf{Z}^{-1} \mathbf{P} \mathbf{Z}^{-1\dagger} = \mathbf{Z}^\dagger \mathbf{P} \mathbf{Z}, \qquad (9)$$

where $\mathbf{Z}$ is a block diagonal matrix with diagonal blocks consisting of the transformation matrices for the individual atoms. The second equality in (9) is valid only if the basis set on each atom is (separately) orthonormalized, then $\mathbf{Z}$ is unitary ($\mathbf{Z}^{-1} = \mathbf{Z}^\dagger$). Consequently, $\mathbf{S}'^{1/2} = \mathbf{Z}^\dagger \mathbf{S}^{1/2} \mathbf{Z}$, and the Löwdin population on A in the newly rotated coordinate system is

$$N_A'^L = \sum_{k \in A} (\mathbf{S}'^{1/2} \mathbf{P}' \mathbf{S}'^{1/2})_{kk} = \sum_{k \in A} (\mathbf{Z}^\dagger \mathbf{S}^{1/2} \mathbf{Z} \mathbf{Z}^\dagger \mathbf{P} \mathbf{Z} \mathbf{Z}^\dagger \mathbf{S} \mathbf{Z})$$

$$= \sum_{k \in A} (\mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2})_{kk} = N_A^L. \quad (10)$$

Equation (10) results from the block-diagonal character of the $\mathbf{Z}$ transformation matrix. Thus, the Löwdin population on each atom A is guaranteed to be rotationally invariant if the transformation of the basis is unitary, which will be true if the basis set of atomic orbitals on A is previously orthogonalized, and so $\mathbf{P}' = \mathbf{Z}^\dagger \mathbf{P} \mathbf{Z}$. The orthogonality of the atom-centered basis set is a sufficient, but not necessary, condition of rotational invariance. The necessary condition is the orthogonality of those basis orbitals that transform between themselves under rotation. As an example, consider an atomic basis that is composed of several sets of pure s, p, d, or f spherical harmonics. A rotational transformation will not mix the different s, p, d, etc., sets of spherical harmonics, neither will it those basis orbitals of the same type which belong to different "shells" (i.e., different Gaussian exponents). A sufficient condition for rotational invariance is the use of pure spherical harmonics because they (the p, d, f orbitals of the same shell) are orthogonal to one another. The pure spherical harmonics occur in the 5d-, 7f-component basis, but not the 6d-, 10f-component one. In the latter, the transformation matrix $\mathbf{Z}$ is not unitary. Consequently, $\mathbf{S}'^{1/2}$ will not be related to
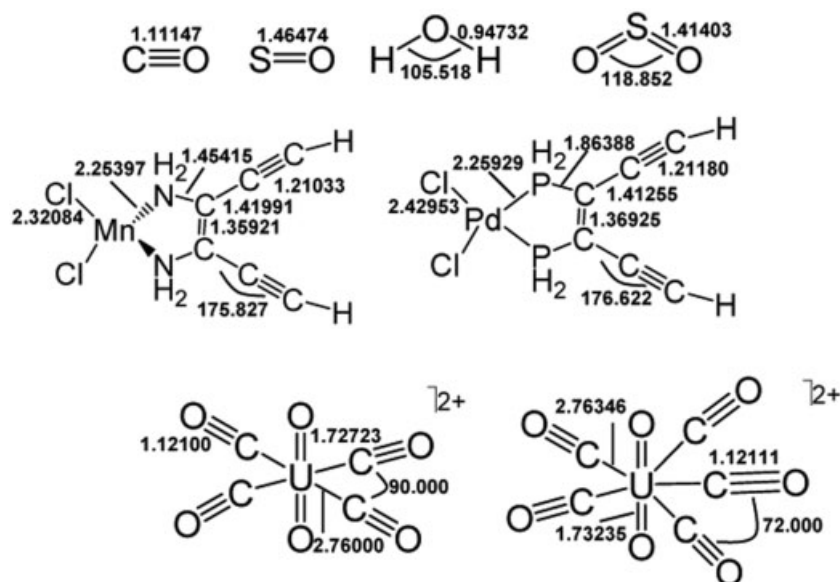
FIGURE 1. Hartree–Fock/6-31G* optimized geometries of main group molecules and the structures for the transition metal, and actinide complexes obtained with density functional theory [17, 18].

