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From the Wave Function to Structural Formula

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The recently proposed pairon population analysis based on geminal expansion of pair densities is applied to the investigation of the molecular structure of several simple molecules. It has been shown that the values of pairon populations straightforwardly reproduce the classical structural formula and, thus provide a new and surprisingly simple means of extracting structural information from the wave function.

INTRODUCTION

It is one of the basic postulates of quantum mechanics that all the available information about the system is contained in its wave function. Applied to a molecular system, this postulate requires the wave function to contain also information about molecular structure. While for observable properties the extraction of the required information is quite straightforward and reduces to the calculation of the expectation value of the corresponding operators, the situation with structural information is much more complex. This is due to the fact that the basic structural unit, the chemical bond, is not associated with any operator. As a consequence, the concept of chemical bond is extremely difficult to analyze and the best that can be done is to discuss the nature of chemical bond from various points of view.¹⁻¹⁰ In spite of numerous attempts at such a discussion, the problem of the compatibility of the chemical bond concept with quantum mechanics is still far from being completely exhausted.

This is especially true of the relation of this concept to the classical Lewis's model of (covalent) chemical bond as a shared electron pair.¹¹ The immense debt which chemistry owes to this idea has stimulated the numerous attempts to substantiate the postulated pair nature of chemical bond by theoretical arguments. The first attempt in this respect is represented by the so-called loge theory.¹²⁻¹⁴ Closely related to this theory is also the more recent approach by Bader, Mel Levy and Julg,¹⁵⁻¹⁷ who proposed to simplify the procedure of finding the borderlines of indi-

vidual loges from the condition of minimization of fluctuation of electron pairs. Unfortunately, these and other attempts¹⁸ to support the expected role of electron pair in bonding were not entirely successful and the situation finally led Prof. Bader to the rather pessimistic conclusion that atoms, rather than chemical bonds, are to be regarded as the basic building block of the molecules.¹⁹

In spite of these discouraging results, the intuitive faith in the deep physical meaning of the Lewis electron pair idea is strong enough and attempts to prove the pair nature of chemical bonds still continue. As an example, it is possible to mention Salem's analysis of electron reorganization in allowed and forbidden pericyclic reactions in terms of pair correlation functions.²⁰ The closely related analyses of pair density matrices have also been performed by us in the past few years²¹⁻²⁴ and our experience in this field stimulated us to extend our efforts also towards investigation of the role of electron pairing in chemical bonds. The procedure we have been using is the population analysis of pair densities²⁵ and, as it will be shown, this approach is indeed able to throw some new light on the old problem of the nature of chemical bond and, particularly, to revive the old Lewis idea of a bond as a shared electron pair.

Our aim in this study is to summarize the results of our previous studies in this field and to demonstrate that the formalism of pairon population analysis can provide the long sought but still missing link between the quantum and classical pictures of chemical bond. The most important result of this approach is the precise reproduction of structural formula, including not only molecular connectivity but also the multiplicity of individual bonds, as well as detection of the possible presence of free electron pairs.

THEORETICAL

According to quantum mechanics, the most complete source of information about the microscopic system is contained in the corresponding wave function. This quantity is, however, rather abstract and, in order to extract the information hidden in it, the wave function is to be subjected to subsequent mathematical manipulations. One of the very general treatments of this type consists of extracting information about the behaviour of only a limited number of particles from the total many electron function. This is the philosophy of introducing the reduced density matrices. In our case, where we are interested in analyzing the role of electron pairing in chemical bonds, the above philosophy allows us to concentrate only on the description of two electrons contributing to the electron pair. The quantity providing just this reduced relevant information is the so-called pair density matrix $\pi(1,2)$. This matrix is generally defined by equation (1), where $d\sigma_i$, dx_j denote the integration over spin

$$\pi(1,2) = \frac{N(N-1)}{2} \int \Psi^2(1,2,3\dots N) d\sigma_1 d\sigma_2 dx_3 dx_4 \dots dx_N \quad (1)$$

and/or spin-space coordinates of electrons, i and j , respectively. This density is given by the well-known formula (2),

$$\pi(1,2) = \sum_{\alpha,\beta} \sum_{\gamma,\delta} \Omega_{\alpha\beta\gamma\delta} \chi_\alpha(1) \chi_\beta(1) \chi_\gamma(2) \chi_\delta(2) \quad (2)$$

which, in the case of Hartree-Fock approximation, can be further simplified to form (3), expressing the matrix elements of the four index matrix Ω terms of matrix elements of the usual charge density bond order matrix P .

