

An Extension of the Hirshfeld Method to Open Shell Systems Using Fractional Occupations

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ABSTRACT: In this work, a new partitioning method is presented which allows one to calculate properties of radicals, in particular, atomic spin populations. The method can be seen as an extension of the Hirshfeld-I method [Bultinck, P. et al. *J. Chem. Phys.* **2007**, *126*, 144111], in which the atomic weight functions, defining the atoms-in-molecules, are constructed by means of an iterative scheme in which the charges of the atoms-in-molecules are altered but the spin remains fixed. The Hirshfeld-I method is therefore not suitable for the calculation of atomic spin populations of open-shell systems. The new fractional occupation Hirshfeld-I (FOHI) uses an iterative scheme in which both the atomic charge and spin are optimized, resulting in a self-consistent method for the calculation of atomic spin populations. The results obtained with the FOHI method are compared with experimental results obtained using polarized neutron diffraction, thus serving as a validation of the FOHI method as well as the Hirshfeld definition of atoms-in-molecules in general.

1. INTRODUCTION

Atomic charges are one of the quantities most frequently addressed by chemists when rationalizing structure and reactivity of molecules. Organic chemists tend, for example, to use partial charges when interpreting reaction mechanisms,¹ where they can be used to calculate interaction energies between molecules and to construct potential energy surfaces. Since no unique definition of the charge of an atom can be formulated, different methods have been developed to calculate this property. These methods can be divided into two categories. The first category uses LCAO coefficients of the basis functions, which are used to represent the wave function. The first method developed along these lines, and until now the most widely used due to its simplicity, is the Mulliken population analysis.² The main drawback of the method is its strong basis set dependence, which becomes particularly problematic when diffuse functions are used, leading to results which have no physical meaning.³ The natural population analysis^{4,5} is at this moment the most elaborate population-analysis-based method, being less sensitive to the choice of the basis set but challenging for extensions to other properties than charges.⁶ The other category is based on the electron density in real space. In these methods, the electron density $\rho(\vec{r})$ is divided into atomic densities $\rho_A(\vec{r})$ by making use of atomic weight functions $w_A(\vec{r})$

$$\rho_A(\vec{r}) = w_A(\vec{r})\rho(\vec{r}) \quad (1)$$

Different approaches are possible to define the weight function. In Bader's quantum chemical topology,⁷ the weight function is discrete and can only be equal to one or zero. At every point, the molecular density is thus assigned to one single atom. This atom is enclosed in a basin, separated from the rest of the atoms by a surface constructed using the zero density flux condition. Another example is the method by Becke, which is an overlapping atoms-in-molecules method,⁸ in which the atoms are separated from each other by means of Voronoi polyhedra, and the

Voronoi deformation density (VDD),⁹ which also uses Voronoi polyhedra, but in combination with the deformation density rather than the full density. The Hirshfeld method¹⁰ also uses diffuse boundaries where the weight function of an atom A can be in principle nonequal to zero at any point \vec{r} of the space. The "share" of each atom at point \vec{r} is relative to the share of the free atom in the promolecular density.

$$w_A^H(\vec{r}) = \frac{\rho_A^0(\vec{r})}{\sum_B \rho_B^0(\vec{r})} \quad (2)$$

In economics terms, an atom can thus be seen as owning a share of the molecule's stock of electrons, wherefrom the original name of this procedure, "stockholder method", was derived. The promolecular density is defined as the sum of the densities of the isolated atoms, positioned at the same coordinates as the atomic nuclei in the real molecule. Integration of the atomic density leads to the population of every atom:

$$N_A = \int \rho_A(\vec{r}) d\vec{r} = \int w_A(\vec{r}) \rho(\vec{r}) d\vec{r} \quad (3)$$

In this first version of the Hirshfeld method, the isolated atoms are usually chosen as neutral atoms. The arbitrary character of the choice of the isolated atomic densities to build up the promolecular density is one of the major criticisms on this method.¹¹ One actually assumes that the atoms-in-molecules resemble best the free spherically symmetric neutral atoms. This may be the case for molecules consisting of covalently bonded atoms with no significant electronegativity differences but questionable for molecules such as LiF. For example, the atomic charges in the molecule LiF will depend strongly on whether the promolecular density is composed of Li^0 and F^0 , Li^+ and F^- , or Li^- and F^+ , the second being evidently the more chemically reasonable choice.

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But since making a chemically sensible guess is not always as straightforward in more extended systems, one would prefer a method which does not require any prior knowledge about the chemical properties of the substrate. Moreover, this scheme is clearly problematic when partitioning charged systems, since in that case the actual system and the promolecule contain a different number of electrons.

