

Electron pairing and chemical bonds. Chemical structure, valences and structural similarities from the analysis of the Fermi holes

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A new method of visualisation of bonding in molecules is introduced. The method is based on the analysis of Fermi holes associated with conditional probabilities of finding one electron of the pair provided the second, reference, electron is localised in a certain molecular region. Based on this analysis it is possible to get a clear and highly visual insight into the structure of molecular fragments (functional groups) in molecules. In addition to this visualisation, the new approach opens the possibility of the new definition of atomic and group valence and, also, can be applied as a new means of the quantitative characterisation of similarity of structural fragments in the series of related molecules.

1. Introduction

The concept of chemical bond is one of the most fundamental concepts of the whole modern chemistry [36]. Despite numerous attempts to elucidate the factors responsible for the strength and the existence of chemical bonds [4,5,9,13–15,23,25,26,49,52] the nature of the chemical bond is still not completely understood. This is especially true of the mutual relation or compatibility of the classical Lewis picture of chemical bond as composed of shared electron pair [27] and the quantum chemical description based on the concept of many electron wave function. The first attempts in this respect were based on the idea of the so-called localised orbitals [12,18,19,31,35,37,38] and even if these orbitals have the basic features attributed to chemical bonds, namely the localisation in a certain region of space and the approximate transferability, this approach cannot be regarded as completely satisfactory from the theoretical point of view. This is due to the fact that the localised orbitals, like any other orbitals, are only one electron quantities and as such they are inherently unable to say anything about the behaviour of electron pairs. It is thus clear, that any attempt at the evaluation of the role of electron pairing in chemical bonds has to be based on inherently two-electron quantities. The simplest of such quantities is the pair density and several attempts based on the analysis of this density was recently reported in the literature

[9,10,17,23–25,50,51,54]. Among them it is necessary to mention the studies by Bader [9] and Julg [25] who came with the idea to identify the chemical bond with the region of small fluctuation of electron pair. Unfortunately, neither this approach was found to be entirely satisfactory and, consequently, the electron pair model of chemical bond was seriously questioned [2]. Despite this discouraging conclusion the situation is not, however, as desperate as it seemed to be since as we have recently shown [48], the criterion of low pair fluctuation is not completely satisfactory. This can very simply be demonstrated by a simple example of H_2 molecule for which the pair fluctuation over the region involving both atoms is identically zero irrespective of the inter-atomic distance, i.e., both for bond lengths close to equilibrium where the bond certainly exists and for the completely dissociated state without any bond. This implies that the low fluctuation criterion is not a good measure of the existence of chemical bond and cannot thus serve as a basis for the evaluation of the role of electron pairing in chemical bonding. Much more convenient criterion for the evaluation of the accuracy of the Lewis electron pair model was found to arise from the recently introduced formalism of the so-called pair population analysis [11,40,41,46]. The basis of this criterion is the interesting normalisation criterion (1), which says that the total sum of mono- and biatomic effective pair populations equals $N/2$ which for the molecule with N electrons is just the number of bonds plus free and core electron pairs:

$$\sum_A \Pi_A^{\text{eff}} + \sum_{A<B} \Pi_{AB}^{\text{eff}} = N/2. \quad (1)$$

The important and interesting feature of this relation is that it can frequently be simplified to the form (2)

$$\sum_A \Pi_A^{\text{eff}} + \sum_{A<B}^{\text{bonded}} \Pi_{AB}^{\text{eff}} \cong N/2, \quad (2)$$

where the summation of biatomic terms runs only over pairs of atoms directly bonded in the classical formula. In this way the accuracy of the Lewis model could straightforwardly be checked and we found [48] that it is usually high enough to represent a good basis for the interpretation of the structure.

Stimulated by this result we decided to pursue the idea of the analysis of the pair density and our aim in this study is to show that useful structural information can be extracted not only from the formalism of the pair population analysis but also from other closely related approaches. In the following part some examples of such approaches will be given.

