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Comparative study of theoretical partial charges of Zn and Mn-Schiff base complexes

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Abstract

Different partial charge distribution methodologies (Mulliken, Löwdin, Hirshfeld, Natural Population Analysis, Merz–Kollman Electrostatic Potential) were used for charge determination in manganese and zinc Schiff base complexes that are isostructural analogs. Chemical reliable clusters were chosen on the ground of experimental X-ray data. Packing effect on charges was found to be negligible. All calculation employed non hybrid *ab-initio* GGA PBE density functional method with conjunction of different basis sets to show small influence of basis set incompleteness. On the ground of chemical bonding theory Hishfeld partial charge definition was found to be most reliable in different situation – different spin states, H–bonding, molecular crystal and clusters.

Keywords: partial charges, Mulliken, Löwdin, Hirshfeld, NPA, MK ESP, density functional theory

1. **Introduction**

Schiff base complexes of manganese and zinc generally offer attractive properties with a dual role of electron intramolecular and intermolecular transport [1-3], which can be estimated via partial atomic charges. The charge distributions may not solely involve a prediction approach of regioselectivity in electrophilic addition and substitution reactions (of which there are unenumerated examples). For instance, it is possible to cite studies on the reaction of radicals [4, 5]. The charge distributions can also be used as an interpretation tool in comparative analysis of the series of compounds specified in the work presented here. Partial charges can have a very important place in quantitative molecular modeling [6, 7].

There are several approaches to define the charge distributions in molecules (and radicals) in all phases (eg gas-phase, solid-state), which implies that any definition of an atomic domain is essentially imagined. Therefore, it is not possible to canonize any single partition scheme as more ‘correct’ than any other, or acceptable for all purposes, particularly in the presence of various alternatives [8]. The theoretical groundwork of these insights has been extensively developed for several decades on the basis of quantum-mechanical calculations.

For definitions of atomic charges [9] the methods are commonly divided into two major groups: i) methods based on representation of the molecular wave function in a given Hilbert space, and ii) methods based on the 3D electron density presented in Euclidean space.

The oldest definition of atomic charges is the Mulliken population analysis [10-12]. This method exploits the basis functions whereby the wave function is expanded. The half-and-half division of the overlap population does not take into account the difference of properties between two adjacent atoms. This approach is therefore too crude to be correct and (quasi)-degenerate effects can lead to an extremely sensitive outcome; it can result in unrealistic atomic charges [13, 14]. Löwdin’s method [15] attempts to overcome the arbitrariness of equal partitioning of overlap densities by transforming them into a symmetrically orthogonalized basis before population analysis is carried out. In general, the Mulliken charges do not achieve convergence with an increasing basis set size.

Both Mulliken’s and Löwdin’s approach to assign values of partial atomic charges [13] is not only sensitive to the basis set size but, in particular, the results often do not improve with the increasing basis set. Furthermore, the approach provides unphysical charges when using extended basis sets or basis sets that include diffuse functions.

Improvements [13, 16, 17] have been proposed to eliminate the shortcomings associated with atomic charge schemes based on a population of atom-centered basis functions. The most important one is the Natural Population Analysis (NPA) developed by Reed and Weinhold [16, 17]. The NPA charges [17] employ explicitly orthogonalized (natural) atomic orbitals. Thus, the method treats the overlap population problem from a mathematical point of view. Nevertheless, it was found [14] that the NPA analysis still yields unphysically large charges, giving an overly ionic picture of covalent bonds. This is presumably due to competition between localization and resonance of chemical bonding pictures. Mulliken’s and Löwdin’s charges have been referred to as chemically derived (CD) charges [18].

A second class of methods, which is based on the wave function (but not directly), is potential-derived (PD). This approach exploits the electrostatic potential, which is observable and can be directly calculated from the wave function (thus, it is the reason of dependence on a quantum chemical reference). One can calculate partial atomic charges that best reproduce [19, 20] this electrostatic potential in some regions of space surrounding the molecule (thus, it provides dependence on the choice of evaluation points). However, PD charges [18] are often ill–defined [21, 22].

Well-known PD charges (such as Merz-Kollman (MK) [23], CHelp [24] or CHelpG [25]) are derived from computational schemes. The MK partial charges are presented in this work. The method used for fitting the charges differs mainly in the atomic domain choice, resulting in atomic charges that are strongly method-dependent [26].

