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# Electron Pairing and Chemical Bonds. Anatomy of Bond Formation

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Several methods of the correlated pair density analysis are introduced. Based on these analyses, the splitting of the chemical bond in $H_2$ has been investigated in detail. It has been found that the splitting does not proceed as a smooth continuous process but rather that it has the character of an abrupt change.

## INTRODUCTION

There is probably no other concept that contributed to the development of chemistry so remarkably as the concept of chemical bond. The crucial step in the understanding of the nature of chemical bond was made by Lewis[1] whose idea that chemical bonds are formed by shared electron pairs has played the central role in the development of modern chemistry. The unusual fertility of this idea was certainly the reason why the Lewis classical model survived the advent of quantum theory, even if the quantum picture of bonding with the wave function spread over the whole molecule is considerably different from the classical picture of isolated localized chemical bonds. The apparent incompatibility of quantum and classical descriptions stimulated many studies aiming at reconciliation of these alternative pictures of bonding.[2–11] The important role in this respect belongs to the evaluation of the role of electron pairing in chemical bonds. This problem was studied most systematically by Bader[4,5] but, according to his conclusions, the crucial role of electron pairs as suggested by the Lewis model does not seem to be reflected by the quantum theory. Despite this discouraging result, the intuitive faith in the deeper meaning of classical structural formulas still continued to attract the attention of researchers and some recent results based on the formalism of the pair population analysis[12–15] do indeed suggest that the original conclusions are perhaps not as discouraging as they seemed to be.

Most of these previous studies were based, only on the simplest HF SCF approximation so that its applicability was restricted only to the investigation of systems close to equilibrium geometry for which the correlation effects are not so important. Our aim in this study is to pursue our recent effort at a systematic investigation of the role of electron pairing in chemical bonds[12–16] and to modify the methodology previously developed at SCF level to the analysis of correlated pair densities. This is of crucial importance for investigation of the processes of structural changes which are generally accompanied by the splitting of chemical bonds.

## THEORETICAL

The basic quantity describing the behaviour of electron pairs is the so-called pair density $\rho(r_1, r_2)$,[17] defined as a diagonal element of second order density matrix $\rho(r_1, r_2 \mid r_1', r_2')$ Eq. (1),

$$\rho(r_1, r_2) = \frac{N(N-1)}{2} \int \Psi^2 (1,2,3 \ldots N)\, \mathrm{d}\sigma_1 \mathrm{d}\sigma_2 \mathrm{d}x_3 \ldots \mathrm{d}x_N. \qquad (1)$$

This density is, however, a rather complex quantity and, in order to extract the desired information about the behaviour of electron pairs from it, some additional mathematical processing is necessary. One of such methodologies is based on the formalism of the so-called pair population analysis[12–15] and, as demonstrated in previous studies,[12,13,16] the important role of electron pairing in chemical bonds does indeed seem to be revived by this approach. In this study, we are going to apply another approach to the analysis of electron pairs, *viz.* the investigation of conditional probabilities of finding the electron in a position of the space, provided the reference electron is fixed in a certain point or a region. A consequence of this fixation is that the conditional probability given by Eq.(2) is a simple function of 3 variables which can normally be visualized, *etc.*

$$P_{r_2}(r_1) = \frac{2\rho\,(r_1, r_2)}{\rho\,(r_2)}. \qquad (2)$$

This is very useful since, using this visualization, the information about how the second electron of the pair is distributed around the fixed reference electron can be obtained.

In addition to conditional probabilities, it is also useful to analyze the closely related quantities, sometimes called the Fermi holes.[5,9] Eq. (3),

$$h(r_1, r_2) = \rho(r_1) - P_{r_2}(r_1). \tag{3}$$

These quantities were used some time ago by Luken,[9] who demonstrated that they are not sensitive to the precise location of the reference electron and, if its position is fixed near the midpoint of the inter-nuclear axis, the resulting pictures closely resemble the localized orbitals corresponding to individual bonds. In this way, the important role of electron pairing in chemical bonds was directly confirmed. Similar conclusions were then also drawn in our recent study.[16]

The fixation and, consequently, the strict localization of the reference electron in a single point is not, however, quite consistent with the quantum mechanical uncertainty principle. A much more interesting and also more realistic picture would result if the position of the reference electron were not fixed in a certain point but allowed to vary within a certain region Ω. In this case, the original Eq. (2) could be rewritten as:

$$f_\Omega(r_1) = \frac{2 \int\limits_\Omega \rho(r_1, r_2)\, dr_2}{\int\limits_\Omega \rho(r_2)\, dr_2}. \tag{4}$$

The resulting quantity is again a function of only 3 variables but, in contrast to Eq. (2), it averages the conditional probabilities over all positions of the reference electron within region Ω.