2. Theoretical

The simplest quantity which is of fundamental importance for any attempt to evaluate the role of electron pairing in chemical bonds is the pair density which is defined

as a diagonal element of the (spin-less) second density matrix [28,32] $\rho(r_1, r_2|r'_1, r'_2)$,

$$\rho(r_1, r_2) = \rho(r_1, r_2|r_1, r_2) = N(N-1)/2 \int \Psi^2(1, 2, \dots, N) d\sigma_1 d\sigma_2 dx_3 \dots dx_N, \quad (3)$$

where the integration is performed over the spin coordinates of the first two electrons and over the spin and space coordinates of remaining $N - 2$ electrons.

In spite of considerably reducing the extent of information compared to the wave function, this density is still rather complex quantity and in order to extract the desired information from it, it has to be subjected to further mathematical processing. One of such methods is, e.g., the recently proposed pair population analysis. In this study we are going to introduce another kind of analysis which is based on the exploitation of conditional probabilities describing the distribution of one electron of the pair provided the second, reference, electron is fixed in a certain position or region. This conditional probability, with the reference electron fixed in a point r_2 is given by

$$P_{r_2}(r_1) = 2\rho(r_1, r_2)/\rho(r_2). \quad (4)$$

In addition to conditional probabilities themselves it is also useful to analyse the closely related quantities (5), the so-called Fermi holes [7,29,30,55]:

$$h_{r_2}(r_1) = \rho(r_1) - P_{r_2}(r_1). \quad (5)$$

These quantities were introduced long time ago by Wigner in solid state physics [55] and only relatively recently were used also in chemistry [7,29,30]. Thus, e.g., Luken [29,30] demonstrated that these holes are not very sensitive to the precise location of the reference electron and if this position is fixed near the midpoint of the inter-nuclear axis, the resulting pictures closely resemble the localised orbitals corresponding to individual bonds. In this way the important role of electron pairs in chemical bonds was directly confirmed. Similar conclusion were then also obtained in our recent study [47].

The fixation and, consequently, the localisation of the reference electron in a single point is not, however, very compatible with the quantum mechanical uncertainty principle. Much more useful and realistic picture would result if the position of the reference electron is not fixed in a point but is allowed to vary within a certain region Ω . In this case the original equation (4) becomes

$$f_{\Omega}(r_1) = \frac{\int_{\Omega} 2\rho(r_1, r_2) dr_2}{\int_{\Omega} \rho(r_2) dr_2}. \quad (6)$$

The conditional probabilities satisfy the universal normalisation condition (7) which holds for the arbitrary shape of the region Ω :

$$\int f_{\Omega}(r_1) dr_1 = N - 1. \quad (7)$$

Parallel to Fermi hole (5) it is also useful to define an “integrated” Fermi hole (8):

$$h_{\Omega}(r_1) = \rho(r_1) - f_{\Omega}(r_1), \quad (8)$$

which identically satisfies the normalisation

$$\int h_{\Omega}(r_1) dr_1 = 1. \quad (9)$$

Although the validity of the normalisation is not influenced by how the region Ω is actually chosen, there is a certain definition which is of special importance for chemistry. This definition is based on the virial partitioning of the function $\rho(r_1)$ proposed by Bader [3]. According to this partitioning the molecular space is divided into regions associated with individual atoms. Adopting this type of partitioning it is reasonable to identify the regions Ω with some of the atomic regions of the Bader's partitioning.

In addition to restricting the position of the reference electron into single atomic region it is also useful to investigate the conditional probabilities and Fermi holes for some other specific forms of Ω . Thus, e.g., one of such possibilities would be to analyse the biatomic regions defined as a union of neighbouring atomic regions especially for the classically bonded atoms. In certain cases even more complex forms of the region Ω can also be useful to analyse. The important feature of this analysis is that these holes associated with the region Ω are predominantly localised in the same region so that the information they contain is to a considerable extent specific just for the given region (functional group). As we shall see below, this may be especially useful for the visualisation of the structure of molecular fragments and, also, for the evaluation of similarity of these fragments (functional groups) in a series of structurally related molecules. Before this becomes possible it is necessary to introduce yet some other related quantities and, also, to specify the methods of their analysis

First of them is based on the idea of the Mulliken population analysis [34]. The quantity which is analysed is not, however, the total electron density but the "charge weighted" Fermi hole which is defined by

$$g_{\Omega}(r_1) = N_{\Omega}h_{\Omega}(r_1), \quad (10)$$

and where the proportionality factor equals to the number of electrons in a region Ω .