These problems have recently been solved for the atomic charges in the Hirshfeld-I method¹¹ (HI), by making use of an iterative scheme. In this method, the promolecule in each iteration is constructed from atomic densities obtained in the previous iteration, thus allowing the atomic populations of the atoms-in-molecules to change. As a result, the resulting promolecular density and atomic weight functions no longer depend on the first guess: in the case of LiF, identical atomic charges are obtained when the iterative procedure is started from any of the three possibilities mentioned above. This procedure brings the Hirshfeld method more in line with information theory, on the basis of which expression 3 can be derived.¹² The validity of this improved definition of the Hirshfeld weight-function was confirmed also for other quantities such as polarizabilities,^{13,14} electrostatic potentials,¹⁵ and dispersion interactions.^{16,17}

In principle, atomic spin populations, which are useful in the field of molecular magnetism, can be calculated with the partitioning methods mentioned above.^{18,19} However, straightforward application of these methods to the spin density leads to results which suffer from the same inconsistencies as the charges in the classic Hirshfeld method, namely, the arbitrariness of the choice of spin. In the case of the Hirshfeld-I method, the total number of electrons in each atom in the promolecule is allowed to vary until convergence, but no constraints are laid upon the spin of the atoms. As a result, the Hirshfeld-I method does not seem suitable for open-shell systems when atomic spin populations need to be calculated. In this article, we propose a new method (fractional occupation Hirshfeld-I, FOHI) which extends the Hirshfeld-I method so that the atomic spin populations are also calculated in an iterative way.

The outline of this paper is as follows. Section 2 contains the details of the new method, followed by computational details in section 3. In section 4, the atomic spin populations of both methods will be compared for a set of radicals using different levels of theory. In order to validate the new method, experimental results will be used to compare different partitioning methods. Finally, section 5 contains a brief summary and the conclusions of this paper.

2. METHOD

In order to solve the problem of the fixed isolated atomic densities in the original Hirshfeld method,¹² the HI method¹¹ used the following interpolation formula:

$$\rho_A^{N_A}(r) = \rho_A^{\text{lint}(N_A)}(r)[\text{uint}(N_A) - N_A] + \rho_A^{\text{uint}(N_A)}(r)[N_A - \text{lint}(N_A)] \quad (4)$$

for the calculation of the atomic densities (N_A) needed to construct the promolecular density during the different iterations of their procedure. In eq 4, $\text{lint}(x)$ represents the integer part of x (i.e., lower integer), while $\text{uint}(x) = \text{lint}(x) + 1$ (i.e., upper integer). This function interpolates the atomic density between two atoms with an integer population to compute the atomic density of an atom with a noninteger number of electrons. On

the basis of these atomic densities, a new promolecule is constructed, and a new weight function is calculated. The atomic densities of every atom ranging from integer charges -2 up to $+2$ in their respective spectroscopic ground state are calculated and stored beforehand. Finally, integration leads to new atomic populations, and this process is repeated until the atomic populations are converged for all atoms.

For open-shell systems, atomic spin populations can be obtained by integrating the molecular spin density with the atomic weight functions.

$$N_A^{\text{spin}} = \int w_A(\vec{r})(\rho^\alpha(\vec{r}) - \rho^\beta(\vec{r})) d\vec{r} \quad (5)$$

In the HI method, the weight function $w_A(\vec{r})$ obtained after convergence of the atomic charges is used to calculate the atomic spin populations. However, during the iterations which determine the weight function, the molecular spin density is not used.

The weight function in the HI method was shown to minimize the loss of information entropy by equalizing the number of electrons in the atoms building up the promolecule with the number of electrons in the actual atoms-in-molecules.^{11,12} For example, in a diatomic molecule AB, the loss of information due to the partitioning of the density $\rho(\vec{r})$ into a sum of the approximate atomic densities $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$, instead of the “true” (but unknown) atomic densities $\rho_A^0(\vec{r})$ and $\rho_B^0(\vec{r})$, is given by the following function:

$$I = I_A + I_B = N_A \int \sigma_A(\vec{r}) \ln \left(\frac{\sigma_A(\vec{r})}{\sigma_A^0(\vec{r})} \right) d\vec{r} + N_B \int \sigma_B(\vec{r}) \ln \left(\frac{\sigma_B(\vec{r})}{\sigma_B^0(\vec{r})} \right) d\vec{r} + N_A \ln \left(\frac{N_A}{N_A^0} \right) + N_B \ln \left(\frac{N_B}{N_B^0} \right) \quad (6)$$

where N_A and N_B are the atomic populations of the atoms constituting the promolecule, N_A^0 and N_B^0 are the “true” atomic populations of the atoms in the molecule, and $\sigma(\vec{r})$ is the shape function, defined as²⁰

$$\sigma_A(\vec{r}) = \frac{\rho_A(\vec{r})}{N_A} \quad (7)$$

One can see that eq 6 is minimized if the normalization constraints $N_A = N_A^0$ and $N_B = N_B^0$ are fulfilled, which is achieved by means of the iterative procedure in the HI method.