Conditional probabilities satisfy the universal normalization condition (5), which holds irrespective of the form of the region Ω.

$$\int f_\Omega(r_1) dr_1 = N - 1. \tag{5}$$

Despite the independence of normalization (5) of the form of region Ω, there is a definition that is of special importance for chemistry. This definition is based on the virial partitioning of function $\rho(r_1)$ proposed by Bader.[18] 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 regions Ω in Eq. (4) with individual atomic regions of Bader's partitioning. Using this approach, the information about how the second electron of the pair is distributed on a molecule, provided the first, reference, electron is on a given atom can be obtained.

Our aim in this study is to demonstrate how this information can be used to get a detailed insight into the role of electron pairing during the formation and/or splitting of a chemical bond. This, of course, requires going beyond the level of simple SCF approximation and analyzing the pair densities derived from correlated wave functions. Such correlated pair densities are not, however, readily available from the existing quantum chemical programs so that we had to restrict our analysis only to the simplest model case of $H_2$ dissociation, for which the correlated pair density can be simply obtained from 2 × 2 CI wave function. Here, it is necessary to say that such a pair density represents, of course, only a crude approximation to the true correlated pair density but, as it will be possible to see bellow, the basic qualitative features of the dissociation process are correctly reflected even at this approximate level. In the following part, the results of the analysis of an approximate pair density will be reported.

## RESULTS AND DISCUSSION

As already stressed above, a correct description of dissociation requires taking into account the electron correlation. In the case of $H_2$, this can simply be done *via* CI wave function, which with a minimal basis set involves only two configurations, the ground state and the HOMO-LUMO biexcited configuration.

$$\Psi(1,2) = c_1|\varphi_1\overline{\varphi_1}| + c_2|\varphi_1^*\overline{\varphi_1^*}|. \tag{6}$$

Based on this wave function, a correlated pair density $\rho(r_1, r_2)$ can straightforwardly be calculated and this pair density is exact at this level of approximation. In the following pair density analysis, it is useful to pursue the methodology of the pair population analysis and expand the pair density in the basis of two-electron functions, the so-called geminals. As demonstrated in Ref. 12, if the basis geminals are defined as Eqs. (7)–(9):

$$\lambda_{\alpha\alpha}(r_1, r_2) = \chi_\alpha(r_1)\chi_\alpha(r_2) \tag{7}$$

$$\lambda^{s}_{\alpha\beta}(r_1, r_2) = \frac{1}{\sqrt{2}}(\chi_\alpha(r_1)\chi_\beta(r_2) + \chi_\beta(r_1)\chi_\alpha(r_2)) \tag{8}$$

$$\lambda^{t}_{\alpha\beta}(r_1, r_2) = \frac{1}{\sqrt{2}}(\chi_\alpha(r_1)\chi_\beta(r_2) - \chi_\beta(r_1)\chi_\alpha(r_2)) \tag{9}$$

the pair density can be represented by a normal two-index matrix $\gamma$ Eq. (10),

$$\rho(r_1, r_2) = \sum_{i,j} \gamma_{ij}\lambda_i(r_1, r_2)\, \lambda_j(r_1, r_2) \tag{10}$$

which is much simpler to work with than the four-index matrices required for the orbital based expansions. In the case of $H_2$, the only electron pair in the molecule is a singlet coupled so that all basis geminals Eqs. (11)–(13) describing the pair density at this level are of singlet type.

$$\lambda_1(r_1, r_2) = \chi_A(r_1)\chi_A(r_2) \tag{11}$$

$$\lambda_2(r_1, r_2) = \chi_B(r_1)\chi_B(r_2) \tag{12}$$

$$\lambda_3(r_1, r_2) = \frac{1}{\sqrt{2}}\chi_A(r_1)\chi_B(r_2) + \chi_B(r_1)\chi_A(r_2). \tag{13}$$

The first two geminals Eqs. (11) and (12) describe the ionic situation where both electrons are on one of the atoms while the third one is of covalent type. Using these basis functions, the pair density is given by 3 × 3 matrix $\gamma$ Eq. (14),

$$\rho(r_1, r_2) = (\lambda_1, \lambda_2, \lambda_3)\begin{pmatrix}\gamma_{11} & \gamma_{12} & \gamma_{13}\\ \gamma_{21} & \gamma_{22} & \gamma_{23}\\ \gamma_{31} & \gamma_{32} & \gamma_{33}\end{pmatrix}\begin{pmatrix}\lambda_1\\ \lambda_2\\ \lambda_3\end{pmatrix}. \tag{14}$$