$$\Omega_{\alpha\beta\gamma\delta} = \frac{1}{2} \left(P_{\alpha\beta} P_{\gamma\delta} - \frac{1}{2} P_{\alpha\gamma} P_{\beta\delta} \right) \quad (3)$$

Although the above introduced pair density is much simpler to analyze than the original wave function, it is still a rather complex quantity and the extraction of the desired information about the behaviour of electron pairs still requires some additional mathematical processing. One such technique is the so-called population analysis. Although attempts to introduce the population analysis of matrix Ω have been reported,²⁶⁻²⁸ such attempts have, in our opinion, one important conceptual disadvantage. This is due to the fact that the usual expansion of pair density in the basis of atomic orbitals (2) leads to a four index matrix Ω , for which manipulations with the individual elements is unnecessarily complicated. In this connection, it is interesting to note that the form of the expansion matrix of the pair density can be considerably simplified using the basis of true two-electron functions – geminals – instead of the usual basis of one-electron orbitals. As demonstrated in the previous study,²⁵ and also in,²⁹ if the geminal basis is chosen in form (4), the pair density $\pi(1,2)$ can be expressed by Eq. (5).

$$\begin{aligned} s_{\alpha\alpha} &= \lambda_k(1,2) = \chi_\alpha(1) \chi_\alpha(2) \\ s_{\alpha\beta} &= \lambda_e(1,2) = \frac{1}{\sqrt{2}} \left[\chi_\alpha(1) \chi_\beta(2) + \chi_\alpha(2) \chi_\beta(1) \right] \end{aligned} \quad (4)$$

$$\begin{aligned} t_{\alpha\beta} &= \lambda_m(1,2) = \frac{1}{\sqrt{2}} \left[\chi_\alpha(1) \chi_\beta(2) - \chi_\alpha(2) \chi_\beta(1) \right] \\ \varphi(1,2) &= \sum_{ij} g_{ij} \lambda_i(1,2) \lambda_j(1,2) \end{aligned} \quad (5)$$

We can thus see that in this basis the pair density has the simple form of a normal two-index matrix similar to the form of the first order density matrix in the basis of orbitals. On the basis of this analogy, it is then possible to use the formalism of the common Mulliken population analysis³⁰ and to introduce the pairon populations. Prior to presenting the final expression for the pairon populations, some specific features of the above procedure are worth mentioning. First of all, it is necessary to note that, in the case of orthogonal basis geminal function (6), only the diagonal elements g_{ii} of the pair density analogous to »net« quantities of the Mulliken population can be taken into account.

$$\int \lambda_i(1,2) \lambda_j(1,2) dr_i dr_j = \delta_{ij} \quad (6)$$

As a consequence, the natural normalization condition (7), expressing the conservation of the total number of electron pairs, is satisfied.

$$\sum_i g_{ii} = \frac{N(N-1)}{2} \quad (7)$$

In this connection it is, however, fair to say that the orthogonality constraint is not at all necessary and the same population scheme can be generalized to nonorthogonal geminal bases as well. Moreover, such a generalization is not restricted only to the Hartree-Fock wave functions but correlated wave functions can be also analyzed.³¹

Another important feature of the proposed population analysis stems from the fact that individual basis functions (4) correspond to the situation where either both participating orbitals α, β are associated with one atom or shared between atoms. As a consequence, the final populations can also be associated with mono- and biatomic contributions. This is an important simplification since, in previous population schemes,²⁶ the contributions involving three- and four-atomic contributions appeared. In addition to this simplification, there is yet another specific difference. This difference arises from the fact that in constructing the geminal basis functions it was necessary to take into account the existence of spin pure singlet and triplet states of the electron pair. As a consequence, and because of the special block-diagonal form of the pair density expansion^{25,29}, it is possible to introduce the populations corresponding to separate contributions of singlet and triplet states of electron pair. The individual populations are then given by Eq. (8):