In open shell molecules, where the electrons of opposite spin are described by separate densities $\rho^\alpha(\vec{r})$ and $\rho^\beta(\vec{r})$, additional constraints must be added, namely, $N_A^\alpha = N_A^{0,\alpha}$, $N_A^\beta = N_A^{0,\beta}$, $N_B^\alpha = N_B^{0,\alpha}$, and $N_B^\beta = N_B^{0,\beta}$. The information loss is then described for each atom as

$$I_A^{\text{open-shell}} = N_A^\alpha \int \sigma_A^\alpha(\vec{r}) \ln \left(\frac{\sigma_A^\alpha(\vec{r})}{\sigma_A^{0,\alpha}(\vec{r})} \right) d\vec{r} + N_A^\beta \int \sigma_A^\beta(\vec{r}) \ln \left(\frac{\sigma_A^\beta(\vec{r})}{\sigma_A^{0,\beta}(\vec{r})} \right) d\vec{r} + N_A^\alpha \ln \left(\frac{N_A^\alpha}{N_A^{0,\alpha}} \right) + N_A^\beta \ln \left(\frac{N_A^\beta}{N_A^{0,\beta}} \right) \quad (8)$$

where the atomic shape function is now defined for α and β densities separately

$$o_A^\alpha(\vec{r}) = \frac{\rho_A^\alpha(\vec{r})}{N_A^\alpha} \quad (9)$$

In the HI method, these constraints are not met, so there is no guarantee that the atoms in the promolecule have the same spin as the atoms in the molecule. In order to minimize the information loss, the α and β densities must be iterated separately. An additional complication is that a certain inconsistency is present in the interpolation formula (eq 4), even for closed shell molecules. The atomic densities are usually interpolated between atoms of different charge, but calculated at the Hartree–Fock level and at their spectroscopic ground-state, which is not necessarily a singlet. This means that for closed-shell molecules, the atoms in the promolecule do not have zero spin, as one assumes they should.

A solution for the problems outlined above is proposed by extending the HI procedure in such a way that both charge and spin are calculated every iteration. However, extending this procedure by using the interpolation formula eq 4 requires a 2D interpolation scheme of both charge and spin in every iteration, which in our view is not practical. Inspired by ref 6, we propose to use another approach to build up the promolecule. The orbitals for a spherically symmetric atom with a given charge and multiplicity are calculated in the unrestricted approach using fractional occupations for degenerate valence orbitals while all other orbitals lower in energy are fully occupied. A calculation of this type is performed for every atom in the molecular system at the same level of theory (DFT functional and basis set) as the molecular system in every step of the iterative procedure. For example, in a given iteration, for a carbon atom with a charge of -0.1 and a spin ($\alpha - \beta$) of $+0.3$, the occupation of the $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals would be 1 , 1 , 0.4 , 0.4 , and 0.4 for the α electrons and 1 , 1 , 0.3 , 0.3 , and 0.3 for the β electrons, respectively. In every iteration, the promolecular density is constructed using the atomic densities calculated using the description described above, for every atom in the system. The weight function of the HI method based on eq 2 cannot be used, because this weight function is only based on the total density $\rho(\vec{r}) = \rho^\alpha(\vec{r}) + \rho^\beta(\vec{r})$. Two new weight functions are defined, one based on the α density and one based on the β density. The weight function for the α density is defined as:

$$w_A^\alpha(\vec{r}) = \frac{\rho_A^\alpha(\vec{r})}{\sum_B \rho_B^\alpha(\vec{r})} \quad (10)$$

The molecular α density is converted to atomic α densities by integration:

$$N_A^\alpha = \int \rho_A^\alpha(\vec{r}) d\vec{r} = \int w_A^\alpha(\vec{r}) \rho^\alpha(\vec{r}) d\vec{r} \quad (11)$$

Equivalent formulas are used for the β density.

