

**Padeleimon KARAFILOGLOU**  
*Aristotle University of Thessaloniki, Faculty of Chemistry*

## UNDERSTANDING DELOCALIZATION AND HYPERCONJUGATION IN TERMS OF (COVALENT AND IONIC) RESONANCE STRUCTURES

*Received 10 January 2002; revised 28 March 2002; accepted 2 April 2002*

**ABSTRACT:** Electron transfer (from bonding to anti-bonding orbitals) effects, as delocalization and hyperconjugation, are translated into a language referring to resonance structures of covalent and ionic components of bonds. These effects are presented as examples destined to familiarize students with the translation of molecular orbital wave functions into the chemically meaningful language of resonance structures. ‘Structural multiplication tables’ are introduced as a pedagogical tool, allowing one to generate resonance structures in a pictorial manner. It is shown that the transfer of one electron from a bonding orbital,  $\omega_{ij}$  (donor), to an anti-bonding one,  $\omega_{kl}^*$  (acceptor), creates an odd (an unpaired) electron in region (i,j) and another odd electron in region (k,l); the coupling of these two odd electrons provides the necessary covalent component(s) of the new bond(s) between the donor and the acceptor. [*Chem. Educ. Res. Pract. Eur.*, 2002, 3, 119-127]

**KEY WORDS:** *delocalization; hyperconjugation; resonance structures; electron transfer; natural bond orbitals – Slater determinants*

### INTRODUCTION

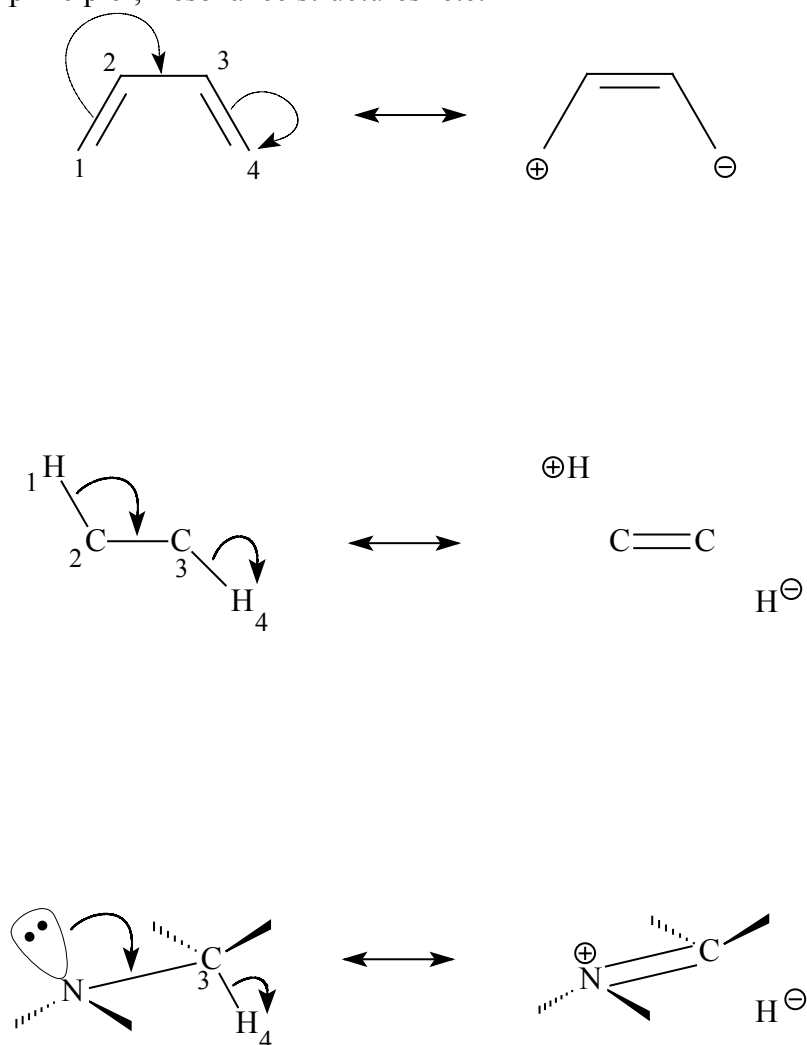
Molecular Orbital and ‘Resonance’ (or ‘Mesomeric’) theories can provide equivalent descriptions of various chemical effects even though use two totally different languages. The possibility to translate, even in freshman students, Molecular Orbital (MO) wave functions (Karafiloglou & Ohanessian, 1991; Karafiloglou 1992) into a language referring to usual covalent and ionic resonance structures is presented elsewhere (Karafiloglou & Launay, 1998). In this context, the fundamental chemical concept of ‘resonance’ can be looked from a probabilistic point of view, in which the required probabilities are expressed in terms of coefficients involved in the optimal superposition orbitals (Weinhold, 1999), as the usual MOs. Natural Resonance Theory (NRT) (Glendening & Weinhold, 1998; Weinhold & Landis, 2001; Glendening *et al.*, 2001), provides also weights of resonance structures, in the framework of a very compact description of the chemical bonding, in which, however, one cannot distinguish covalent and ionic components of bonds, because each bond is treated as one entity.