$$\begin{aligned} \Pi_{AA}^s &= \frac{1}{4} \sum_{\mu}^A p_{\mu\mu}^2 + \frac{1}{4} \sum_{\mu < \nu}^A \sum_{\mu < \nu}^A (p_{\mu\mu} p_{\nu\nu} + p_{\mu\nu}^2) \\ \Pi_{AA}^t &= \frac{3}{4} \sum_{\mu < \nu}^A \sum_{\mu < \nu}^A (p_{\mu\mu} p_{\nu\nu} - p_{\mu\nu}^2) \\ \Pi_{AB}^s &= \frac{1}{4} \sum_{\mu}^A \sum_{\nu}^B (p_{\mu\mu} p_{\nu\nu} + p_{\mu\nu}^2) \\ \Pi_{AB}^t &= \frac{3}{4} \sum_{\mu}^A \sum_{\nu}^B (p_{\mu\mu} p_{\nu\nu} - p_{\mu\nu}^2) \end{aligned} \quad (8)$$

Having introduced these final expressions, let us demonstrate, in the following part, the practical application of the resulting population scheme. One of the main goals will be the demonstration that properly defined pair quantities provide a new simple means of extracting structural information, such as *e.g.* the connectivity between atoms, including the multiplicity of bonds as well as detection of the possible presence of free electron pairs on some atoms.

In this connection it is perhaps fair to say that a certain visualization of structural formula is available also using various localization procedures³²⁻³⁶ or the recent definition of bond order by Cioslowski³⁷ but these, in principle, one-electron approaches are inherently unable to say anything about the role of electron pair in bonding. Thus, in this respect, our approach provides not only a duplication of what is already known but, and this is new, also brings a clear theoretical evidence in favour of the Lewis electron pair model of chemical bond.

The calculated values of pairon populations for a series of simple molecules are summarized in Table I-III. Calculations were performed by the standard MNDO method³⁸ for optimized molecular geometries.

RESULTS AND DISCUSSION

In order to demonstrate the role of electron pairing in chemical bonds, it is first necessary to introduce the so-called effective pairon populations [16] defined by Eq. (9).

$$\begin{aligned}\Pi_{AA}^{\text{eff}} &= \Pi_{AA}^s - \frac{1}{3} \Pi_{AA}^t \\ \Pi_{AB}^{\text{eff}} &= \Pi_{AB}^s - \frac{1}{3} \Pi_{AB}^t\end{aligned}\quad (9)$$

Although introduction of these quantities may seem rather artificial at first sight, it is *via* their values that the parallel between chemical bonds and electron pairs becomes especially clear and transparent. One of the most important results, which speaks in favour of these effective populations, is that by using their values it is possible to reproduce the classical structural formula, including the multiplicity of the bonds, as well as detect the eventual presence of free electron pairs on some atoms. While the reproduction of the structural formula is based on biatomic contributions, detection of the presence of free electron pairs requires a knowledge of monoatomic populations.

Let us start our analysis by examining the values of biatomic contributions. The most surprising result that can be seen from the tables is that, despite the great variety of atoms involved, the effective pairon populations display remarkable regularity and their values can be roughly divided into only three or four basic groups. For the first group, corresponding to single bonds, the values of effective populations are, irrespective of the type of the bonded atoms, close to 0.5. Another group, characterized by the populations close to 1, is then typical of the double bonds while for the third group, corresponding to triple bonds, the contributions are closed to 1.5. At the same time, the effective populations between formally nonbonded atoms are practically negligible. This result is even more interesting if we look at pure singlet and triplet populations whose values display much less regularity and nonnegligible contributions are observed between all, even nonbonded, atoms. We can, thus, see that the proposed population scheme is able not only to detect the presence of bonds between the atoms but also to give more detailed information about the multiplicity of individual bonds. This is the first, indirect, indication of the convenience of introducing effective pairon populations. Another, perhaps even more important, indication of the specific role of effective pairon populations arises from the following identity (10).

$$\sum_A \Pi_{AA}^{\text{eff}} + \sum_{A<B} \Pi_{AB}^{\text{eff}} = \frac{N}{2}\quad (10)$$

The proof of this identity immediately follows from the definition of effective populations (9). Using this equation, the individual terms in Eq. (10) can be replaced by identities (11), from which it is evident that the left hand side of Eq. (10) is equal