The new method can be summarized as follows:

- On the basis of the atomic charge and spin, atomic SCF calculations are performed on the basis of fractional occupations to compute the corresponding densities for every atom in the system. In the first step, both the charge and spin of every atom are set equal to zero.
- Two promolecular densities are constructed: one based on the atomic α density and one based on the atomic β density.

Table 1. Atomic Charges for a Set of Closed-Shell Systems Obtained Using the HI and FOHI Methods Obtained with the RB3LYP Functional

molecule	atom	HI		FOHI	
		6-31G	6-31++G**	6-31G	6-31++G**
C ₂ H ₂	C	−0.211	−0.217	−0.215	−0.219
	H	0.211	0.217	0.215	0.219
CH ₄	C	−0.680	−0.597	−0.716	−0.571
	H	0.170	0.149	0.179	0.142
CO ₂	C	0.838	0.950	0.832	0.942
	O	−0.419	−0.475	−0.416	−0.470
H ₂ CO	C	0.276	0.304	0.270	0.262
	O	−0.326	−0.380	−0.320	−0.365
	H	0.025	0.038	0.025	0.052
H ₂ O	O	−0.841	−0.920	−0.830	−0.900
	H	0.421	0.459	0.415	0.450
H ₂ S	S	−0.264	−0.276	−0.245	−0.255
	O	0.132	0.138	0.123	0.128
HCN	N	−0.235	−0.283	−0.239	−0.289
	C	0.023	0.066	0.022	0.067
	H	0.212	0.217	0.217	0.223
HF	F	−0.472	−0.513	−0.464	−0.511
	H	0.472	0.513	0.464	0.511
NH ₃	N	−1.070	−1.065	−1.066	−1.001
	H	0.357	0.355	0.356	0.334
N ⁽¹⁾ N ⁽²⁾ O	N ⁽¹⁾	−0.259	−0.271	−0.254	−0.258
	N ⁽²⁾	0.567	0.595	0.552	0.567
	O	−0.308	−0.325	−0.298	−0.309
PH ₃	P	−0.117	−0.062	−0.076	−0.009
	H	0.039	0.021	0.025	0.003
SO ₂	S	1.015	1.072	0.995	1.079
	O	−0.507	−0.536	−0.497	−0.539

- A Hirshfeld partitioning of the α and β molecular density is performed using the respective promolecular densities constructed in the previous step.
- The atomic charge and spin of every atom is compared with the corresponding values in the previous iteration. If convergence is not reached, the previous steps are repeated.

Whether or not the level of theory (method/basis set) of the atomic self-consistent field calculations is the same as that with which the molecular density is calculated is not a prerequisite of the partitioning procedure. In section 4, self-consistent atomic densities obtained with the UB3LYP level of theory will be used to partition molecular densities obtained at the same level of theory, as well as densities obtained using the UMP2 and the UCCSD levels of theory.

3. COMPUTATIONAL DETAILS

For the molecules used in this article, the geometry of every structure was optimized using the Gaussian 03 program²² with the UB3LYP functional²³ using the 6-31++G**²⁴ basis set. Additional single points were also performed at the UMP2 and UCCSD levels using the aug-cc-pVTZ²⁵ basis set and at the DFT/UB3LYP level using the 6-31G,²⁶ 6-311++G**,²⁷ and aug-cc-pVTZ basis sets. Mulliken partitioning of the spin density

Table 2. Atomic Spin Populations for a Set of Radicals Based on HI and FOHI Using the aug-cc-pVTZ Basis Set^a