It is well known that transfer of electron(s) from a bonding bond orbital,  $\omega_{ij}$ , (defining a region, i,j) to an anti-bonding one,  $\omega_{kl}^*$  (defining another region, k,l) describes the delocalization between  $\pi$  bonds or hyperconjugation (i.e. delocalization between  $\sigma$ , or  $\pi$  and  $\sigma$  bonds) (Weinhold, 1999; Goodman *et al.*, 1999). In general, it is admitted (Weinhold, 2001) (without to be shown explicitly) that such transfer of electron(s) has as consequence to

increase the weights of resonance structures exhibiting bonds between the centers of the donor and centers of the acceptor, i.e. bonds of the type i-k or j-l etc.

Electron transfer between bonding and anti-bonding orbitals is considered within usual MO theory, while delocalization and hyperconjugation are often presented by means of resonance structure arguments within ‘Resonance’ (or ‘Mesomeric’) theory. Figure 1 presents the usual pictures of resonance structures involving the quite familiar to chemists ‘curved arrows’, which are frequently used in basic textbooks or research papers of various topics. This type of practice in chemistry is widely discussed in this issue by Laszlo (2002).

Since students mainly, but not solely, cannot easily understand how transfer of electron(s) between orbitals can be expressed into resonance structures, in the present work we wish (i) translate the MO description of such electron transfer effects into resonance structures referring to covalent and ionic components of chemical bonds, and (ii) show the isomorphism between the quantum and the experimental chemist points of view concerning resonance structures and ‘curved arrows’. Furthermore, by means of the presented process, a student can easily realize that there is an underlying framework for some basic concepts as ‘orbital interactions’, ‘Slater determinants’ (and ‘anti-symmetrization’), ‘Pauli exclusion principle’, ‘resonance structures’ etc.



**FIGURE 1:** *Electron delocalization (for a  $\pi$ -system) and hyperconjugation (for  $\sigma$ -systems) effects within ‘Resonance’ (or ‘Mesomeric’) theory.*

## DESCRIBING DELOCALIZATION BY MEANS OF LOCALIZED STRUCTURES

Let us consider that  $\omega_{1,2}$  is the  $\pi$  bonding bond orbital between two atoms (1,2) of a  $\pi$ - system, as butadiene, or the  $\sigma$  orbital between  $sp^3$  hybrid of C and H in a  $\sigma$ - system, as ethane, or the lone pair of nitrogen in methylamine, and  $\omega_{3,4}$  is a similar bond orbital between two adjacent atoms (3,4) (see Figure 1). By using these orbitals and without conceptual difficulty, one can construct the corresponding anti-symmetrical wave function, i.e. the Slater determinant  $\Omega_1$ :

$$\Omega_1 = \begin{vmatrix} \omega_{1,2} & \overline{\omega_{1,2}} & \omega_{3,4} & \overline{\omega_{3,4}} \end{vmatrix} \quad (1)$$

$\Omega_1$  provides the totally localized picture of chemical bonding. Starting from this electronic configuration, one can establish the communication (e.g. delocalization) between bonds, by considering the transfer of electron(s) from one bonded region to other. For example, the transfer from region (1,2) to (3,4) refers to the transfer from the bonding  $\omega_{1,2}$  to the anti-bonding  $\omega_{3,4}^*$ , and thus the whole process can involve:

### (i) Transfer of one electron

The transfer of an  $\alpha$ - spin electron from  $\omega_{1,2}$  to  $\omega_{3,4}^*$  is described by means of the Slater determinant  $\begin{vmatrix} \omega_{3,4}^* & \overline{\omega_{1,2}} & \overline{\omega_{3,4}} & \overline{\omega_{3,4}} \end{vmatrix}$ , which is derived from  $\Omega_1$  by replacing spin-orbital  $\omega_{1,2}$  by  $\omega_{3,4}^*$ ; the transfer of a  $\beta$ - spin electron between the same orbitals is described by  $\begin{vmatrix} \omega_{1,2} & \overline{\omega_{3,4}^*} & \overline{\omega_{3,4}} & \overline{\omega_{3,4}} \end{vmatrix}$ . The transfer of one electron from  $\omega_{1,2}$  to  $\omega_{3,4}^*$ , regardless to its spin, is described by  $\Omega_2$ :

$$\Omega_2 = \frac{1}{\sqrt{2}} \left( \begin{vmatrix} \omega_{3,4}^* & \overline{\omega_{1,2}} & \overline{\omega_{3,4}} & \overline{\omega_{3,4}} \end{vmatrix} + \begin{vmatrix} \omega_{1,2} & \overline{\omega_{3,4}^*} & \overline{\omega_{3,4}} & \overline{\omega_{3,4}} \end{vmatrix} \right) \quad (2)$$

### (ii) Transfer of two electrons

Similarly, the transfer of two electrons (of opposite spin) from  $\omega_{1,2}$  to  $\omega_{3,4}^*$  is described by means of the Slater determinant  $\Omega_3$ :

$$\Omega_3 = \begin{vmatrix} \omega_{3,4}^* & \overline{\omega_{3,4}^*} & \overline{\omega_{3,4}} & \overline{\omega_{3,4}} \end{vmatrix} \quad (3)$$

Taking into account the transfer of electron(s) from region (1,2) to (3,4), the totally localized  $\Omega_1$  can be improved by considering its mixing with  $\Omega_2$  and  $\Omega_3$ :

$$\Psi(\text{ground}) = C_1\Omega_1 + C_2\Omega_2 + C_3\Omega_3 + \dots \quad (4)$$

It is worth to notice that in wave function (4) one may consider all the other types of 'excitations', which can be generated from  $\Omega_1$ .

Let us consider now as bond orbitals the well known Natural Bond Orbitals (NBOs) (Reed *et al.*, 1988; Weinhold & Landis, 2001; Glendening *et al.*, 2001); these orbitals can be

expressed in terms of Natural Atomic Orbitals (NAOs) for  $\pi$ - systems or the Natural Hybrid Orbitals (NHOs) for  $\sigma$ - systems. If  $\varphi_i$  represent NAOs or NHOs then the bonding NBOs have the form

$$\omega_{1,2} = c_1\varphi_1 + c_2\varphi_2 \quad (5)$$

$$\omega_{3,4} = c_3\varphi_3 + c_4\varphi_4 \quad (6)$$

and the anti-bonding NBOs the form (because NBOs are obtained by unitary transformations of  $\varphi_i$  )

$$\omega_{1,2}^* = -c_2\varphi_1 + c_1\varphi_2 \quad (7)$$

$$\omega_{3,4}^* = -c_4\varphi_3 + c_3\varphi_4 \quad (8)$$

(For example,  $\varphi_1$  and  $\varphi_2$  in butadiene are the valence  $p_z$  –NAOs of the first two C atoms and  $\varphi_3$  and  $\varphi_4$  those of the other C atoms).

When the usual MO wave function (in Hartree-Fock or correlated level) is known, then the expansion coefficients  $C_i$  involved in (4) can be expressed in terms of the known LCAO (Linear Combination of Atomic Orbitals) and CI (Configuration Interaction) coefficients (Karafiloglou, 2001). In this case the weight,  $C_i^2$ , of a given configuration,  $\Omega_i$ , can be calculated independently from the other configurations, i.e. without to be necessary to generate and storage the whole determinantal basis set  $\{\Omega_i\}$  (Karafiloglou, 2001). A  $C_i^2$  provides also the probability of finding simultaneously electron pairs or electrons in various bonding and anti-bonding NBOs.

