

ELECTRON PAIRING AND CHEMICAL BONDS

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The recently proposed population analysis of pair densities is applied to the investigation of molecular structure of several simple molecules. The values of pairon populations straightforwardly reproduce the classical structural formula including the multiplicity of the bonds and provide thus the so far missing link between quantum chemical and Lewis's classical picture of bonding. As demonstrated, the formalism of the proposed approach provides strong theoretical evidence for the frequently expected but so far elusive role of electron pairing in chemical bonding.

One of the most fruitful concepts of modern chemistry is the concept of chemical bond¹. Because of its immense impact for chemistry, this concept has become the subject of numerous investigations aiming at disclosure of its exact meaning. The first successful attempt in this respect is due to Lewis², whose idea of chemical bond as a shared electron pair allowed a clear physical interpretation of classical structural formulae. This, in principle localized picture of bonding was supported by the approximate validity of empirical additivity rules for various molecular properties.

The really quantitative theory of chemical bonding was, however, created only after the formulation of quantum mechanics. This quantum chemical description leads, however, to an entirely different picture of bonding. Instead of the concept of more or less independent chemical bonds localized in different regions of space, quantum mechanics operates with the wave function which is usually spread over the whole molecule. This considerable conceptual difference as well as the immense debt which chemistry owes to classical Lewis's electron pair theory has stimulated from early days of quantum theory the attempts at the reconciliation of these two alternative pictures of bonding³⁻²⁶.

If we disregard the concept of the so-called localized orbitals³⁻¹¹ which, because of their one-electron nature are inherently unable to describe the two-electron phenomena, the first serious attempt to evaluate the role of electron pairing in bonding explicitly is represented by the so-called loge theory¹⁸⁻²². According to this theory the molecular volume is to be dissected into several nonoverlapping regions in a way to minimize the so-called missing information function $I(P_n, \Omega)$, where $P_n(\Omega)$ is the probability that n

electrons occupy the region (loge) Ω when the remaining $(N - n)$ electrons are confined in the remainder of the system

$$I(P_n, \Omega) = - \sum_n P_n(\Omega) \ln P_n(\Omega) .$$

Using this definition it was indeed possible to obtain the best loges for a number of simple molecules and the most probable partitioning did indeed localize two electrons in regions which are usually associated with core, bonded and nonbonded electron pairs. In spite of this success, the parallel between the loge and chemical bond is not, however, entirely complete since quite simple molecules were also found, for which the partitioning into loges is impossible.

Another approach closely related to the loge theory is due to Bader^{23,24}, Levy²⁵ and Julg²⁶, who proposed to determine the boundaries of individual regions from the condition of minimization of fluctuation of electron pair in these regions. Nevertheless, the parallel between the bond and the localized electron pair was not completely convincing in this approach either since there are molecules for which the possibility of pair localization is unacceptably small. In view of this result Bader²⁷ has even proposed not to consider as fundamental building blocks of the molecules the individual chemical bonds but, instead, he rather prefers the dissection of molecule into what he calls atoms in molecule.

In spite of this, the intuitive faith in the role of electron pair in bonding is still strong enough and the attempts to disclose such a role still continue²⁸⁻³⁰. Into the framework of this effort can be included also our recent study³¹ in which a new formalism, the so-called population analysis of pair density was proposed. Using this approach we have been able to demonstrate that properly defined pair quantities do indeed support the electron pair nature of chemical bond.

Our aim in this study is to pursue the general methodology of the pair population analysis and to demonstrate that its formalism leads to the picture of chemical bond that is remarkably close to classical Lewis idea of shared electron pair.

THEORETICAL

Since the mathematical formalism of the proposed population analysis is sufficiently described in our previous study³¹ we will not go into details here and, instead, only a brief review of the basic ideas and formulas to the extent necessary for the purpose of this study will be given. The philosophy of the proposed population analysis arises from simple idea that in order to assess the role of electron pair in bonding it is necessary to work with quantities which are able to describe the desired pair behavior¹³. The simplest of such quantities is the second order density matrix or, more precisely, only the diagonal element of this matrix, the so-called pair density

$$\gamma(1,2) = \frac{N(N-1)}{2} \int \Phi^2(1, 2, \dots, N) d\sigma_1 d\sigma_2 dx_3 dx_4 \dots dx_N. \quad (1)$$

Within the framework of SCF approximation, which is of our concern here, the pair density is given by the well known formula (2),

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

where the expansion coefficients $\Omega_{\alpha\beta\gamma\delta}$ are given by Eq. (3).