TABLE I
*Calculated values of singlet, triplet and effective pairon populations for
 a series of simple molecules with single bonds*

| molecule | type | Π_{AA}^s | Π_{AA}^t | Π_{AA}^{eff} | Π_{AB}^s | Π_{AB}^t | Π_{AB}^{eff} |
|---------------------------------|-------|--------------|--------------|-------------------------|--------------|--------------|-------------------------|
| H ₂ | H | 0.250 | 0.0 | 0.250 | - | - | - |
| | H-H | - | - | - | 0.500 | 0.0 | 0.500 |
| F ₂ | F | 7.750 | 13.500 | 3.250 | - | - | - |
| | F-F | - | - | - | 12.500 | 36.0 | 0.500 |
| H-F | H | 0.127 | 0.0 | 0.127 | - | - | - |
| | F | 8.345 | 14.792 | 3.414 | - | - | - |
| | H-F | - | - | - | 1.528 | 3.208 | 0.459 |
| H ₂ O | H | 0.175 | 0.0 | 0.175 | - | - | - |
| | O | 6.341 | 10.988 | 2.678 | - | - | - |
| | O-H | - | - | - | 1.566 | 3.244 | 0.485 |
| | H...H | - | - | - | 0.176 | 0.523 | 0.002 |
| NH ₃ | H | 0.213 | 0.0 | 0.213 | - | - | - |
| | N | 4.353 | 7.441 | 1.873 | - | - | - |
| | N-H | - | - | - | 1.455 | 2.882 | 0.494 |
| | H...H | - | - | - | 0.214 | 0.638 | 0.001 |
| CH ₄ | H | 0.259 | 0.0 | 0.259 | - | - | - |
| | C | 2.422 | 4.314 | 0.984 | - | - | - |
| | C-H | - | - | - | 1.245 | 2.264 | 0.490 |
| | H...H | - | - | - | 0.260 | 0.772 | 0.002 |
| CH ₃ F | H | 0.253 | 0.0 | 0.253 | - | - | - |
| | C | 2.205 | 3.873 | 0.914 | - | - | - |
| | F | 8.246 | 14.634 | 3.368 | - | - | - |
| | C-H | - | - | - | 1.179 | 2.101 | 0.479 |
| | C-F | - | - | - | 7.012 | 19.604 | 0.477 |
| | H...H | - | - | - | 0.255 | 0.749 | 0.005 |
| | H...F | - | - | - | 1.826 | 5.446 | 0.011 |
| CH ₃ OH | H (O) | 0.168 | 0.0 | 0.168 | - | - | - |
| | H (C) | 0.265 | 0.0 | 0.265 | - | - | - |
| | O | 6.339 | 11.026 | 2.664 | - | - | - |
| | C | 2.280 | 4.032 | 0.936 | - | - | - |
| | C-H | - | - | - | 1.218 | 2.228 | 0.475 |
| | C-O | - | - | - | 6.275 | 17.320 | 0.501 |
| | O-H | - | - | - | 1.534 | 3.180 | 0.474 |
| CH ₃ NH ₂ | H (N) | 0.204 | 0.0 | 0.204 | - | - | - |
| | H (C) | 1.205 | 2.165 | 0.483 | - | - | - |
| | C | 2.363 | 4.197 | 0.964 | - | - | - |
| | N | 4.443 | 7.631 | 1.900 | - | - | - |
| | C-H | - | - | - | 1.205 | 2.165 | 0.484 |
| | N-H | - | - | - | 1.437 | 2.856 | 0.485 |
| | C-N | - | - | - | 5.377 | 14.628 | 0.501 |
| C ₂ H ₆ | H | 0.253 | 0.0 | 0.253 | - | - | - |
| | C | 2.488 | 4.437 | 1.009 | - | - | - |
| | C-H | - | - | - | 1.245 | 2.272 | 0.488 |
| | C-C | - | - | - | 4.214 | 11.157 | 0.495 |

TABLE II

Calculated values of singlet, triplet and effective pairon populations for a series of simple molecules with double bonds.