The second major group of charge distribution analysis methods is based directly on electron density. An example of such an atomic charge scheme is the Hirshfeld method [27, 28]. The method makes use of the electronic density of the molecule and of a fictitious promolecule, made up of overlapping ground-state atoms prior to any charge migration between or within these atoms; it yields neutral atomic charges. Hirshfeld charges have received considerably less attention in studies than other population analysis methods. It is possible that the situation will change since Hirshfeld analysis methodology of charge distribution was implemented as an experimental feature in the widely used Gaussian03 [29] program package.

Promolecule density is defined as the sum over the (usually spherically averaged) ground-state atomic densities $\rho_B(\boldsymbol{r})$:

$$\rho_{molecule}(\mathbf{r}) = \sum_{B} \rho_B(\mathbf{r})$$

The electronic density ($\rho_{molecule}$) of the real molecule at each point in space is then distributed over the atoms A. This is done in the same ratio as simultaneously contributed by the atomic densities $\rho_A(\mathbf{r})$ to the promolecule density:

$$\rho_A^{molecule}(\mathbf{r}) = \frac{\rho_A(\mathbf{r})}{\rho_{promolecule}(\mathbf{r})} \rho_{molecule}(\mathbf{r})$$

The Hirshfeld atomic charge is then obtained by subtracting the integral of the density associated with atom A from the corresponding nuclear charge Z_A:

$$Q_A^{Hirshfeld} = Z_A - \int \frac{\rho_A(\mathbf{r})}{\rho_{molecule}(\mathbf{r})} \rho_{molecule}(\mathbf{r})\, d\mathbf{r}$$

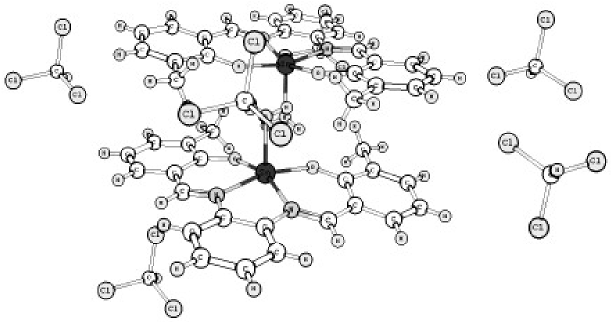
The proposed charge decomposition has been extensively developed, and the recently extended version of this approach is available through the Hirshfeld-I [30]. This remarkable new way of exploring molecular crystals is carried out by isosurface rendering of smooth, non-overlapping molecular surfaces arising from partitioning crystal space based on Hirshfeld's stockholder scheme [31].

It is vital to prove whether the charges agree with the deductions from the great body of various and experimental chemical knowledge.

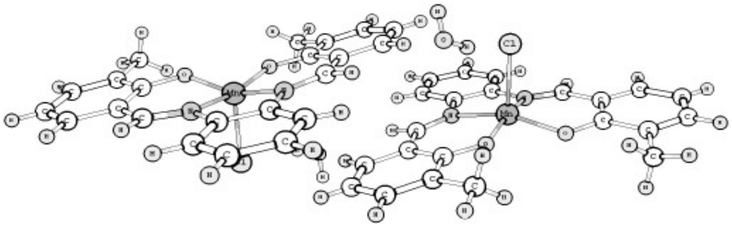
Our aim is to evaluate if the partial charges, obtained (from the different methods on Schiff base complexes) in the series of molecular systems (manganese and zinc Schiff base complexes), have been assigned in a trustworthy (reliable) manner and are chemically correct. In this paper we summarize, present and discuss the atomic charges *averaged* in chemically meaningful groups. Using the results from the five different methods (Mulliken, Löwdin, Hirshfeld, NPA, MK's ESP), the computed values will be the subject of analysis.

2. Computational details

A computer simulation based on a unit cell composed of several *hundreds* of atoms is extremely time consuming. The level model should be decreased. In this paper, molecular crystals are presented as reliable molecular clusters that are 'cut' from molecular crystals. Atoms are fixed in their positions obtained from the experimental X-ray data [1-3]. Our charge distribution study comprises two 'big' clusters and two 'small' clusters isolated *in vacuo* (Fig. 1). Only 'big' clusters are shown on Fig. 1 because every 'small' cluster is a monomeric sub–unit of a 'big' cluster surrounded of solvate molecules.



a) Zn Schiff base complex



b) Mn Schiff base complex

Fig. 1. The structure of the clusters, a) Zn Schiff base complex, and b) Mn Schiff base complex

In our opinion, the most suitable choice of a molecular cluster is a more secluded molecular unit. It is therefore very probable that inner interactions will be more important, with a staggered dimeric pair for O-, N-chelate Zn(H_2O)- and MnCl- complexes surrounded with six corresponding $HCCl_3$ molecules and two corresponding H_2O molecules, and a staggered trimeric cluster of chelating agent's molecules. To verify the transferability of partial charges from molecular cluster to crystal, we performed a qualitative estimation of the crystal packing effects on charge distributions as an influence of cluster cage on charges.