### COVALENT AND IONIC RESONANCE STRUCTURES INVOLVED IN $\Omega_i$

In order to know what is the chemical meaning and the role of each determinantal basis function  $\Omega_i$  in expansion (4), one must translate Slater determinants into a language familiar to chemists. For this purpose, each  $\Omega_i$  is developed in terms referring to covalent and ionic resonance structures of chemical bonds. Substituting (5)-(8) in various  $\Omega_i$ , one can decompose (Karafiloglou & Ohanessian, 1991; Karafiloglou 1992; Bachler & Schaffner, 2000) them in terms of Slater determinants involving  $\varphi_i$ . These decompositions are obtained straightforwardly by recalling the very simple operational rule stating that ‘a MO- Slater determinant written in its diagonal form can be developed as if it were a simple product of summations’; for example,

$$\begin{aligned} \left| \overline{\omega_{1,2}} \overline{\omega_{1,2}} \overline{\omega_{3,4}} \overline{\omega_{3,4}} \right| &= \left| (c_1\varphi_1 + c_2\varphi_2) \overline{\omega_{1,2}} \overline{\omega_{3,4}} \overline{\omega_{3,4}} \right| \\ &= c_1 \left| \overline{\varphi_1} \overline{\omega_{1,2}} \overline{\omega_{3,4}} \overline{\omega_{3,4}} \right| + c_2 \left| \overline{\varphi_2} \overline{\omega_{1,2}} \overline{\omega_{3,4}} \overline{\omega_{3,4}} \right| . \end{aligned}$$

The most simple decomposition is for  $\Omega_3$ , in which, applying the Pauli exclusion principle, we obtain:

$$\Omega_3 = \left| \overline{\omega_{3,4}^*} \overline{\omega_{3,4}^*} \overline{\omega_{3,4}} \overline{\omega_{3,4}} \right| = \left| (-c_4\varphi_3 + c_3\varphi_4) \overline{(-c_4\varphi_3 + c_3\varphi_4)} (c_3\varphi_3 + c_4\varphi_4) \overline{(c_3\varphi_4 + c_4\varphi_4)} \right|$$

$$= c_4^4 \left| \overline{\varphi_3 \varphi_3} \overline{\varphi_4 \varphi_4} \right| + c_3^4 \left| \overline{\varphi_4 \varphi_4} \overline{\varphi_3 \varphi_3} \right| - c_3^2 c_4^2 \left| \overline{\varphi_4 \varphi_3} \overline{\varphi_3 \varphi_4} \right| - c_3^2 c_4^2 \left| \overline{\varphi_3 \varphi_4} \overline{\varphi_4 \varphi_3} \right|$$

Taking into account the change of the sign of a determinant by interchanging two vicinal columns (or rows), and the fact that  $c_3^2 + c_4^2 = 1$ , we obtain:

$$\Omega_3 = (c_3^4 + c_4^4 + 2c_3^2 c_4^2) \left| \overline{\varphi_3 \varphi_3} \overline{\varphi_4 \varphi_4} \right| = \left| \overline{\varphi_3 \varphi_3} \overline{\varphi_4 \varphi_4} \right| \quad (9)$$

Therefore,  $\Omega_3$  represents the fully ionic structure 1(+)-2(+)-3(-)-4(-), i.e. a structure composed from the ionic components of both 2-3 and 1-4 bonds.

### Structural multiplication tables

Let us consider now the decomposition of  $\Omega_2$ , which involves longer (even though very simple) algebraic developments. Chemistry students, who, in general, do not feel comfortable with long mathematical manipulations, can be rapidly disappointed. For these reasons we introduce the ‘structural multiplication tables’, as a pedagogical tool allowing one to simplify in a great extent the algebraic developments, and obtain the final electronic structures in a pictorial manner. The whole procedure is as follows: Firstly, each NBO Slater determinant is formally divided into two (or more) parts, as this is dictated from the spatial location of the involved bond orbitals. For example,  $\left| \overline{\omega_{1,2}} \overline{\omega_{3,4}^*} \overline{\omega_{3,4}} \overline{\omega_{3,4}} \right|$  is divided into two parts referring to regions (1,2) and (3,4):  $\left| \overline{\omega_{1,2}} \dots \right|$  and  $\left| \dots \overline{\omega_{3,4}^*} \overline{\omega_{3,4}} \overline{\omega_{3,4}} \right|$ . The first part, because of relation (5) gives:

$$\left| \overline{\omega_{1,2}} \dots \right| = c_1 \left\{ \left| \overline{\varphi_1} \dots \right| \right\} + c_2 \left\{ \left| \overline{\varphi_2} \dots \right| \right\} \quad (10)$$

$$\begin{array}{c} \cdot \text{-----} \cdot \\ 1 \quad \quad \quad 2 \end{array} \quad \begin{array}{c} + \text{-----} \\ 1 \quad \quad \quad 2 \end{array}$$