| molecule | type | Π_{AA}^s | Π_{AA}^t | Π_{AA}^{eff} | Π_{AB}^s | Π_{AB}^t | Π_{AB}^{eff} |
|-------------------------------|-------|--------------|--------------|------------------|--------------|--------------|------------------|
| ethene | H | 0.230 | 0.0 | 0.230 | - | - | - |
| | C | 2.609 | 4.657 | 1.056 | - | - | - |
| | C-H | - | - | - | 1.220 | 2.214 | 0.482 |
| | C=C | - | - | - | 4.658 | 10.994 | 0.993 |
| | H...H | - | - | - | 0.232 | 0.684 | 0.004 |
| CH ₂ O | H | 0.251 | 0.0 | 0.251 | - | - | - |
| | C | 2.170 | 3.799 | 0.903 | - | - | - |
| | O | 6.254 | 10.909 | 2.618 | - | - | - |
| | C-H | - | - | - | 1.153 | 2.110 | 0.450 |
| | C=O | - | - | - | 6.330 | 15.984 | 0.970 |
| | H...H | - | - | - | 0.262 | 0.717 | 0.023 |
| CH ₂ NH | H (N) | 0.205 | 0.0 | 0.205 | - | - | - |
| | H (C) | 0.241 | 0.0 | 0.241 | - | - | - |
| | C | 2.427 | 4.304 | 0.992 | - | - | - |
| | N | 4.368 | 7.497 | 1.869 | - | - | - |
| | C-H | - | - | - | 1.199 | 2.192 | 0.468 |
| | C=N | - | - | - | 5.651 | 13.944 | 1.003 |
| | N-H | - | - | - | 1.425 | 2.837 | 0.480 |
| | H...H | - | - | - | 1.237 | 3.694 | 0.005 |
| N ₂ H ₂ | H | 0.201 | 0.0 | 0.201 | - | - | - |
| | N | 4.157 | 7.061 | 1.803 | - | - | - |
| | N=N | - | - | - | 7.019 | 18.007 | 1.016 |
| | N-H | - | - | - | 1.382 | 2.717 | 0.476 |
| | H...H | - | - | - | 0.209 | 0.580 | 0.016 |
| | N...H | - | - | - | 1.145 | 3.428 | 0.002 |
| allene | H | 0.236 | 0.0 | 0.236 | - | - | - |
| | C (1) | 2.615 | 4.696 | 1.050 | - | - | - |
| | C (2) | 2.423 | 4.354 | 0.972 | - | - | - |
| | C=C | - | - | - | 4.522 | 10.583 | 0.994 |
| | C-H | - | - | - | 1.229 | 2.270 | 0.472 |
| | C...C | - | - | - | 4.181 | 12.538 | 0.004 |
| ketene | H | 0.213 | 0.0 | 0.213 | - | - | - |
| | C (1) | 2.806 | 5.004 | 1.138 | - | - | - |
| | C (2) | 2.128 | 3.779 | 0.868 | - | - | - |
| | O | 6.159 | 10.735 | 2.581 | - | - | - |
| | C-H | - | - | - | 1.209 | 2.236 | 0.463 |
| | C=C | - | - | - | 4.373 | 10.238 | 0.960 |
| | C=O | - | - | - | 6.226 | 15.782 | 0.965 |
| C...O | - | - | - | 6.634 | 19.701 | 0.067 | |

TABLE III

Calculated values of singlet, triplet and effective pairon populations of a series of simple molecules with triple bonds

| molecule | type | Π_{AA}^s | Π_{AA}^t | Π_{AA}^{eff} | Π_{AB}^s | Π_{AB}^t | Π_{AB}^{eff} |
|----------------|-------|--------------|--------------|-------------------------|--------------|--------------|-------------------------|
| CH=CH | H | 0.179 | 0. | 0.179 | - | - | - |
| | C | 2.705 | 4.528 | 1.196 | - | - | - |
| | C-H | - | - | - | 1.115 | 1.925 | 0.473 |
| | C≡C | - | - | - | 5.054 | 10.727 | 1.478 |
| | H...H | - | - | - | 0.181 | 0.531 | 0.004 |
| | C...H | - | - | - | 0.884 | 2.618 | 0.011 |
| HCN | H | 0.164 | 0.0 | 0.164 | - | - | - |
| | C | 2.626 | 4.662 | 1.072 | - | - | - |
| | N | 4.153 | 7.055 | 1.801 | - | - | - |
| | C-H | - | - | - | 1.060 | 1.787 | 0.464 |
| | C=N | - | - | - | 5.955 | 13.423 | 1.481 |
| | H...N | - | - | - | 1.041 | 3.073 | 0.017 |
| N ₂ | N | 4.000 | 6.750 | 1.750 | - | - | - |
| | N=N | - | - | - | 7.000 | 16.500 | 1.500 |
| CO | C | 2.432 | 3.458 | 1.279 | - | - | - |
| | O | 6.072 | 10.737 | 2.493 | - | - | - |
| | C=O | - | - | - | 6.496 | 15.805 | 1.227 |