molecule doublet	atom	HI			FOHI		
		UB3LYP	UMP2	UCCSD	UB3LYP	UMP2	UCCSD
CN	C	0.790	0.512	0.877	1.003	0.589	1.140
	N	0.209	0.488	0.123	−0.003	0.411	−0.140
CF ₃	C	0.654	0.681	0.681	1.007	1.058	1.058
	F	0.115	0.106	0.106	−0.002	−0.019	−0.019
COH	C	0.562	0.509	0.589	0.655	0.567	0.704
	O	0.288	0.344	0.264	0.187	0.266	0.151
	H	0.150	0.147	0.146	0.159	0.167	0.145
H ₂ NCO	C	0.512	0.421	0.544	0.711	0.559	0.768
	O	0.221	0.343	0.203	0.103	0.266	0.070
	N	0.255	0.231	0.243	0.227	0.225	0.204
	H	0.006	0.003	0.005	−0.020	−0.025	−0.021
C ⁽¹⁾ H ₃ C ⁽²⁾ ONH	C ⁽¹⁾	0.006	0.018	0.004	0.025	−0.074	0.026
	H	0.004	0.010	0.001	0.005	0.026	0.002
	C ⁽²⁾	−0.006	0.228	−0.015	−0.157	0.314	−0.176
	O	0.277	−0.136	0.230	0.321	−0.210	0.272
	N	0.702	0.841	0.762	0.872	0.962	0.950
	H	0.019	0.028	0.020	−0.057	−0.053	−0.065
	C ⁽¹⁾	0.466	0.458	0.477	0.788	0.764	0.821
	C ⁽²⁾	−0.032	−0.018	−0.052	−0.350	−0.315	−0.398
C ₃ H ₅	H ⁽¹⁾	0.024	0.026	0.023	−0.067	−0.060	−0.072
	H ⁽²⁾	0.028	0.030	0.027	0.026	0.011	0.029
triplet							
HCN	N	0.382	0.388	0.285	−0.004	0.009	−0.191
	C	1.539	1.555	1.646	1.897	1.929	2.076
	H	0.080	0.058	0.069	0.107	0.063	0.115
NF	N	1.709	1.742	1.752	1.862	1.905	1.915
	F	0.291	0.258	0.248	0.138	0.096	0.085
singlet							
C ₆ H ₄	C ⁽¹⁾	0.757	0.734		1.166	1.070	
	C ⁽²⁾	0.010	0.107		−0.258	−0.036	
	C ⁽³⁾	−0.010	−0.107		0.258	0.036	
	C ⁽⁴⁾	−0.757	−0.734		−1.166	−1.070	
	C ⁽⁵⁾	−0.010	−0.107		0.258	0.036	
	C ⁽⁶⁾	0.010	0.107		−0.258	−0.036	

^a The UB3LYP functional is compared with the UMP2 and UCCSD level of theory.

was performed using the Gaussian 03 program.²² Bader analysis²⁸ was performed using Gaussian cube files. For the fractional occupation Hirshfeld-I partitioning (FOHI), the atomic densities were calculated at every iteration using the BRABO package²⁹ with the UB3LYP method and with the same basis set used for the molecule. These SCF calculations were performed using fractional occupations as described above. Both HI and FOHI charge and spin populations were evaluated by using the STOCK program.³⁰ In the HI method, convergence is reached when $\text{abs}(N_A^i - N_A^{i-1}) < 0.001$. Convergence in the FOHI method is reached when two conditions are met: $\text{abs}(N_A^i - N_A^{i-1}) < 0.001$ and $\text{abs}(S_A^i - S_A^{i-1}) < 0.001$, where S stands for the spin population of an atom.

4. RESULTS AND DISCUSSION

4.1. Charges of Closed-Shell Systems. It is possible to calculate the atomic densities necessary to build up the promolecule using

two methods: the interpolation method (HI), where the atomic density of an atom containing a noninteger number of electrons N_A is interpolated between two atomic densities with an integer number of electrons according to eq 4, and the fractional occupation method described above (FOHI), in which the density is obtained directly through an SCF calculation using fractional occupation numbers. For closed-shell systems, the spin density is zero in every point of the space. Strictly speaking, this does not mean that the atomic spin density of each atom at each point in space should be zero, but only their sum at each point in space. However, since we are working with spherically symmetric promolecular atoms, this condition can only be met by restricting the spin density of these atoms to zero. Both methods were applied for a set of closed-shell molecules: C₂H₂, CH₄, CO₂, H₂CO, H₂O, H₂S, HCN, HF, NH₃, N₂O, PH₃, and SO₂. Table 1 compares the atomic charges calculated with both methods, using the 6-31G and 6-31++G** basis sets. The very high regression coefficients ($R^2 = 0.9996$ and $R^2 = 0.9993$ for the basis

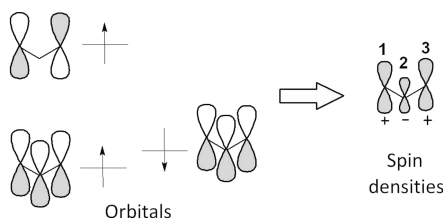


Figure 1. The second highest occupied orbitals and the SOMO for the allyl radical.