The second part, because of relations (6) and (8), and taking into account the Pauli exclusion principle, gives:

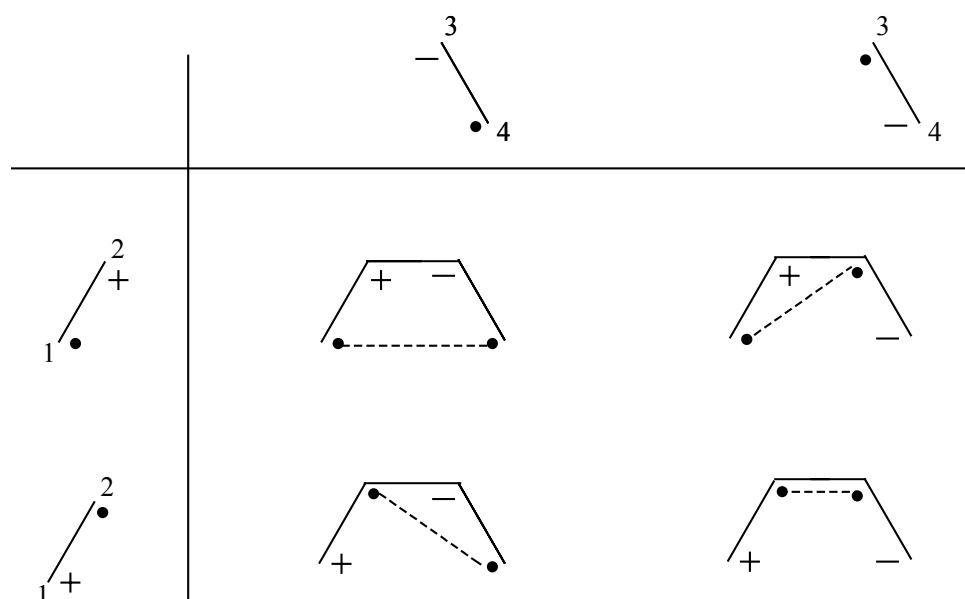
$$\left| \dots \overline{\omega_{3,4}^*} \overline{\omega_{3,4}} \overline{\omega_{3,4}} \right| = c_3 \left\{ \left| \dots \overline{\varphi_3 \varphi_3} \overline{\varphi_4} \right| \right\} - c_4 \left\{ \left| \dots \overline{\varphi_3} \overline{\varphi_4 \varphi_4} \right| \right\} \quad (11)$$

$$\begin{array}{c} \cdot \text{-----} \cdot \\ 3 \quad \quad \quad 4 \end{array} \quad \begin{array}{c} \cdot \text{-----} \cdot \\ 3 \quad \quad \quad 4 \end{array}$$

In order to obtain the result of the decomposition of  $\left| \overline{\omega_{1,2}} \overline{\omega_{3,4}^*} \overline{\omega_{3,4}} \overline{\omega_{3,4}} \right|$ , we multiply (10) and (11), according to the ‘structural multiplication table’ given in Figure 2; this multiplication provides four Slater determinants, represented by the four electron schemes of Figure 2:

$$\left| \overline{\omega_{1,2}} \overline{\omega_{3,4}^*} \overline{\omega_{3,4}} \overline{\omega_{3,4}} \right| = c_1 c_3 \left\{ \left| \overline{\varphi_1 \varphi_3} \overline{\varphi_3} \overline{\varphi_4} \right| \right\} - c_1 c_4 \left\{ \left| \overline{\varphi_1} \overline{\varphi_3} \overline{\varphi_4 \varphi_4} \right| \right\}$$

$$+ c_2 c_3 \left\{ \left| \overline{\varphi_2 \varphi_3} \overline{\varphi_3} \overline{\varphi_4} \right| \right\} - c_2 c_4 \left\{ \left| \overline{\varphi_2} \overline{\varphi_3} \overline{\varphi_4 \varphi_4} \right| \right\} \quad (12)$$



**FIGURE 2:** Structural multiplication table for  $\Omega_2$ . Broken lines represent the covalent components of bonds formed between donor, 1 — 2, and acceptor, 3 — 4, regions.