$$\sum_A \Pi_{AA}^s + \sum_{A<B} \Pi_{AB}^s = N^{(s)} = \frac{N(N+2)}{8}$$

$$\sum_A \Pi_{AA}^t + \sum_{A<B} \Pi_{AB}^t = N^{(t)} = \frac{3N(N-2)}{8} \quad (11)$$

to the total number of singlet minus one third of the total number of triplet pairs that can be formed in a closed shell system with N electrons. As it can be verified by direct calculation, the difference between the number of singlet and (one third) triplet pairs is identically equal to $N/2$. This result is very interesting since $N/2$ just gives the total number of bonds plus free electron pairs that can be formed in a closed shell system with N valence electrons. We can thus see that, while there is no simple correlation between the molecular structure and the number of pure singlet and triplet pairs, such a parallel clearly exists for effective pairs.

While the straightforward interpretation of effective populations exactly parallels what was already found in previous studies, it is perhaps interesting to give a short remark on the values of individual singlet and triplet populations. The simplest situation is the case of monoatomic populations Π_{AA}^s and Π_{AA}^t , whose values can be interpreted as the total number of singlet and triplet pairs on a given atom. For the system of N electrons with zero net spin, the number of these pairs is given by Eq. (11) and, as it can be easily verified by direct calculation, the values resulting from the use of Eq. (11) for the values of N given by the Mulliken population analysis are quite close to the actual values of Π_{AA}^s and Π_{AA}^t . In contrast to simple interpre-

tation of the values of monoatomic contributions, the case of individual singlet and triplet biatomic populations is much more complex and we can offer no explanation for them except for a rough rule that triplet biatomic pair populations are usually higher than the singlet ones simple because there are more triplet than singlet pairs.

Having demonstrated the reproduction of a molecular graph by biatomic (effective) pairon populations, let us turn our attention to another interesting feature of the proposed population scheme, namely detection of the presence of free electron pairs on atoms. For this purpose, monoatomic populations play the decisive role. In order to demonstrate the above features, it is convenient to start with the simplest case of the H_2 molecule. As it can be seen from Table I, the pairon populations are in this case distributed in such a way that half of the pair resides in covalent biatomic contribution Π_{AB} while the remaining half is evenly distributed between two atomic ionic populations.* In this connection it is perhaps interesting to mention that, for this particular system, the same result can be obtained also from simple VB analysis of the MO wave function and, as such an analysis has shown, the relatively high contributions of ionic terms are a direct consequence of the inability of the MO function to describe correctly the dissociation of the molecule. This specific drawback of the MO wave function is not, however, important here since, for the molecules close to ground state equilibrium geometries, the MO description is fairly good.

After this short explicatory excursion, let us return to our examples of the H_2 molecule and let us focus our attention on the values of monoatomic populations. As expected, the symmetry of the molecules finds its reflection in the equality of the corresponding contributions Π_{AA} and Π_{BB} . This result is quite general and the same distribution of monoatomic terms is observed for any ideally nonpolar A-A bond (Table I). On the other hand, the inherent polarity of bonds A-B will find its reflection in the change of relative contributions of Π_{AA} and Π_{BB} . As an example, let us analyze from this point of view the electron distribution in the H-Cl molecules. In this case, the resulting values of effective pairon populations are the following (Eq. 12):

$$\begin{aligned}\Pi_H^{\text{eff}} &= 0.167 \\ \Pi_{Cl}^{\text{eff}} &= 3.352 \\ \Pi_{H,Cl}^{\text{eff}} &= 0.483\end{aligned}\tag{12}$$