Using this equation, conditional probabilities can be calculated for any choice of region $\Omega$ and the process of dissociation can be monitored by the variation of these quantities with the systematic change of the inter-atomic distance. As already stressed above, some choices of the region are of particular interest. One of them is to identify region $\Omega$ with Bader's region of one of the hydrogen atoms. Unfortunately, because the programs for the integration over Bader's regions were not available to us, we could not use this approach straightforwardly but, instead, we used an alternative approximation where the integration over the region is approximated by appropriately restricting the summations over the basis functions. Within this approach, which is analogous to Mulliken like partitioning[19] of the first order density, the electron is assumed to be in the region of atom A if it resides in an orbital centred on this atom. Using this approximation and taking into account the ZDO approximation Eq. (15) for the necessary integrals,

$$\chi_A(r_1)\chi_B(r_1) = \delta_{AB} \tag{15}$$

the integrated conditional probability for reference electron localized on atom A is given by Eq. (16),

$$f_{\Omega_A}(r_1) = (\chi_A\ \chi_B)\begin{pmatrix}f_{AA} & f_{AB}\\ f_{BA} & f_{BB}\end{pmatrix}\begin{pmatrix}\chi_A\\ \chi_B\end{pmatrix} = (\chi_A\ \chi_B)\begin{pmatrix}2\gamma_{11} & \gamma_{13}\sqrt{2}\\ \gamma_{31}\sqrt{2} & \gamma_{33}\end{pmatrix}\begin{pmatrix}\chi_A\\ \chi_B\end{pmatrix}. \tag{16}$$

In keeping with the general normalization (5), matrix (16) satisfies the equation (17)

$$f_{AA} + f_{BB} = 1 \tag{17}$$

so that the individual elements $f_{AA}$ and $f_{BB}$ can straightforwardly be interpreted as probabilities that, provided the reference electron is on atom A, the second electron of the pair is on atoms A and B, respectively. These quantities thus naturally provide the »weights« of ionic ($f_{AA}$) and covalent ($f_{BB}$) contributions, well known from the VB description of the molecules. The effect of stretching on the nature of the bond can thus be analyzed by monitoring the $f_{AA}$and $f_{BB}$ values for systematically varying inter-atomic distances. The results of these calculations are summarized in Table I.

TABLE I

Calculated matrix elements of the conditional probability Eq. (16) in dependence on the inter-atomic distance The reference electron is on atom A.

| $r_{H...H}$ (in A) | $f_{BB}$ | $f_{AA}$ | $f_{AB}$ |
|---|---|---|---|
| 0.5 | 0.538 | 0.463 | 0.499 |
| 0.75 | 0.586 | 0.414 | 0.493 |
| 1.00 | 0.660 | 0.340 | 0.474 |
| 1.25 | 0.768 | 0.232 | 0.422 |
| 1.50 | 0.872 | 0.128 | 0.334 |
| 1.75 | 0.942 | 0.058 | 0.233 |
| 2.00 | 0.977 | 0.022 | 0.150 |
| 2.25 | 0.991 | 0.009 | 0.093 |
| 2.50 | 0.997 | 0.003 | 0.057 |
| 3.00 | 1.000 | 0.000 | 0.021 |
| 5.00 | 1.000 | 0.000 | 0.000 |
| SCF | 0.500 | 0.500 | 0.500 |

Let us discuss now the conclusions resulting from this Table. First of all, it is possible to see that for inter-atomic distances close to equilibrium (where the effects of electron correlation are small), the second electron of the pair is spread nearly uniformly between both atoms. This is clearly reminiscent of SCF picture of the bond which at this approximation is 50% ionic and 50% covalent. This, of course, is not very realistic for purely nonpolar H-H bond but it is the well known artefact of averaging the electron repulsion at SCF level. This picture of bonding changes, however, for greater inter-nuclear distances where the role of electron correlation becomes important. As it is can be seen, the introduction of correlation manifests itself in increasing the probability of finding the second electron of the pair on atom B, provided the reference electron is on atom A. In other words, the effect of correlation couples the electron motions of both electrons so as to avoid each other maximally. This effect is so strong that within the limits of complete dissociation the second electron is completely localized on the other atom than the reference electron. This result is clearly consistent with the classical picture of the homolytic bond scission and with the biradical nature of the dissociated state. We can thus see that, in spite of the approximate nature of our pair density, the description of the dissociation is qualitatively correct.