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

As shown, however, in previous study, such a straightforward expansion in the basis of atomic orbitals is not very convenient since the four index form of the expansion coefficient matrix Ω is for the work with pair density unnecessarily complicated. In order to overcome this complication we proposed to expand the pair density in the basis of true two-electron functions – the so-called geminals (spingeminals) λ . Using this approach the original expansion formula simplifies to the form Eq. (4) from which it is evident that in geminal basis the pair density has the form of usual two-index matrix γ

$$\gamma(1,2) = \sum_{\alpha\beta} \gamma_{\alpha\beta} \lambda_{\alpha}(1) \lambda_{\beta}(1,2). \quad (4)$$

We can thus see that in the geminal basis the pair density has the same simple form as normal first order density matrix in the basis of orbitals. This allows us to use the idea of Mulliken population analysis³² and to introduce pairon population analysis in which, owing to orthogonality of geminal basis, only the diagonal elements of the pair density can be taken into account. Since these elements unambiguously correspond to individual geminals which, in turn, can be directly associated with electron pair either localized on atoms or shared between atoms, it is possible to introduce the atomic and biatomic pairon populations analogous to “net” quantities of Mulliken analysis. This is an important simplification since in alternative pairon population analysis³³ the three- and four-atomic contributions appeared. In spite of straightforward parallel with Mulliken analysis, the situation with pairon populations is nevertheless slightly more compli-

cated. This is due to the fact that the matrices γ representing geminal and/or spingeminal expansion of pair densities have a special block diagonal form with individual blocks corresponding to singlet and triplet states of electron pair. This suggests that in our approach it is possible to distinguish between the singlet and triplet pairon populations. The resulting expressions are given by the following equations (5)

$$\Pi_{AA}^s = \frac{1}{4} \sum_{\mu}^A p_{\mu\mu}^2 + \frac{1}{4} \sum_{\mu < \nu}^A (p_{\mu\mu} p_{\nu\nu} + p_{\mu\nu}^2) \quad (5a)$$

$$\Pi_{AA}^t = \frac{3}{4} \sum_{\mu < \nu}^A (p_{\mu\mu} p_{\nu\nu} - p_{\mu\nu}^2) \quad (5b)$$

$$\Pi_{AB}^s = \frac{1}{4} \sum_{\mu}^A \sum_{\nu}^B (p_{\mu\mu} p_{\nu\nu} + p_{\mu\nu}^2) \quad (5c)$$

$$\Pi_{AB}^t = \frac{3}{4} \sum_{\mu}^A \sum_{\nu}^B (p_{\mu\mu} p_{\nu\nu} - p_{\mu\nu}^2), \quad (5d)$$

where $p_{\mu\mu}$ and $p_{\mu\nu}$ are the elements of ordinary charge density bond order matrix defined by Eq. (6)

$$p_{\mu\nu} = 2 \sum_i^{\text{occ}} c_{\mu i} c_{\nu i}. \quad (6)$$

The individual populations fulfill the natural normalization conditions (7), where the quantities $N^{(1)}$ and $N^{(3)}$ give the total number of singlet and the triplet pairs in the system with N electrons.

$$\begin{aligned} \sum_A \Pi_{AA}^s + \sum_{A < B} \Pi_{AB}^s &= N^{(1)} = \frac{N(N+2)}{8} \\ \sum_A \Pi_{AA}^t + \sum_{A < B} \Pi_{AB}^t &= N^{(3)} = \frac{3N(N-2)}{8} \end{aligned} \quad (7)$$

The total number of pairs which is equal to $N(N-1)/2$ is given by the sum of $N^{(1)}$ and $N^{(3)}$. As demonstrated in previous study³¹, the above introduced pairon populations

have a number of interesting applications. Among them the most important is the possibility to reproduce the classical structural formulae including the multiplicity of the bonds. The quantity on the basis of which such a reproduction is possible is the effective population Π_{AB}^{eff} defined by the relation (8).

$$\Pi_{AB}^{\text{eff}} = \Pi_{AB}^{\text{s}} - \frac{1}{3} \Pi_{AB}^{\text{t}} \quad (8)$$

Using these quantities we have been able to show that these populations attain nonnegligible values only between the atoms joined by a classical bond while for nonconnected atoms the populations are close to zero. Moreover, where the populations indicate the presence of the bonds, the values are little sensitive to the nature of bond, and rather than on the type of bonded atoms depend on the multiplicity of the bond. Thus, for example, the values for all single bonds are close to 0.5, whereas for double and triple bonds the populations are close to 1 and 1.5, respectively.