sets 6-31G and 6-31++G**, respectively) clearly show that the choice of method has, for closed shell systems, little influence on the charge of the atom. Indeed, according to the information theory, the constraint of charge is fulfilled equally well in the HI method (eq 6) as in the FOHI method (eq 8), regardless of whether we are dealing with closed-shell or open-shell systems. The main difference between the two methods, when applied to charges, comes from the manner of obtaining the atomic densities, namely, through interpolation or through a fractional occupations calculation. This high correlation between both methods is not surprising, since the spectroscopic state of the atom has a negligible effect on the atomic density.³⁰ This finding serves as a validation of the fact that the interpolation method is a good approximation for the calculation of atomic charges of closed shell systems. This high correlation between the results is also in agreement with a previous study by Ayers,³¹ who has shown that the density of a system with an irrational number of electrons is equivalent with the density acquired through interpolation (eq 4). Finally, one can also see that the basis set dependence of both methods is small, as was to be expected from a previous study.³²

4.2. Spin Densities of Open-Shell Systems. In order to further compare both methods, now for open-shell systems, the spin populations of a set of small radicals were calculated using both the HI and the FOHI methods. The list of radicals and their corresponding spin populations can be found in Table 2 for a number of doublets, triplets, and a singlet diradical. As mentioned above, the results for the charges are very similar for both methods and are therefore not present in the table. The spin populations were calculated using the UB3LYP, UMP2, and UCCSD methods and the aug-cc-pVTZ²⁵ basis set. The unrestricted formalism is used throughout this work since it has been shown that the restricted open-shell methods cannot reproduce spin polarization effects, which are of importance for spin densities.³³ As mentioned above, it is known that the spin density is influenced by two major effects: spin delocalization and spin polarization.³⁴ The first effect describes the spreading out of the spin over the molecule, which is a direct consequence of the delocalization of the SOMO (singly occupied molecular orbital). Spin polarization is a consequence of the minimization of electron–electron repulsion of two electrons of parallel spin sharing the same space, according to the Pauli principle. Consequently, one may expect induced negative spin density on the nodal atoms of the SOMO if there is an underlying π orbital which is localized on the same atoms as the SOMO.³⁴ An example is given for the allyl radical in Figure 1, which can also be found in ref 6, where the upper part of the scheme represents the SOMO orbital and the lower part of the scheme represents the α and β π orbitals in the unrestricted case. One can see that if the SOMO orbital has a node, as is the case for the second carbon atom, the polarization of the π -orbital due to the presence of the radical leads to a negative spin density on the nodal atom. In the

RODFT formalism, no polarization of the π orbital is possible, and no negative spin densities are possible. Unlike negative electronic populations, negative spin populations have in fact physical meaning and can be observed experimentally.

The HI and FOHI methods are compared in Table 2 for the three levels of theory. First, we will discuss the HI and FOHI methods based on the DFT level of theory. For the CN and CF₃ radicals, the FOHI method localizes the unpaired electron on the carbon atom, whereas the HI method spreads the spin density over several atoms. As we have mentioned for the allyl radical, a negative spin density is expected to be found on the central carbon atom. Both HI and FOHI indeed show a negative spin density for this carbon atom, although this is more pronounced in the FOHI method. With the exception of the UMP2 method, the amide radical has a large negative spin density on the carbon atom in the FOHI method, which is again very small in the HI method. Also for the triplet molecules, one can see that the HI method has more difficulties localizing the spin populations in comparison with the FOHI method. For example, in the HCN molecule in the triplet state, the HI method localizes one unpaired electron on the C atom while the other is spread out over the C and the N atoms, whereas in the FOHI method both unpaired electrons are localized on the C atom. The singlet diradical 1,4-didehydrobenzene has two unpaired electrons in the para position from each other with opposite spin. The position of the two unpaired electrons in the para position having opposite spins is found in both methods, but the alternation of the spin density over the carbon atoms due to spin polarization on the ortho- and meta-carbons is only showing in the FOHI method, while the HI method divides the molecule in a spin-positive and spin-negative part.

Both methods were further compared in partitioning molecular densities obtained at the UMP2 and UCCSD level of theory. For both methods, one can state that the DFT and UCCSD levels are in agreement for the doublet radicals. The UMP2 level shows significant differences for doublet radicals for both methods. The spin density on the CN radical is spread over both atoms. For the H₂NCO radical, the spin density on the oxygen atom is much larger compared to DFT and UCCSD. Finally, for the amide radical, the UMP2 level is the only one which localizes a negative spin density on the oxygen atom. The results for the molecules in the triplet state are alike between the different levels of theory in the HI method. For the FOHI method, the UCCSD level shows a significant negative spin density on the nitrogen atom for the HCN triplet. For the singlet diradical, the spin polarization is much more pronounced with the DFT level of theory than with the UMP2 level of theory in the FOHI method.