$S^{1/2}$, using Z, and so the Löwdin population on atom A may vary with rotation. The difference between the rotational dependence of the Löwdin formalism and that of Mulliken lies in the fact that the Löwdin populations are expressed via the matrix $S^{1/2}$, whereas the Mulliken populations are expressed via S. The Mulliken populations can be related to S' via any nonsingular transformation of the orbitals on the same center, while the Löwdin populations are invariant only under unitary transformations, because $S^{1/2}$ is calculated by using the eigenvalues of S, and nonunitary transformations do not leave the eigenvalues invariant (see discussion by Mayer [9]).

Computational Details

The geometries of CO, SO, H_2O, and SO_2 were optimized using Hartree–Fock theory (HF), with the 6-31G* basis set [14, 15] as implemented in Gaussian 03 [16] (Fig. 1). Population analyses of the *cis*-1,5-hexadiyne-3-ene transition metal complexes $MnCl_2(NH_2)_2C_6H_2$ (**1**), $PdCl_2(PH_2)_2C_6H_2$ (**2**), and the $UO_2(CO)_4^{2+}$ (**3**), and $UO_2(CO)_5^{2+}$ (**4**), actinide compounds were performed at the highest symmetry DFT optimized structures that have been discussed elsewhere [17, 18] (Fig. 1). The LANL2DZ basis set [19] with the LANL2 effective core potential [19] was used to describe elements beyond row

three in the transition metal complexes. The Stuttgart relativistic effect core potential was used to replace the inner 60 electrons of the U atom in each of the actinide complexes, while the outer core 5*d*, 6*s*, and 6*p* electrons and valence 5*f*, 6*d*, 7*s*, and 7*p* electrons were explicitly treated using a [6*s*6*p*5*d*3*f*] contracted Gaussian basis [20]. The 6-31G* basis [15] was used to treat the main group elements. Within the single-point Gaussian calculations the "NOSYM" and "SCF=TIGHT" keywords were used. Density functional theory (DFT), with the B3LYP exchange-correlation functionals [21, 22] (with integrals performed over an ultra-fine grid), was used to calculate the energies, densities, and Kohn–Sham orbitals for the transition metal and actinide complexes, while restricted HF theory was used to determine these properties for the simple main group molecules. Wave functions were generated from DFT by constructing a single Slater determinant from the Kohn–Sham orbitals. Calculations were made using both the "pure" 5*d*, 7*f* basis sets and with the 6*d*-, 10*f*-component Cartesian ones, respectively.

The Mulliken and Löwdin analyses were performed with Gaussian 03 [16], while the Davidson–Löwdin results were obtained with MELD [23] and a small ad hoc program based upon APOST [24] (using different pre-orthogonalization schemes, which, however, do lead to identical results for identical systems). The charges were determined

TABLE I

Mulliken (M), Davidson–Löwdin (DL), and Löwdin (L) atomic charges (calculated with 6d- and 10f-component Cartesians in the 6-31G* basis) for main group molecules under rotation in 15° increments from the standard orientation, $\theta = 0°$.*