The same multiplication table holds for  $|\omega_{3,4}^* \overline{\omega_{1,2}} \overline{\omega_{3,4}} \overline{\omega_{3,4}}|$  (but inverting  $\alpha$ - and  $\beta$ - spins in singly occupied AOs):

$$\begin{aligned}
 |\omega_{3,4}^* \overline{\omega_{1,2}} \overline{\omega_{3,4}} \overline{\omega_{3,4}}| &= c_1 c_3 \{ |\overline{\varphi_1} \overline{\varphi_3} \overline{\varphi_3} \varphi_4| \} - c_1 c_4 \{ |\overline{\varphi_1} \overline{\varphi_3} \varphi_4 \overline{\varphi_4}| \} \\
 &+ c_2 c_3 \{ |\overline{\varphi_2} \overline{\varphi_3} \overline{\varphi_3} \varphi_4| \} - c_2 c_4 \{ |\overline{\varphi_2} \overline{\varphi_3} \varphi_4 \overline{\varphi_4}| \} \quad (13)
 \end{aligned}$$

Finally, substituting (12) and (13) in (2) we obtain the resonance structures (having the form of spin-eigenfunctions in AO-positions) which are contained in determinantal basis function  $\Omega_2$ . These structures are represented also by the four-electron schemes of Figure 2. One must note that the structural multiplication table of Figure 2 holds for both Slater determinants and spin-eigenfunctions. It is noticeable that the graphical process given in Figure 2 (and 3) is not equivalent to the well known Rumer diagrams, which allow to construct linearly independent spin-eigenfunctions for a given set of orbitals (while the multiplication tables of the present work concern the decomposition of Slater determinants).

Another conclusion which one can draw from the above analysis is that the transfer of one electron from a bonding  $\omega_{1,2}$  (donor) to an anti-bonding  $\omega_{3,4}^*$  (acceptor) creates an odd (an unpaired) electron in region defined by centers (1,2) and another odd electron in region (3,4); *the coupling of these two odd electrons provides the necessary covalent components of the new bonds between the donor and the acceptor*. This is described schematically by resonance structures of the right-side of Figure 1.

In order to examine which resonance structures are involved in the determinantal basis function  $\Omega_1$ , we divide the corresponding Slater determinant into the following two parts:

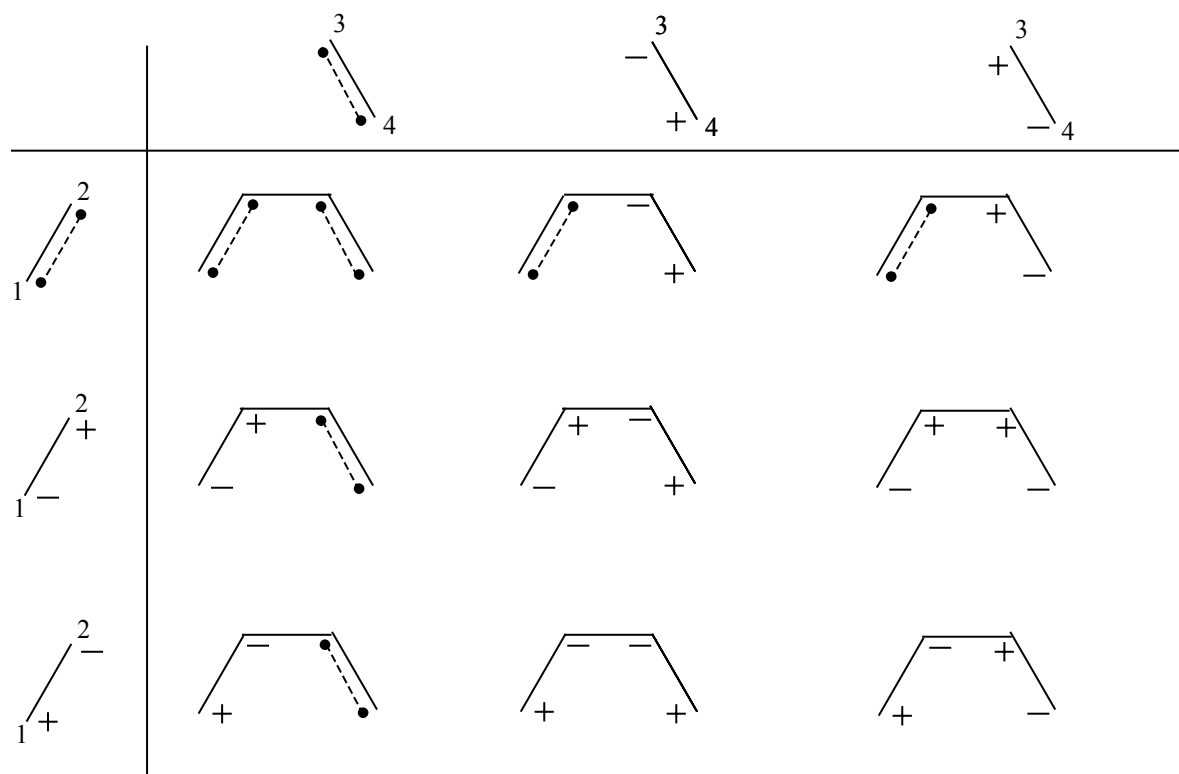
$$|\overline{\omega_{1,2} \omega_{1,2} \dots} = c_1 c_2 \{ |\overline{\varphi_1 \varphi_2 \dots} + |\overline{\varphi_2 \varphi_1 \dots} \} + c_1^2 \{ |\overline{\varphi_1 \varphi_1 \dots} \} + c_2^2 \{ |\overline{\varphi_2 \varphi_2 \dots} \} \quad (14)$$