While in previous study³¹ the effective bond populations were introduced rather intuitively, our aim in this report is to attempt at more sound theoretical justification of these quantities and to demonstrate the important role they play in the qualitative understanding of the nature of chemical bond.

RESULTS AND DISCUSSION

In order to analyze the role of electron pairing in bonding it is first convenient to discuss the applicability of pairon populations by several practical examples. For this purpose we present in Tables I and II the calculated values of singlet, triplet and effective populations for a series of simple molecules. The calculations were performed by standard MNDO method³³. The molecules were considered in their respective optimized geometries.

Let us attempt now to discuss the conclusions suggested by the presented values. First what can be seen are again the already reported trends in the values of effective populations³¹, whose values display much higher regularity than the values of individual singlet and triplet populations themselves. The most important in this respect is the remarkable independence of the effective populations on the type of bonded atoms and, on the other hand, their proportionality to the multiplicity of the bond. This opens the possibility to reproduce the classical structural formula just from the quantities directly derivable from the wave functions. In this connection it is perhaps fair to say that a certain visualization of the structural formula is available, even in graphical form, using various localization procedures incorporated into modern quantum chemical programs but as already stressed above this, in principle one-electron approach, is inherently unable to say anything about the presumed role of electron pair in bonding. In this

respect thus our approach does not provide only a simple duplication of what was already known but, and this is new, also brings a clear theoretical evidence in favor of Lewis's electron pair model of chemical bond.

Since the role of the effective bonding populations in reproducing the structural formula was sufficiently demonstrated in previous study³¹, we concentrate ourselves here to another interesting feature which is the exploitation of monoatomic populations Π_{AA}^{eff} defined by Eq. (9).

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

As we shall see these values allow one to enrich the primary structural information by the detection of eventual presence of free electron pairs and, also, by a rough estimate of the asymmetry in shared electron pair resulting from the differences in electronega-

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

Molecule	One-center terms				Two-center terms			
	type	Π_{AA}^s	Π_{AA}^t	Π_{AA}^{eff}	type	Π_{AB}^s	Π_{AB}^t	Π_{AB}^{eff}
H ₂	H	0.250	0.000	0.250	HH	0.500	0.000	0.500
HF	H	0.127	0.000	0.127	HF	1.528	3.208	0.459
	F	8.345	14.792	3.414				
H ₂ O	H	0.175	0.000	0.175	OH	1.566	3.244	0.485
	O	6.341	10.988	2.678	H...H	0.176	0.523	0.002
NH ₃	H	0.213	0.000	0.213	NH	1.455	2.882	0.494
	N	4.353	7.441	1.873	H...H	0.214	0.638	0.001
CH ₄	H	0.259	0.000	0.259	CH	1.245	2.264	0.490
	C	2.422	4.314	0.984	H...H	0.260	0.772	0.002
HCl	H	0.167	0.000	0.167	HCl	1.708	3.674	0.483
	Cl	8.126	14.326	3.351				
H ₂ S	H	0.229	0.000	0.229	SH	1.705	3.618	0.499
	S	5.904	10.078	2.545	H...H	0.229	0.686	0.000
PH ₃	H	0.297	0.000	0.297	PH	1.537	3.122	0.496
	P	3.610	5.963	1.622	H...H	0.297	0.890	0.000
SiH ₄	H	0.331	0.000	0.331	SiH	1.203	2.255	0.451
	Si	1.840	3.134	0.795	H...H	0.337	0.974	0.012

tivity of bonded atoms. In order to demonstrate this particular feature it is convenient to analyse first the simplest case of homonuclear biatomic molecule like H_2 . In this case the situation is especially simple since the MO wave function leads to the well-known result according to which half of the pair resides in biatomic (covalent) populations while remaining half is uniformly distributed between two atomic (ionic) populations.

$$|\Phi\bar{\Phi}\rangle = \frac{1}{4} |\chi_a \bar{\chi}_a\rangle + \frac{1}{4} |\chi_b \bar{\chi}_b\rangle + \frac{1}{2} {}^1\Psi$$

$${}^1\Psi = \frac{1}{\sqrt{2}} \{ |\chi_a \bar{\chi}_b\rangle + |\chi_b \bar{\chi}_a\rangle \} \quad (10)$$