	CO		SO		H_2O		SO_2			
Angle	C	O	S	O	O	H	H	S	O	O
M	0.26572	−0.26572	0.44656	−0.44656	−0.86879	0.43440	0.43440	1.07507	−0.53754	−0.53754
DL	0.01277	−0.01277	0.39699	−0.38699	−0.56923	0.28461	0.28461	0.86898	−0.43449	−0.43449
L, $\theta = 0$	0.06551	−0.06551	0.45519	−0.45519	−0.72975	0.36487	0.36487	1.12869	−0.56435	−0.56435
L, $\theta = 15$	0.06692	−0.06692	0.45457	−0.45457	−0.72806	0.36435	0.36372	1.12873	−0.56403	−0.56470
L, $\theta = 30$	0.06757	−0.06757	0.45332	−0.45332	−0.72471	0.36267	0.36204	1.12889	−0.56412	−0.56477
L, $\theta = 45$	0.06785	−0.06785	0.45299	−0.45299	−0.72305	0.36152	0.36152	1.12902	−0.56451	−0.56451
L, $\theta = 60$	0.06757	−0.06757	0.45332	−0.45332	−0.72471	0.36267	0.36204	1.12889	−0.56477	−0.56412
L, $\theta = 75$	0.06692	−0.06692	0.45457	−0.45457	−0.72806	0.36435	0.36372	1.12873	−0.56470	−0.56403
L, $\theta = 90$	0.06655	−0.06655	0.45519	−0.45519	−0.72975	0.36487	0.36487	1.12869	−0.56435	−0.56435

* Mulliken and Davidson–Löwdin charges were invariant to rotation. For the main group molecules, the atomic charges were only invariant to the fifth decimal place due to finite accuracy in the MO coefficients when computed separately at each orientation by convergence of the energy.

for molecules under rotation in the y,z-plane in increments of 15° from the standard orientation. This amounts to shifts of both the atomic coordinates, as well as the molecular center of mass. It has been shown that the Davidson–Löwdin and Mulliken populations are always rotationally invariant, however finite accuracy in the MO coefficients due to convergence of the energy leads to inaccuracy of the computed value in the fifth decimal place for the main group molecules, and the third decimal place in the metal complexes.

Results and Discussion

MAIN GROUP DIATOMIC AND TRIATOMIC MOLECULES

Beginning with a series of main group diatomic and triatomic molecules, Table I illustrates the rotational dependence of the Löwdin charges when calculated in a 6-component d Cartesian basis. No such variance can be observed in the Davidson–Löwdin and Mulliken charges; hence, only a single value is indicated. Although the magnitude of rotational dependence is not large in the Löwdin method, rotation in 15° increments within the y,z plane of the molecule alters not only the atomic populations, but also the distribution of charge between symmetry equivalent atoms. In both H_2O and SO_2, rotation causes unequal distribution of charge between identical centers. For example, ro-

tation of 15° from the standard orientation of SO_2 alters the charge on the sulfur atom by 10^{-4} electrons and leads to an unequal charge distribution between the oxygen atoms. Such discrepancies represent less than 1% of the total calculated charge of the main group elements.

As shown in Figure 2, the variance of the Löwdin atomic charges depends upon rotation from the standard orientation, with a periodicity of 90°. Significant differences in the amplitudes of the vari-
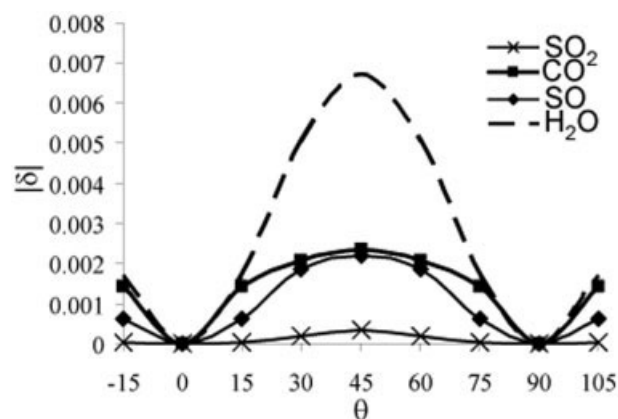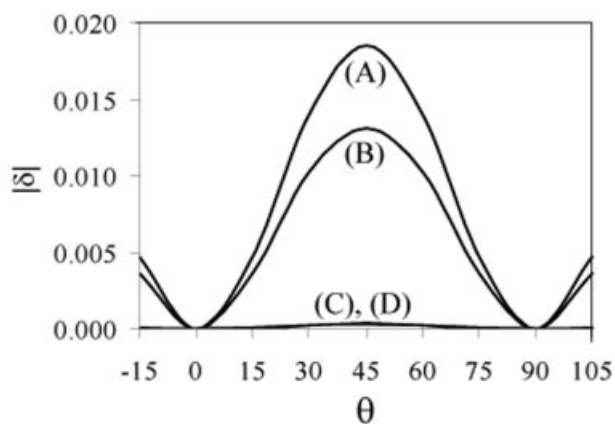