Another interesting and in some respects complementary picture of dissociation process can also be obtained from the alternative analysis of conditional probability represented by the diagonalization of the matrix (16). As it can be checked easily, the progress of dissociation does not alter the eigenvalues of this matrix (they remain 0 and 1 irrespective of the inter-atomic distance) but what is changing dramatically are the corresponding eigenvectors. Qualitatively, it is possible to say that while for shorter inter-atomic distances the occupied orbital corresponding to eigenvalue 1 is delocalized over both nuclei, for longer bond lengths the shape of the orbital changes and it becomes rather strongly localized on only one centre, the atom B. In order to characterize this change of the shape more quantitatively, it is useful to use the so-called localization index introduced some time ago by Pipek and Mezey within their localization scheme.[11] The values of these indices are included in Table II and the dissociation progress can be simply visualized by monitoring their dependence on inter-atomic distances. Such a dependence is shown in Figure 1. As it can be seen for $r_{HH}$ up to roughly 1.25

TABLE II

Calculated values of localization index of »occupied« orbital resulting from the diagonalization of the matrix Eq. (16) in dependence on the inter-atomic distance.

| $r_{H...H}$ (in A) | $L_1$ |
|---|---|
| 0.50 | 1.989 |
| 0.75 | 1.942 |
| 1.00 | 1.814 |
| 1.25 | 1.552 |
| 1.50 | 1.287 |
| 1.75 | 1.122 |
| 2.00 | 1.047 |
| 2.25 | 1.017 |
| 2.50 | 1.006 |
| 3.00 | 1.001 |
| 5.00 | 1.000 |
| SCF | 2.000 |

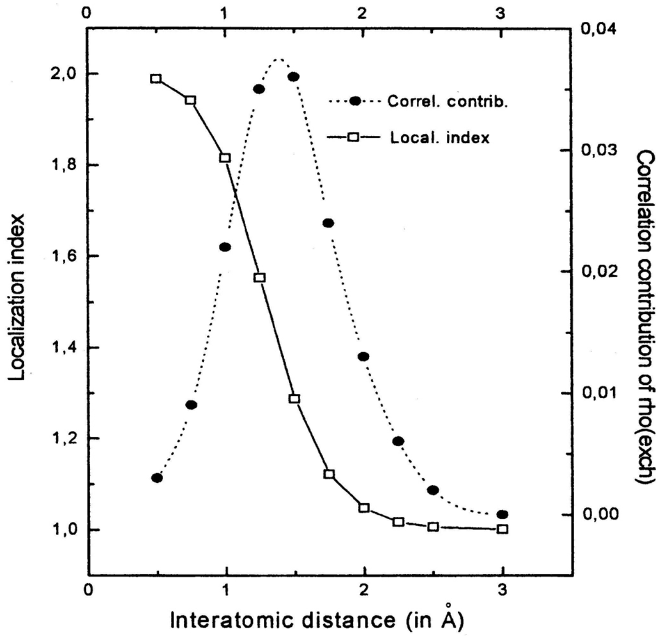

Figure 1. Calculated dependence of localization index and of diatomic contribution of the correlation part of exchange pair density on the inter-atomic distance.

A, the values of localization index do not differ too much from the idealized value 2 characterizing the orbital spread over the two centres. Such an orbital is characteristic of the bonded $H_2$ molecule. This picture of the molecule changes, however, dramatically for larger bond lengths and during the relatively narrow interval 1.25–1.75 A the values of the localization index sharply drop from nearly 2, characteristic of the bonded molecule, to roughly 1 which is characteristic of a practically split bond. Further elongation of the bond length over this critical interval has again only very small effect. This clearly implies that the splitting of the bond does not proceed as a smooth process but that it rather has the character of an abrupt change. This result is very interesting since it provides a new indirect support for earlier findings of Cioslowski,[20] who reported similar sudden changes on the basis of his isopycnic localization method and, also for the results of the general analysis of structural stability done by Bader.[21] The close parallel of our results with the results of Cioslowski is especially important since his conclusions were derived from correlated ab-initio calculations with rather flexible basis sets so that we can see again that, in spite of its approximate and crude nature, our pair density correctly describes the basic correlation effects on the splitting of the bond.