4.3. Comparing Hirshfeld with Other AIM Methods and Experimental Results. As could be concluded from the previous section, the DFT level of theory gives satisfactory results when compared to higher levels of theory. In this section, we will compare FOHI with other AIM methods for a set of larger systems for which we will use the UB3LYP functional and 6-311++G** basis set. The first molecules we compared are based on a phenalenyl system³⁵ and are stable radicals with a highly delocalized spin density. The structures of both molecules can be found in Figure 2. The results for the different AIM methods are summarized in Table 3. Although all three methods seem to account for the spin polarization, the negative spin density is more pronounced in the Mulliken and FOHI method, while the Bader analysis shows rather small values of negative spin density.

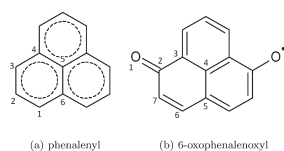


Figure 2. Lewis structures of phenalenyl systems.

Table 3. Comparison of Atomic Spin Populations of the Phenalenyl Structures, TCNE and Nitph, Based on Different AIM Methods Using the UB3LYP Functional and 6-311++G Basis Set^a**

molecule	atom	Mulliken	Bader	FOHI	experiment
phenalenyl	C ⁽¹⁾	0.312	0.224	0.338	
	C ⁽²⁾	−0.137	−0.070	−0.169	
	C ⁽³⁾	0.312	0.225	0.338	
	C ⁽⁴⁾	−0.142	−0.060	−0.159	
	C ⁽⁵⁾	0.062	0.032	0.085	
	C ⁽⁶⁾	−0.142	−0.060	−0.159	
6-oxophenalenoxyl	C ⁽¹⁾	0.213	0.176	0.213	
	C ⁽²⁾	−0.070	0.003	−0.086	
	C ⁽³⁾	0.083	0.061	0.109	
	C ⁽⁴⁾	−0.089	−0.041	−0.118	
	C ⁽⁵⁾	0.399	0.281	0.421	
	C ⁽⁶⁾	−0.186	−0.093	−0.211	
TCNE	C ⁽⁷⁾	0.335	0.245	0.365	
	N ⁽¹⁾	0.165	0.117	0.168	0.12
	C ^{(2)(sp)}	−0.107	0.008	−0.081	−0.05
	C ^{(3)(sp²)}	0.385	0.252	0.326	0.33
	C ^{(4)(sp)}	−0.107	0.008	−0.081	−0.03
	N ⁽⁵⁾	0.165	0.117	0.168	0.13
	C ^{(6)(sp²)}	0.385	0.252	0.326	0.33
	C ^{(7)(sp)}	−0.107	0.008	−0.081	−0.04
	N ⁽⁸⁾	0.165	0.117	0.168	0.12
	C ^{(9)(sp)}	−0.107	0.008	−0.081	−0.08
NitPh	N ⁽¹⁰⁾	0.165	0.117	0.168	0.16
	O ⁽¹⁾	0.357	0.327	0.320	0.277
	N ⁽²⁾	0.263	0.219	0.315	0.278
	C ⁽³⁾	−0.169	−0.065	−0.245	−0.121
	N ⁽⁴⁾	0.263	0.219	0.314	0.278
	O ⁽⁵⁾	0.357	0.327	0.320	0.247
	C ⁽⁶⁾	−0.009	−0.032	0.063	0.024
	C ⁽⁷⁾	−0.025	0.013	−0.053	0.000
	C ⁽⁸⁾	0.022	0.000	0.029	0.025
	C ⁽⁹⁾	−0.045	0.000	−0.050	−0.016
	C ⁽¹⁰⁾	0.022	0.000	0.028	0.011
	C ⁽¹¹⁾	−0.025	−0.032	−0.053	−0.037

^a Experimental values are listed for the TCNE and NitPh radicals.

The spin populations obtained using different partitioning methods were also compared with experimental results obtained with polarized neutron diffraction. This technique is able to quantify the spin density on every atom, which gives the unique opportunity to compare values of atoms-in-molecules, which are generally unobservable, with experimental data. Two molecules were examined, the first one being tetracyanoethylene (TCNE). The structure of this radical anion can be found in Figure 3. The

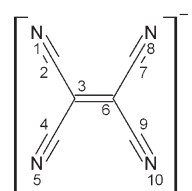


Figure 3. Lewis structure of TCNE.

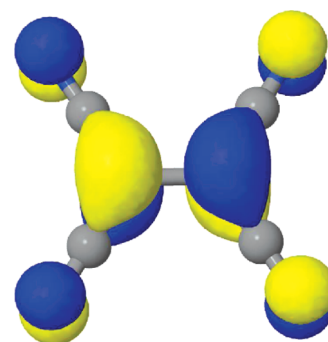


Figure 4. Singly occupied molecular orbital (SOMO) of the radical anion TCNE. The SOMO shows nodes on the sp carbon atoms.