FIGURE 2. Absolute value of the deviation $|\delta|$ in Löwdin atomic charges for the heaviest elements in CO, SO, H_2O, and SO_2, as a function of rotation (θ) from the standard orientation ($\theta = 0°$) in the plane of the molecule (y,z-plane), calculated by HF with the 6-31G* basis set.

ance at the peak maxima ($\theta = 45°$) are also observed. The rotational variance increases with basis set size, as participation of the nonpure spherical d harmonics increases in the wave function. As shown in Figure 3 for SO_2, increasing the basis set from 6-311G* to 6-311++G(3df,3pd) enhances the rotational variation by two orders of magnitude.

TRANSITION METAL AND ACTINIDE COMPLEXES

When metal complexes are computed in a non-pure spherical harmonic basis, the inappropriate behavior of the Löwdin charges is amplified due to enhanced participation of the d and f orbitals in the molecular wave function. Here, the d and f orbitals are true valence orbitals rather than merely polarization functions. Table II shows the atomic charges of the transition metal and actinide centers in compounds **1**–**4**, at the standard orientation and upon rotation by 45° (the maxima in the periodicity if the rotational variance). Table II demonstrates that the Löwdin charges deviate as a function of rotation by 10^{-1} or 10^{-2} electrons in the metal complexes as compared with 10^{-3} or 10^{-4} electrons in the main group molecules (cf. Table I). The large discrepancies in the former can amount to a significant percentage of the total predicted charge. For example, the maximum deviation in metal charge for the planar Pd complex (**2**) is 0.04, approximately 5% of

FIGURE 3. Absolute value of the deviation $|\delta|$ in Löwdin atomic charges for the sulfur atom in SO_2, as a function of rotation (θ) from the standard orientation ($\theta = 0°$) in the plane of the molecule, calculated by Hartree–Fock with (A) the 6-311++G(3df,3pd) basis set, (B) the 6-31G(3df,3pd) basis set, (C) the 6-311G basis set, (D) the 6-31G* basis set.

TABLE II _____

Mulliken (M), Davidson–Löwdin (DL), and Löwdin (L) metal atomic charges for 1–4, obtained by B3LYP, at the standard orientation ($\theta = 0$) and upon rotation by 45° using both the 5d7f- and 6d10f-component Cartesian basis sets.*

Molecule	M	DL	L θ = 0	L θ = 45°
	5d7f Cartesian basis			
$MnCl_2(NH_2)_2C_6H_2$	0.752	−0.589	0.010	0.010
$PdCl_2(PH_2)_2C_6H_2$	−0.166	−1.471	−0.808	−0.808
$UO_2(CO)_4^{2+}$	1.365	−1.104	−0.293	−0.293
$UO_2(CO)_5^{2+}$	1.217	−1.558	−0.622	−0.622
	6d10f Cartesian basis			
$MnCl_2(NH_2)_2C_6H_2$	0.609	−0.630	−0.071	−0.063
$PdCl_2(PH_2)_2C_6H_2$	−0.362	−1.550	−0.928	−0.888
$UO_2(CO)_4^{2+}$	1.424	−1.374	−0.677	−0.904
$UO_2(CO)_5^{2+}$	1.309	−1.888	−1.130	−1.355