$$\dots \overline{\omega_{3,4} \omega_{3,4}} = c_3 c_4 \{ \dots \overline{\varphi_3 \varphi_4} + \dots \overline{\varphi_4 \varphi_3} \} + c_3^2 \{ \dots \overline{\varphi_3 \varphi_3} \} + c_4^2 \{ \dots \overline{\varphi_4 \varphi_4} \} \quad (15)$$

Multiplication of (14) and (15), given in structural multiplication table of Figure 3, provides the resonance structures (having the form of spin-eigenfunctions in AO-positions), which are contained in  $\Omega_1$ . From this table one can conclude (in accord with intuition) that the bonding is limited in regions defined by centers (1,2) and (3,4) (both covalent and ionic components), and not between these regions. This is described schematically by resonance structures of the left-side of Figure 1.

### WEIGHTS OF RESONANCE STRUCTURES

Substituting in (4) the various  $\Omega_i$  by the resonance structures which they involve, one can evaluate quantitatively the weights of resonance structures describing  $\Psi(\text{ground})$ , following a process quite similar to the general method presented elsewhere (Karafiloglou, 2001). In the present paper we present only qualitatively the trends in weights. If we are limited to  $\Omega_1$ , then the weights of resonance structures shown in Figure 3 are different from zero, but other structures as those of Figure 2 should have zero weights. Since wave function (4) is normalized to one, the inclusion of  $\Omega_2$  and  $\Omega_3$  in  $\Psi(\text{ground})$  has as consequence to increase the weights of structures responsible for bonds between the couple of centers 1,2 and the couple 3,4 (e.g. bonds 2-3 or 1-4), while simultaneously decreases the weights of structures responsible for the chemical bonds 1-2 and 3-4.



**FIGURE 3:** Structural multiplication table for  $\Omega_1$ . Broken lines represent the covalent components of bonds existing in donor, 1 — 2, or acceptor, 3 — 4, regions.

Looking at chemical resonance effect from a probabilistic point of view, the above weights provide also the probabilities (Karafiloglou & Launay 1998; Karafiloglou 2001) of finding various bonding schemes between orbitals (i.e. those which are involved in each resonance structure) inside the considered molecule. In this context, the electron transfer from one region to other is characterized from the increasing of probabilities of structures responsible for the bonding between donor and acceptor regions, as well as the decreasing of probabilities of structures responsible for the bonding within both donor and acceptor regions.

### THE ROLE OF QUANTUM MECHANICAL RESONANCE STRUCTURES TO UNDERSTANDING CHEMICAL REALITY

According to Laszlo (2002), when teaching chemistry one must not be limited to the Platonic archetypes of structural formulas. In general, structural formulas (and the associated resonance structures) must be viewed only as a pedagogical tool, having as purpose to improve the rational understanding of chemistry and its underlying logic by students; it must be not identified (or confused) with chemical reality. Also, the unguarded practice of ‘curved arrows’ in resonance structures involves a real danger that can easily become a modern counterpart to medieval scholastics (Laszlo, 2002). Quantum chemistry, and precisely ‘Resonance’ (or ‘Mesomeric’) theory can help to avoid to a great extent such a type of misinterpretation.