Prior to discussing the implications arising from the ionic populations let us focus our attention just on another feature of pairon population analysis which is the advantage of introducing effective instead of direct use of primary singlet and triplet populations*. At the first sight such an introduction could seem rather artificial since according to naive expectations the pure singlet pairs should better correspond to bonding. Such is not, however, the case. The first indication of the inconvenience of pure singlet (or triplet) populations arises from the fact that the number of bonds plus core and free electron pairs which a given molecule can form is usually much lower than the number of (singlet or triplet) pairs. It would be therefore quite difficult to have any direct relation between the number of singlet (or triplet) pairs and the number of bonds. For that reason it is also quite difficult to say whether some clearcut physical interpretation can be attributed to individual singlet and triplet populations. The situation is, however, entirely different with the effective populations whose straightforward relation to chemical bonds clearly follows from the Eq. (11). As can be seen, the sum of effective populations represented by the difference between the number of singlet and one third of triplet pairs is equal to $N/2$ which is just the number of bonds plus free electron pairs for a molecule with N valence electrons.

$$\sum_A \Pi_{AA}^{\text{eff}} + \sum_{A < B} \Pi_{AB}^{\text{eff}} = N^{(1)} - \frac{1}{3} M^{(3)} = \frac{N}{2} \quad (11)$$

In our case of hydrogen molecule we thus have just one bond and no free pair.

* In the ground state of H_2 molecule it is possible to form only one singlet and no triplet pair so that the effective populations are in this case identical with pure singlet populations.

After this discussion of the specific role of effective pairon populations let us return back to the problem of monoatomic populations. Their equality ($\Pi_{AA}^{\text{eff}} = \Pi_{BB}^{\text{eff}} = 0.25$) indicates that in this ideally symmetric case the electron pair is shared uniformly between the atoms. As a next example let us consider the case of biatomic heteropolar molecule like H-F. As can be seen from the Table I, the effective populations are the following

$$\begin{aligned}\Pi_{HH}^{\text{eff}} &= 0.127 \\ \Pi_{FF}^{\text{eff}} &= 3.414 \\ \Pi_{HF}^{\text{eff}} &= 0.459.\end{aligned}\quad (12)$$

What can be deduced from these values? First of all it is possible to see that the bond population Π_{HF}^{eff} is again close to ideal value of 0.5, indicating thus the bond as single. Much more interesting are, however, the values of atomic effective populations since their values, as already stressed above, give an information about the asymmetry of the charge distribution and, also, about the presence of free electron pairs. Let us consider, just from this point of view, the atomic populations in H-F molecule. If the electron distribution of the H-F bond were ideally nonpolar, it would be possible to expect a value of 0.25 for atomic populations on hydrogen and, if we take into account 3 free

TABLE II
Calculated values of singlet, triplet and effective pairon populations for a series of molecules with multiple bonds

Molecule	One-center terms				Two-center terms			
	type	Π_{AA}^s	Π_{AA}^t	Π_{AA}^{eff}	type	Π_{AB}^s	Π_{AB}^t	Π_{AB}^{eff}
CH ₂ =CH ₂	H	0.230	0.000	0.230	CH	1.220	2.214	0.482
	C	2.609	4.657	1.056	CC	4.658	10.994	0.993
					H...H	0.232	0.684	0.004
CH ₂ O	H	0.251	0.000	0.251	CH	1.153	2.110	0.450
	C	2.170	3.799	0.903	CO	6.330	15.984	0.970
	O	6.254	10.909	2.618	H...H	0.262	0.717	0.023
					O...H	1.588	4.683	0.027
CH≡CH	H	0.179	0.000	0.179	CH	1.115	1.925	0.473
	C	2.705	4.528	1.196	CC	5.054	10.727	1.478
					H...H	0.181	0.531	0.004

electron pairs on fluorine, a population 3.25 on this atom*. Although as can be seen from the actual values the atomic populations are quite close to these limits, some deviations do exist as well and just these deviations inform us about the asymmetry of the charge distribution. Thus e.g., the fact that the fluorine population is higher than expected while the hydrogen population is less is just an indication of the greater electronegativity of fluorine. The analogous situation holds then also for other molecules. Thus, e.g., for H₂O and H₂S molecules, the ideally nonpolar distribution should require the population of 0.25 on each hydrogen and 2.5 (2 + 2 × 0.25) on oxygen (sulfur) whereas for NH₃ (PH₃) molecule the ideal population should be 0.25 on each hydrogen and 1.75 (1 + 3 × 0.25) on nitrogen (phosphorus). As can be seen from actual values, the individual populations are rather close to these ideal limits and the existing deviations again correctly reflect the differences in electronegativity. In this connection it is perhaps interesting to remark that the parallel between the atomic populations and electronegativity is even of quantitative nature. As can be seen from Fig. 1 corresponding to a series of simple hydrides of the type H_nX (X = F, O, N, C, Cl, S, P, Si) there is a nearly perfect linear correlation between the hydrogen atomic population $\Pi_{\text{HH}}^{\text{eff}}$ and the valence state electronegativity³⁴ of central atom X in the same series. We can thus see that the introduction of the effective pairon populations is not apparently an artificial construction but that these values do indeed reflect real facets of electron structure. Another interesting feature supporting the introduction of effective pairon populations is that their values are closely related to another key chemical concept which is the concept of valence^{35–37}. Classically the valence is understood as a number of electron pairs which a given atom is able to share with its neighbours. On the other hand another quantum chemical definition was proposed by Jug and while the calculated values of valencies are close to classical expectations, the relation of both definitions is not immediately apparent. As we shall see, the effective pairon populations can just provide a missing link between both definitions. As can be seen, namely, from the definitions (5), the sum of effective populations is just equal to Wiberg indices³⁸ W_{AB} , in terms of which the valencies were defined by Jug. It holds:

$$2 \sum_{\text{B} \neq \text{A}} \Pi_{\text{AB}}^{\text{eff}} = \sum_{\text{B} \neq \text{A}} \sum_{\mu}^{\text{A}} \sum_{\nu}^{\text{B}} p_{\mu\nu}^2 = \sum_{\text{B} \neq \text{A}} W_{\text{AB}} = V_{\text{A}}. \quad (13)$$

* The trivial correction of atomic populations for the presence of free electron pairs is a direct consequence of Eq. (11) according to which there is a 1 : 1 correspondence of effective populations and chemical bonds and/or free electron pairs.

In connection with the problem of quantum chemical definition of valency it is also interesting to remark that the ideas requiring the introduction of characteristics analogous to our effective populations were formulated already in the early days of quantum mechanics. To illustrate this point we quote from the commemorative paper by Hund³⁹: "The valence of an atom is the number of electrons which can enter bonding minus the number of electrons which have to enter bond weakening states". Taking into account that the electron pair in singlet geminal corresponds to attraction between nuclei while the pair in triplet geminal is repulsive (see e.g. the differences in the behavior of singlet and triplet states of hydrogen molecule), the parallel with our effective quantities is striking.

Summarizing the above results we would like to express our belief that the proposed pairon population analysis represents a new, perhaps interesting attempt to explain the role of electron pairing in chemical bonding and to contribute thus to the solution of the old but still living problem of the nature chemical bond and of its relation to classical Lewis ideas. In this respect the main conclusion of this study is that if some quantity could be straightforwardly related to chemical bond then it should be some "effective" quantity corresponding, like our effective populations, to the difference between attractive singlet and repulsive triplet contributions. From this point of view it is also perhaps possible to understand the failures of previous attempts to prove the pair nature of chemical bond since the characteristics these studies dealt with were based on manipulations with quantities corresponding to either α,α or α,β electron pairs, but these quantities, not being derived from spin pure states of electron pair are for the correct treatment of pair properties apparently inconvenient.

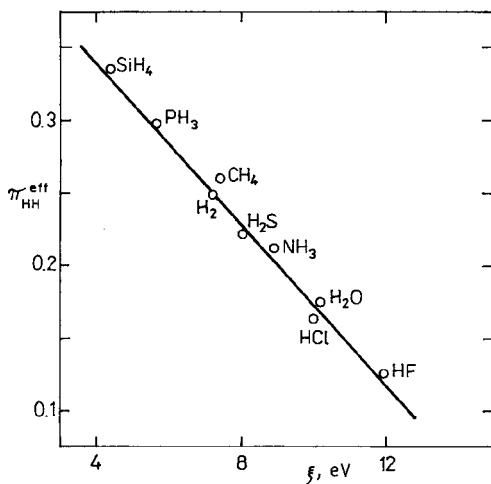


FIG. 1
Dependence of effective atomic populations Π_{HH}^{eff} in a series of simple hydrides H_nX on the values of valence state electronegativity of the hydrogen in the same series. The electronegativities were determined according to procedure reported in the study³⁴

In connection with the above proved role of electron pair in bonding it is, however, necessary to bear in mind, that the straightforward parallel with classical Lewis's ideas supported by our model can be expected to hold only for "normal" closed shell molecules which are correctly described by simple SCF one-determinantal wave function. If such is not the case as, e.g. for excited states, open shell structures or molecules whose description requires the inclusion of electron correlation (1,3 dipoles for instance), the above simple analysis is not convenient in its present form and in order to make it applicable here, the appropriate generalizations will be certainly required. These generalizations are currently being investigated in our laboratory and their results will be described elsewhere.

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