* The 6-31G* basis described the main group atoms, while Mn and Pd used the LANL2DZ basis with the LANL2 effective core potential, and U used the [6s6p5d3f] contracted Gaussian basis, with the Stuttgart relativistic electron effective core potential. For the transition metal and actinide complexes, the M and DL atomic charges calculated using an orthogonal basis were only invariant to the third decimal place due to finite accuracy in the MO coefficients when computed separately at each orientation by convergence of the energy.

the total charge on the Pd center. When both d and f orbitals contribute to bonding, the deviation increases to as much as 34% of the total metal charge, that observed in $UO_2(CO)_4^{2+}$. As in the main group diatomics and triatomics, the asymmetric distribution of charge on symmetry equivalent atoms is of the same magnitude as the deviation in atomic charge upon rotation (Fig. 4). Figure 4 further illustrates that among the oxygen atoms in $UO_2(CO)_5^{2+}$, the largest rotational variance is observed for the doubly bonded uranyl oxygen, as its bonding with the metal center involves the participation of d and f orbitals.

Finally, it is to be noted that the three charge definitions can give quite different results: the same atom (e.g., Mn in $MnCl_2(NH_2)_2C_6H_2$) may appear strongly positive, strongly negative, or nearly neutral, depending on what method is used. Although Mulliken analysis appears to yield results that are more physically intuitive (i.e., positive metal charges), closer inspection reveals the typical problems associated with this method: gross metal atomic orbital populations that exceed two or that
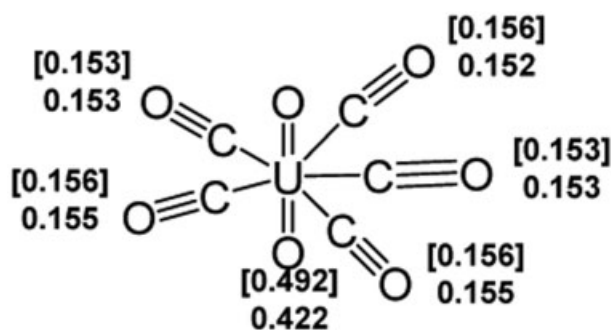
FIGURE 4. Löwdin atomic charges on symmetry equivalent oxygen atoms in the plane of rotation at $\theta = 0°$ and $\theta = 45°$ (in brackets), using the $6d$ $10f$-component Cartesian basis sets. The 6-31G* basis described the main group atoms, while U used the $[6s6p5d3f]$ contracted Gaussian basis, with the Stuttgart relativistic electron effective core potential.

are less than zero. In the case of $UO_2(CO)_4^{2+}$, several of the $6d$ and $7f$ AOs have significant negative electron populations (e.g., -0.38035 in the d_{x2} AO).

Conclusion

It has been demonstrated that the Mulliken and pre-orthogonalized Löwdin population analyses are invariant to a general rotation transformation, while the standard non-pre-orthogonalized implementation of the Löwdin formalism may not be so. In the latter, rotational variance is observed when a nonpure spherical harmonic basis is used that contains d or f components (e.g., with $6d$ $10f$ Cartesians). An asymmetric distribution of the Löwdin atomic charges among symmetry-equivalent atoms is also observed. This incorrect behavior occurs in only the third or fourth decimal place for main group elements with a reasonable basis set (e.g., 6-31G*). However, when the d or f components participate significantly to the wave function, the rotational dependence increases by up to two orders of magnitude. This occurs when the basis set is increased, or, if the d or f orbitals participate in bonding, as in transition metal or actinide complexes.

Although the original work of Löwdin was based on semi-empirical calculations where the one-center bases were orthonormal by assumption, the correct generalization of his scheme to a more general basis set has led to two different implementations. We suggest that the conventional Löwdin population, which uses a non-pre-orthogonalized basis set, is an incorrect generalization of Löwdin's original approach due to its rotational variance.

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