Although the above analysis of conditional probabilities provides a complete and consistent description of the effect of electron correlation on the splitting of the bond, there is yet another alternative, but related, formalism in terms of which the independent support of the above conclusions can be given. This concerns above all the relatively narrow range over which the splitting of the bond takes place. Of special importance in this respect is the analysis of the so-called exchange part of the pair density matrix which is defined as

$$\rho_{\mathrm{exch}}(r_1, r_2) = \frac{1}{2}\rho(r_1)\rho(r_2) - \rho(r_1, r_2). \tag{18}$$

Some time ago, Ruedenberg proposed[22] to dissect this exchange pair density into two components Eq. (19), of which one describes the effect of self-pairing and the other the correlation effects.

$$\rho_{\mathrm{exch}}(r_1, r_2) = \rho_{\mathrm{self}}(r_1, r_2) + \rho_{\mathrm{corr}}(r_1, r_2). \tag{19}$$

Unfortunately, except for presenting the normalization relations (20,21) which these matrices should satisfy, no method of actually performing the dissection was proposed in the study.[22]

$$\int \rho_{\mathrm{self}}(r_1\, r_2)\, \mathrm{d}r_1 \mathrm{d}r_2 = \frac{N}{2} \tag{20}$$

$$\int \rho_{\mathrm{corr}}(r_1\, r_2)\, \mathrm{d}r_1 \mathrm{d}r_2 = 0. \tag{21}$$

Quite recently, we found a procedure based on spectral resolution of appropriate density operators in terms of which the Ruedenberg partitioning could be done.* Using this approach, the extent and the role of correlation effects in the process of dissociation can be straightforwardly analyzed. The approach is based on the use of interesting pairing properties of occupation numbers of natural geminals resulting from the diagonalization of the exchange pair density in geminal basis. Eigenvectors resulting from such diagonalization can always be associated into two groups in such a way that the eigenvalues of the first group satisfy Eq. (22)

$$\sum_{k}^{\text{group 1}} n_k = \frac{N}{2} \tag{22}$$

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* The details of this procedure will be separately published elsewhere.

while for the other group Eq. (23) holds.

$$\sum_{j}^{\text{group 2}} n_j = 0 . \tag{23}$$

Based on this association, the self-pairing and correlation part of exchange density can be defined as Eqs. (24) and (25):

$$\rho_{\text{self}}\,(r_1, r_2) = \sum_{k}^{\text{group 1}} n_k\,|k\rangle\langle k| \tag{24}$$

$$\rho_{\text{corr}}\,(r_1, r_2) = \sum_{j}^{\text{group 2}} n_j\,|j\rangle\langle j|. \tag{25}$$

Having introduced this partitioning. it is already a matter of straightforward generalization to apply the idea of pair population analysis to these matrices and to decompose them further into mono- and biatomic contributions. Variation of these contributions with the systematic change in the interatomic distance allows us to analyze how the self-pairing and the correlation are influenced by the progress of bond scission. Especially interesting for our purposes is the $r$-dependence of diatomic (and of course also of complementary mono-atomic) contributions, which is also included in Figure 1. The form of this dependence, which displays a rather sharp maximum, is also very interesting. It demonstrates, namely, that the role of correlation during the dissociation considerably changes. As it is possible to expect, its effect is very small for $r$ close to equilibrium where the effects of CI are relatively weak and, also for very large $r$ when two H atoms formed by dissociation are already more or less independent. For medium inter-atomic distances, the effects of correlation enter into play and it is interesting that the sharp peak with the maximum in the region 1.25–1.30 A ,which is a clear indicator of the important role of correlation effects, surprisingly well coincides with the region of the most rapid change of the localization indices. We can thus see that all alternative analyses of pair density consistently lead to the conclusion that the process of the bond scission actually proceeds in a relatively narrow range of inter-atomic distances and that they are just the effects of electron correlation, whose assistance is of crucial importance for the splitting of the bond. Summarizing the above results it is perhaps possible to say that even if our analyses were based only on rather crude pair density, the basic factors governing the electron reorganization during the splitting of chemical bond are reflected correctly. Here it is, of course, fair to say that such a close parallel with the results of more sophisticated correlated *ab initio* calculations is probably possible only in this simple case of a two-electron system. For more complex systems, the use of much more realistic pair density would certainly be necessary. This, however, does not detract from the usefulness of the above introduced general methodologies of the pair density analysis and we believe that their application to other more complex systems can hopefully contribute to a better understanding of the factors governing the process of splitting and/or formation of chemical bonds. Such calculations are being prepared in our laboratory and their results will be reported elsewhere.

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## SAŽETAK

### Sparivanje elektrona i kemijske veze. Anatomija stvaranja veze

*Robert Ponec*

Uvedeno je nekoliko metoda za analizu gustoće koreliranog para. S pomoću tih analiza potanko je istraženo cijepanje kemijske veze u $H_2$. Pronađeno je da cijepanje nije kontinuiran proces, već ima karakter nagle promjene.