The philosophy underlying the introduction of these "charge weighted" Fermi holes is the following. The "normal" Fermi holes are derived from the conditional probabilities describing the distribution of one electron of the pair provided the second, reference, electron is localised in a region Ω . The localisation of one and only one electron in a region Ω is, however, rather artificial act which does not reflect the fact that in a real molecule the region Ω is generally populated not by one but by N_{Ω} electrons, where N_{Ω} is given by

$$\int_{\Omega} \rho(r_1) dr_1 = N_{\Omega}. \quad (11)$$

This implies that in order to correct for the statistical probability of distribution of electrons in a molecule, the “normal” Fermi holes are to be multiplied by a factor N_{Ω} . As a consequence, the “charge weighted” Fermi holes satisfy the universal normalisation

$$\int g_{\Omega}(r_1) dr_1 = N_{\Omega}. \quad (12)$$

This identity can be then decomposed into individual atomic populations exactly as in the standard Mulliken population analysis and the resulting populations will be shown to be closely related to the classical concept of valence.

Another general methodology of the analysis of “charge weighted” Fermi holes arises from the fact that the matrix G_{Ω} representing this quantity in AO basis can be diagonalised exactly like the charge density-bond order matrix. Since, as stressed above, the Fermi holes associated with a region Ω are predominantly localised in the same region, the eigenvalues and eigenvectors resulting from such diagonalisation provide a specific information about the structure of corresponding fragment. Thus, e.g., if the region Ω is composed of atomic region of a single atom, the diagonalisation of the matrix G provides the valence state of the atom in a molecule. On the other hand, for more complex regions corresponding, e.g., to certain functional groups, the diagonalisation of the matrix G closely reflects the classical picture of that fragment as composed of localised electron pairs corresponding to bonds, free and/or core electron pairs and some unsaturated free valences. In addition to this, the eigenvalues resulting from the diagonalisation of the “charge weighted” Fermi holes can hopefully be used as a new efficient basis for the classification and the systemisation of similarities in molecular structure. In the following part some examples of this practical use of these holes will be discussed.

3. Results and discussion

Although the above methodology is formulated quite generally and can be applied at any level of theory, the practical applications discussed in this study are based on some simplifying assumptions. First of the concerns the pair densities which, for simplicity, are derived from semiempirical MO methods at SCF level. This restriction was motivated mainly by the simplicity with which the above analysis can be implemented and subsequently tested at this particular level. Moreover, we believe, that at this level the conclusions can still be regarded as reliable enough and certainly they provide a good starting point prior to eventual extension to higher levels of the theory. Second of the approximations concerns the integration over the Bader’s regions. Because of unavailability of programs for such an integration to us we used, as in previous cases [44,48] the approximation replacing the direct Bader’s integration by appropriately restricting the summation over the basis functions. Within this approach the electron is assumed to be in the region of the atom A if it resides in the orbital centred on this atom. Using this approach, combined with the usual ZDO approximation used in semiempirical methods, the general formula (6) for the conditional probability over

the region Ω can be rewritten in the form (13), in which P_Ω denotes the total electron density in this region:

$$f_\Omega(r_1) = \frac{\int_\Omega 2\rho(r_1, r_2) dr_2}{P_\Omega}. \quad (13)$$

The approach was applied to a series of simple molecules restricted, in this introductory study, only to structures well represented by the classical Lewis model of two-center two-electron (2c-2e) bonds. The calculations were performed by standard MNDO method [16] implemented in the MOPAC package [53] and in all cases the molecules were considered in completely optimised molecular geometries.