What can be deduced from these values? Let us first imagine an hypothetical situation where the H-Cl bond is ideally nonpolar. In this case, it is possible to expect that the atomic population on hydrogen will again be 0.25 and the same value can also be expected to contribute from the H-Cl bond to the atomic population of chlorine. However, the chlorine atom also carries three electron pairs, the presence of which should be taken into account. Due to the parallel between the total number of effective pairs and the number of bonds plus free electron pairs (10), such a correction is extremely simple and the contribution is just 3. Thus, the total atomic population on chlorine should be 3.25. Since, however, the H-Cl bond is inherently polar, deviations from this idealized limit can be expected. This is actually the case

* In the ground state of H_2 molecule, only one singlet and no triplet pairs can be formed so that in this case the effective populations are identical to pure singlet populations.

but, as seen from the actual values, the real electron distribution is not very far from this idealized limit. Moreover, the differences clearly correspond to the differences in electronegativity. Thus, *e.g.*, due to greater electronegativity of chlorine, the corresponding atomic population exceeds the idealized limit 3.25 while the population on the less electronegative hydrogen is correspondingly less. In a completely analogous way, it would be possible to analyze any other molecule but, instead of presenting additional examples, we will only give the idealized values of atomic populations for atoms with 2, 1 and 0 electron pairs *e.g.* (H_2O , NH_3 and CH_4). These values are 2.5 (2 free pairs + 2×0.25), 1.75 (1 free pair + 3×0.25) and 1 (0 free pairs + 4×0.25), respectively. As evident from the Tables, these hypothetical values are quite close to the actual values in real molecules and the differences correspond again to the electronegativity of the atoms.

Although the reproduction of the classical structural formula by the values of pairon populations is certainly the main goal of the new approach, there are, nevertheless, also some other interesting features worth mentioning. First such example concerns the possibility to interpret the physical meaning of the quantum chemical definition of the concept of valence. Classically, the valence of a given atom is a measure of its capacity to enter into bonding with its partners and, since the Lewis interpretation connects each covalent bond with a shared electron pair, the valence also gives the number of electron pairs that a given atom is able to share with its neighbours. On the other hand, the quantum chemical definition of valence was proposed by Jug and Gopinathan^{39,40} who defined it in terms of the so-called Wiberg indices W^{41} (Eq. (13)).

$$V_A = \sum_{B \neq A} W_{AB} = \sum_{B \neq A} \sum_{\mu}^A \sum_{\nu}^B p_{\mu\nu}^2 \quad (13)$$

Although the numerical values of Jug's valencies are remarkably close to what can be expected classically, the fact that both definitions are actually completely equivalent was not clear until very recently, when a direct proof based on the use of effective populations was given.²⁵ As it can be seen, the original Jug's definition can be alternatively rewritten in the form of (14) from which the parallel with the classical definition is immediately apparent.

$$V_A = 2 \sum_{B \neq A} \Pi_{AB}^{\text{eff}} \quad (14)$$

Another example of the usefulness of introducing effective pairon populations concerns their nearly perfect transferability. Thus, *e.g.*, if we look at the Tables, it is possible to see that, irrespective of the type of the molecule, the effective pairon populations for the bonds of the same type (C-H or O-H bonds for instance) are very close. This transferability of effective pairon populations is a very useful property since it provides a direct theoretical justification for the empirically well known principle of the additivity of bond energies.⁴² This result, along with all the interesting properties mentioned above, is very important since the ability of effective pairon populations to mimic the properties usually attributed to chemical bonds could considerably help to understand the nature of the chemical bond. Some investigations in this direction are currently under way in our laboratory and their results will be

reported elsewhere.⁴³ This above all, concerns the analysis of the basis set dependence since, like for other Mulliken-like population schemes, the values of pair populations can be expected to display sensitivity to the basis set chosen. This is not particularly important for the semiempirical approach described here but for the interpretation of more accurate ab initio data this factor can be of crucial importance.

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SAŽETAK

Od valne funkcije do strukturne formule

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Nedavno predložena paronska populacijska analiza, zasnovana na geminalnom razvoju gustoće elektronskih parova, primijenjena je u istraživanju molekulske strukture nekoliko jednostavnih molekula. Pokazano je da paronske populacije izravno reproduciraju klasične strukturne formule, pa stoga predstavljaju novo i iznenađujuće jednostavno sredstvo za dobijanje strukturne formule molekule iz pripadne joj valne funkcije.