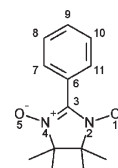


Figure 5. Lewis structure of NitPh.

atomic spin populations based on the different partitioning methods and the experimental results can be found in Table 3. Experimental results¹⁸ show that the density is mostly localized on the sp² carbon atoms. However, due to spin delocalization and spin polarization, there is a considerable amount of spin density on the nitrogen atom and a negative spin density on the sp carbon atoms. The unequal experimental values on the sp carbon atoms and the nitrogen atoms are due to the reduced symmetry of the monoclinic unit cell.¹⁸ The negative spin density is in agreement with the theory, since the SOMO of TCNE clearly shows nodes at the sp carbon atoms (Figure 4). The negative values are also reproduced by the FOHI method and the Mulliken method but not by the Bader method.

The second molecule examined is the nitronyl nitroxide 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl-3-oxide (NitPh), the structure of which can be found in Figure 5. Comparison of the values obtained by means of the partitioning methods and the experimental results can be found in Table 3. Experimental results³⁶ show that most of the spin density is concentrated on the NO groups, where it seems to be equally shared between the nitrogen and oxygen atoms. A large negative spin population is observed on the carbon atom connecting the two NO groups. Also, here, these results are in agreement with the theory, as can be seen from the visualization of the SOMO orbital of NitPh in Figure 6. The spin density in the phenyl ring is very low, although alternation of the spin on the carbon atoms is observed. This has also been confirmed by ¹H and ¹³C NMR

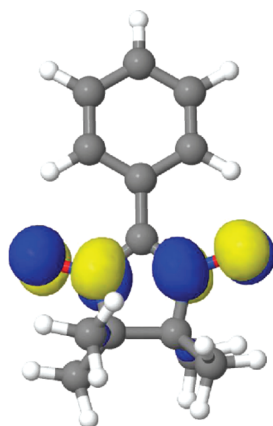


Figure 6. Singly occupied molecular orbital (SOMO) of the nitronyl nitroxide NitPh. The SOMO shows a node on the carbon connecting the two NO groups.

experiments.^{37,38} The almost equal distribution of the spin density between the nitrogen and oxygen atoms, observed in the experimental results, is reproduced in the results obtained by the FOHI method and the Mulliken method but not in the Bader method, where the oxygen has higher spin populations. The alternation of the spin on the phenyl group is only observed in the FOHI method. Although the Bader method seems to underestimate the negative spin density on the carbon atom connecting the two NO groups (C_3), both of the other methods overestimate this negative spin density.

5. CONCLUSION

A new partitioning method, inspired by the iterative procedure in Hirshfeld-I (HI),¹¹ was introduced in order to calculate properties of open-shell systems, in particular, atomic spin populations. The iterative procedure has been expanded so that both the spin and the charge of the atoms are altered during the iterations. This is achieved by performing in each iteration an SCF calculation for each of the atoms using fractional occupation numbers. Because the atomic SCF calculations have to be repeated every iteration for every atom, this can become time-consuming for larger systems. However, the execution time can be reduced drastically, first, by using converged densities of a previous iteration as an initial guess together with fully exploiting the spherical symmetry of the atoms and eventually skipping atoms for which the results are already converged, and second, since the atomic calculations are completely independent, by processing these calculations in parallel, the CPU time can be drastically decreased.

The Hirshfeld-I method is compared with the new fractional occupation Hirshfeld-I method (FOHI). It is found that for properties where only the sum of the α and β density is of importance, such as charges, both methods lead to similar results. Whereas for properties where the difference between the α and β density is of importance, such as spin populations, the FOHI method appears superior. In particular, the ability to reproduce negative spin populations, observed in experimentation, in a consistent manner is a major advantage of the FOHI method. This is due to the fact that the HI method does not make use of the molecular spin density during its iterations and the spin of the atomic densities is arbitrary chosen.

The results obtained by different AIM methods are compared with experimental results obtained with polarized neutron diffraction. The Bader analysis seems to underestimate the spin polarization effect. Therefore, certain atoms have a positive spin density, although experimental results clearly show a negative spin density due to spin polarization. The Mulliken method accounts for the spin polarization, but the results are strongly basis set dependent. The FOHI method is in agreement with the experimental results, but the effect of spin polarization may be overestimated.

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