A non-hybrid *ab-initio* GGA PBE [32, 33] density functional method was employed for the calculation of the partial atomic charges and the electronic population analysis of all molecular clusters and molecules studied here. Different basis sets were applied to estimate the basis set dependence of assigning charges for high-valent complexes and chelating agent's molecules. Employed basis sets are double- (SVP), triple-zeta (TZV and TZVP) and 6-31G(2d,p) for different atoms (for basis sets assignment see title of **Tables 1** and **2**). Electronic structures of the dimeric pair of O, N-chelate MnCl-complex in different spin states were explored since CD charges strongly depend on the type of wave function. Stability analysis of wave functions was performed to choose a more trustworthy solution and ensure multiplicity.

The Mulliken [10-12], Löwdin [32], Hirshfeld [27], NPA [16, 17], Merz–Kollman's (MK's), and ESP [22, 23] methods were used to assign corresponding partial charges. All calculations were performed using the Gaussian03 [29] program. For the manganese atom, the corresponding MK's radii was not implemented in Gaussian03. This explains the absence of MK's ESP charges from our study for cluster and molecules containing Mn atoms. However, it will be shown in this paper that unphysical charges are provided where the required parameters are available.

3. Results and Discussion

Partial atomic charges averaged in groups of structural equivalent atoms are collected in **Table 1** (values in a.u.). From **Table 1** we can see the inapplicability of Löwdin, NPA and MK's ESP methods. This is because all presented basis sets show the Cl–atoms in $HCCl_3$ with positive partial charges and C-and H-atoms with *negative* partial charges that are inconsistent with their electronegativity and chemical intuition.

It was important to establish if this was due to the incompleteness or type of basis sets, together with the limitation of the density functional method. In order to ascertain the reason, we calculated atomic charges at the levels PBE with basis sets cc-pVTZ, aug-cc-pVTZ and cc-pVQZ, and B3LYP with basis sets cc-pVTZ, aug-cc-pVTZ and cc-pVQZ. The values were changed but unphysical partial charges were obtained for the above three mentioned methodologies.

The Mulliken prescription for assigning partial atomic charges predicts unphysical charges on H-atoms connected with an aromatic ring. Only Hirshfeld QT-AIM yielded charges that are not controversial with chemical intuition: C- and H-atoms in $HCCl_3$ have positive partial charges; Cl-atoms – negative; C-atoms in aromatic rings ($C_{aromatic}$) – negative. There was only one expectable exclusion of a C-atom connected with the electropositive methyl-group ($C_{aromatic}$-CH_3) because this

C-atom is influenced by an electronegative O-atom in *orto*-position. These two opposite effects may compensate one another from a chemical point of view.

Table 1. Partial atomic charges averaged in chemical meaningful groups for Zn-Schiff base complex assigned at the PBE/SVP level.

Atom *	Partial averaged atomic charges, a. u.				
	Mulliken	Löwdin	Hirshfeld	NPA	ESP
Cl ($HCCl_3$)	-0.038	0.078	-0.031	0.007	0.050
C ($HClCl_3$)	0.093	0.073	0.054	0.196	0.297
H ($HClCl_3$)	0.067	-0.268	0.076	-0.204	-0.349
$C_{aromatic}$ (C-N)	0.106	-0.001	0.031	0.157	0.234
$C_{aromatic}$ (C-O)	0.188	0.059	0.077	0.396	0.372
$C_{aromatic}$ ($C-CH_3$)	-0.168	-0.031	0.004	-0.046	-0.098
$C_{aromatic}$(C-H)	0.068	-0.073	-0.044	-0.170	-0.187
H ($C_{aromatic}$-H)	-0.144	0.056	0.029	0.176	0.124
Zn	0.768	0.579	0.365	1.094	1.062
H(H_2O)	0.035	0.029	0.111	0.453	0.454
O(H_2O)	-0.009	0.013	-0.195	-0.771	-0.857
O(chelating agent)	-0.362	-0.273	-0.219	-0.751	-0.673
N(chelating agent)	-0.049	-0.063	-0.080	-0.570	-0.602

* presented atoms relate to the discussion. In brackets are molecules or adjacent atom chemically bonded with the target atom

There was no noticeable improvement when considering larger basis sets than a standard double- (SVP) basis set such as triple-zeta (TZVP) basis sets for O, N-chelate Zn(H_2O)-complex. In particular, this was the case for describing the charge distribution in the first coordination shell including Zn, O, and N atoms.