Let us discuss now the results of our calculations. As a first example let us introduce the alternative definition of atomic and group valence based on the analysis of the “charge weighted” Fermi holes. Thus, e.g., if these holes are represented in AO basis by the matrix G_Ω then the atomic valence of the group X can be defined as

$$V_X = 2 \sum_{B \notin X} \sum_{\mu}^B (G_X)_{\mu\mu}. \quad (14)$$

The simplest situation is when the group X is composed of a single atom. In this case the resulting quantity is the atomic valence of the corresponding atom. Values of atomic and group valences calculated according to (14) for a series of several simple molecules are included in table 1. Here it is interesting to remark that at simple SCF level the calculated atomic and group valences are identical with the valences resulting from the Jug’s definition [20,22,45]. Such an equivalence would, however, disappear at correlated post SCF level and it would be certainly interesting to test the new definition of valence for correlated pair densities. This would not only allow to extend the definition of valence to correlated post-SCF level of theory but also to test the applicability and the very usefulness of the valence concept outside the scope of SCF approximation.

In addition to opening a possibility of the alternative definition of the atomic and group valence, the analysis of the “charge weighted” Fermi holes brings also the possibility of the extremely straightforward and visual insight into the molecular structure. Such an insight is based on the diagonalisation of the matrix G_Ω in AO basis. The result of this diagonalisation is several nonzero eigenvalues (together with the corresponding eigenvectors) from which the molecular structure can straightforwardly be deduced. Thus, e.g., in the case of CH_3 -fragment in CH_4 molecule, the diagonalisation of the matrix G_Ω gives four nonzero eigenvalues of which three are exactly equal to 2 and the remaining one is close to 1. This suggests that six of the total number of electron within the fragment are coupled to pairs and the remaining roughly one remains uncoupled. Closer inspection of the corresponding eigenvectors demonstrates that the those with eigenvalue 2 correspond to individual C–H bonds and the remaining, singly occupied eigenvector corresponds to unsaturated “free valence” of the CH_3 -group. We can thus see that the analysis of the Fermi hole associated with a fragment provides a picture completely consistent with the classical structural formula.

Table 1
Atomic and group valences from the analysis of Fermi holes for a series of simple molecules.

Molecule	Group	Valence
CH ₄	C	3.921
	H	1.000
	CH	2.960
	CH ₂	1.987
	CH ₃	1.000
NH ₃	N	2.965
	H	0.994
	NH	1.983
	NH ₂	0.994
H ₂ O	O	1.940
	H	0.973
	OH	0.973

After having discussed the simple case of CH₃-fragment let us analyse also other possible fragments derivable from CH₄, NH₃ and H₂O. The only what is necessary is to include the appropriate atoms into the region Ω and to generate and diagonalise the corresponding “charge weighted” Fermi hole. The diagonalisation yields four nonzero eigenvalues of which those, corresponding to X–H bonds and free electron pairs existing in the fragment, are exactly equal or very close to 2 while eigenvalues corresponding to “unsaturated free” valences are close to 1. This suggests the possibility to introduce simple topological definition of group valence as a number of eigenvectors with eigenvalues close to 1. These topological valences are, like the classical valences, only integer numbers and as it is possible to see from table 2 they completely coincide with the classical valences of the group. Such a result is not, of course, very interesting in this particular case but since the formalism is completely general it can equally well be applied to other more complex systems where the classical structural theory is difficult to use. Such can be, e.g., the case with transition metal complexes where the above formalism can be used as an alternative to the qualitative analysis of the so-called isolobal analogy [21].

In addition to allowing the simple extraction of the structure from the pair density, the diagonalisation of the “charge weighted” Fermi holes is also useful as a new means of the evaluation and the classification of similarity [1,6,8,33,39,42] of various structural fragments (functional groups) in a series of related molecules. As an example let us evaluate the similarity of CH₃-fragment in a series CH₃–Li, CH₃–H, CH₃–CH₃, CH₃–NH₂, CH₃–OH, CH₃–F. Like in previous cases the diagonalisation of the “charge weighted” Fermi holes yields four non-zero eigenvalues of which three (corresponding to three C–H bonds in the fragment) are again equal or very close to 2. This clearly demonstrates that the structure of the CH₃-group in all the molecules is essentially identical. The only place where the effect of varying molecular environment becomes

Table 2
Topological valence of several functional groups from the analysis of the Fermi holes.

Molecule	Fragment	Topological valence
CH ₄	C	4
	CH	3
	CH ₂	2
	CH ₃	1
NH ₃	N	3
	NH	2
	NH ₂	1
H ₂ O	O	2
	OH	1

Table 3
Similarity of CH₃-fragment in a series of molecules CH₃X.

Molecule	Similarity index $S_{X,H}$
CH ₃ Li	0.441
CH ₄	0.0
CH ₃ -CH ₃	0.019
CH ₃ -NH ₂	-0.094
CH ₃ -OH	-0.175
CH ₃ -F	-0.282

more important is on the eigenvalue corresponding to remaining “unsaturated free” valence which systematically decrease on going from CH₃-Li to CH₃-F. We propose here to use this variation as a simple measure of molecular similarity. Thus, e.g., if we take methane as a reference standard then the similarity (or dissimilarity) of the CH₃-fragment in CH₃-X can be defined as

$$S_{X,H} = \eta_X^F - \eta_H^F, \quad (15)$$

a difference between the eigenvalues corresponding to “unsaturated free” valence in a molecule CH₃-X and the reference methane. The resulting values of this index are summarised in table 3 and as it is possible to see from the figure 1, the index reasonably correlate with the Pauling electronegativity of the atom (group) X.

Such a simple index is, of course, only one of the possibilities how to measure the similarity of various fragments and more detailed investigation of possible generalisations is currently under study in our laboratory and we believe that further systematic exploitation of Fermi holes will be found useful in the evaluation and systemisation of molecular similarity.

Summarising the above results it is perhaps possible to conclude that in addition to opening the new ways for the quantitative characterization of molecular similarity, the above introduced analysis of the Fermi holes brings also new interesting possibilities

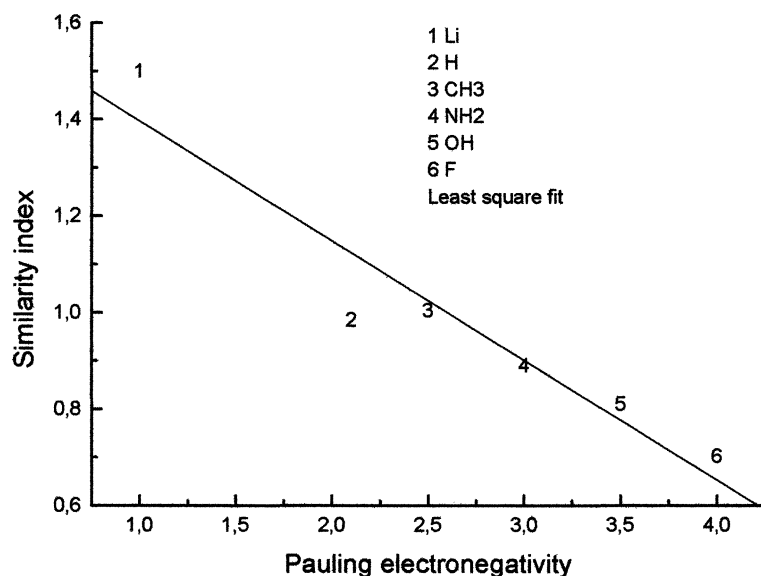


Figure 1. Calculated dependence of similarity of CH₃-fragment in CH₃X on the Pauling electronegativity of the central atom in X.

for the theoretical interpretation and visualization of molecular structure and we believe that further systematic studies of these holes are worth pursuing. In this connection it is, of course, fair to say that in view of the wide potential benefit from these analyses, the extension to more sophisticated levels of the theory would be desirable. One such study aiming at the generalization to more reliable ab-initio description is currently being performed in our laboratory. Another important and especially from the theoretical point of view attractive generalization would be to analyse the conditional probabilities and Fermi holes derived from the correlated pair densities but even if first such attempts were recently reported [43], the low availability of correlated pair densities from existing quantum chemical programs prevents so far wider systematic exploitation of the presented methodology in this direction.

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