Table 2. Partial atomic charges of first coordination shell atoms assigned on the level PBE/TZVP for N, O, Zn + 6-31G(2d,p) for H, C, Cl.

Atom	Partial averaged atomic charges, a. u.				
	Mulliken	Löwdin	Hirshfeld	NPA	ESP
Zn	0.689	0.645	0.354	1.065	1.144
O(H_2O)	-0.554	-0.332	-0.163	-0.214	-0.840
O(chelating agent)	-0.508	-0.313	-0.219	-0.703	-0.755
N(chelating agent)	0.033	-0.071	-0.075	-0.615	-0.510

Therefore, we will use the standard double-(SVP) basis set for O, N-chelate MnCl-complex (staggered dimeric and monomeric), which is in agreement with a very comprehensive study [33]. The main conclusion is that Hirshfeld QT-AIM is the most reliable assigning method for partial charges.

It was established that if two molecules of O and N-chelate Zn(H_2O)-complex are stacked in a staggered dimer with six $HCCl_3$ partial charges of H–atoms in H_2O coordinated with Zn-atom, there was a slight decrease (by 0.05 au). In addition, the values of absolute charges of the O-atoms chelating agent decreased by 0.03 au per atom by H-bonding, and the values of absolute charges of O-atoms in H_2O decreased by 0.03 au. The Hirshfeld charge analysis method uses direct spatial integration of the electronic deformation density, which results in charging effects due to chemical bonding. As can be expected from a chemical point of view, molecules packed in a cluster have a weak influence on partial atomic charges. We can conjecture that the crystal packing effect is small enough if intermolecular H-bonds are not introduced. A similar assumption may be proposed for a chelating agent molecule since intramolecular H-bonds are well recognized. It can be determined that there was a weak influence on charges resulting from inclusion of molecules in a cluster. Some partial charges changed by 0.01 a.u.

Further difficulty for dimeric manganese complexes is experienced with the spin state. We checked stability of wave functions in different multiplicities (11, 9, 7, 5, 1). Total and relative energies of a manganese Schiff base complex are collected in **Table 3** for the above mentioned spin states.

Table 3. Total (E_h) and relative energies (E_{rel}) for staggered dimeric Mn Schiff base complex in different spin state

Multiplicity	E_h, a. u.	E_{rel}, a. u.	E_{rel}, kJ/mol
5	-5587.22	0.0458	124
7	-5587.25	0.0219	60
9	-5587.27	0.0000	0
11	-5587.19	0.0795	216
1	-5587.14	0.1268	344

Surprisingly, all wave functions were found to be stable. The order of relative stability was found from a total energy calculation. The nonet spin configuration (multiplicity=9) is the ground state. The Hirshfeld partial charges were calculated for all atoms. Charges for the first coordination shell are collected in **Table 4**. The packing effect on partial charges was checked for ground state and found to be negligible.

Table 4. Partial atomic charges of first coordination shell atoms assigned on the PBE/SVP level for dimeric Mn Schiff base complex in the ground state

Atom *	Partial averaged atomic charges, a. u.			
	Mulliken	Löwdin	Hirshfeld	NPA
O	-0.282	-0.138	-0.172	-0.564
N	-0.068	0.009	-0.051	-0.485
Mn	0.762	0.281	0.276	0.921
Cl	-0.404	-0.321	-0.333	-0.506

* presented atoms relate to first coordination shell

Conclusion

We have presented calculations of partial atomic charges for a series of compounds, in conjunction with an alternative basis for different atoms with the non-hybrid *ab-initio* GGA PBE [35, 36] density functional method. Five methodologies (Mulliken, Löwdin, Hirshfeld, NPA, MK's ESP) were applied to charge assigning. The Hirshfeld charges are less sensitive to the presence of different basis functions than other charges from the usual population analysis.

The Hirshfeld charge analysis provides charging effects due to chemical bonding like H-bonding. Therefore, as expected, the Hirshfeld charges are the most reliable in different situations (eg different spin states, molecular cluster and association), and give the best results from a chemical point of view. This conclusion is in consensus with the substantial body of experimental chemical knowledge and the chemical bonding theory.

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