In quantum theory, resonance structures are basis wave functions, and have the mathematical form of anti-symmetrized products, i.e. (linear combinations of) Slater determinants. Each basis function represents a certain bonding scheme between orbitals, corresponding to a so-called ‘limit’ resonance structure. The molecular wave function, which constitutes a mathematical representation of the the molecule, can be expressed as a linear combination of such basis wave functions. The movement of electrons inside the molecule, as well as the fractional occupation numbers in atoms, can be understood from the superposition of these basis wave functions (representing, however, integer occupation numbers), i.e. the ‘resonance’ of the corresponding limit resonance structures. For example, the movement of electrons involved in delocalization and hyperconjugation effects can be understood through the resonance of the limit structures involved in  $\Omega_2$  and  $\Omega_3$ . The probabilistic behavior of these structures is a direct consequence of chemical quantum reality. Therefore, looking these structures from a probabilistic perspective, one can *approach chemical reality and simultaneously preserve the useful pedagogical tool of chemical formulas*. Furthermore, in this context, the widely used by experimental chemists ‘curved arrows’ can be considered as a pictorial tool destined to describe schematically the qualitative trends in probabilities.

### CONCLUSION

Without electron transfer, i.e. when we are limited to  $\Omega_1$ , there is a bonding in regions defined by centers (1,2) and (3,4) but not between these regions. This is presented by resonance structures involved in the left-hand side of Figure 1. The movements of electrons included in the transfer from one bonded region to another, within delocalization and hyperconjugation effects, are described by the inclusion of resonance structures exhibiting bonds between donor and acceptor. Such resonance structures are presented in the right-hand side of Figure 1. The necessary covalent components of these bonds are issued from the coupling of the two odd electrons, which are created in donor and acceptor regions (one odd electron in each region), by means of one- electron transfer process.



It is shown that delocalization and hyperconjugation effects are characterized by the increasing of probabilities (i.e. the weights) of structures responsible for bonding between donor and acceptor and the concomitant decreasing of probabilities (i.e. the weights) of structures responsible for bonding in both donor and acceptor regions. In this context, the ‘curved arrows’ of Figure 1 can be considered to describe schematically the qualitative trends of these changes in probabilities.

**CORRESPONDENCE:** Padeleimon KARAFILOGLOU, POB 135, Department of General and Inorganic Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; e-mail: karafilo@ccf.auth.gr

## REREFENCES

- Bachler, V. & Schaffner, K. (2000). The photochemistry of 1,3-butadiene rationalized by means of theoretical resonance structures and their weights. *Chemistry - A European Journal*, 6, 959-970.
- Glendening, E.D., Badenhop, J.K., Reed, A. E., Carpenter, J. E., Bohmann, J.A., Morales, C.M., & Weinhold, F. (2001). Program NBO-5.0, Theoretical Chemistry Institute, University of Wisconsin.
- Glendening, E.D. & Weinhold, F. (1998). Natural resonance theory: I. General formalism. *Journal of Computational Chemistry*, 19, 593-609.
- Goodman L., Pophristic, V. & Weinhold, F. (1999). Origin of methyl rotation barriers. *Accounts of Chemical Research*, 32, 983-993.
- Karafiloglou, P. (1992). Moffitt's theorem as a bridge between the delocalized picture of band theory and the local picture of resonance structures in a solid: Peiers distortions and conductivity. *Journal of Solid State Chemistry*, 99, 29-37.
- Karafiloglou, P. (2001). A method to calculate the weights of NBO electronic structures from Moffitt's theorem. *Journal of Computational Chemistry*, 22, 306-315.
- Karafiloglou, P. & Launay, J.P. (1998). Electron pair (de)coupling in aniline radical cation and its implications for organic “mixed valence” systems. *Journal of Physical Chemistry A*, 102, 8004-8012.
- Karafiloglou, P. & Ohanessian, G. (1991). Understanding molecular orbital wave functions in terms of resonance structures. *Journal of Chemical Education*, 68, 583-586.
- Laszlo, P. (2002). Describing reactivity with structural formulas, or when the push comes to shove. *Chemistry Education: Research and Practice in Europe*, 3, 113-118.  
[[http://www.uoi.gr/conf\\_sem/cerapie](http://www.uoi.gr/conf_sem/cerapie)]
- Reed, A.E., Curtiss, L.A., Weinhold, F. (1988). Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chemical Reviews*, 88, 899-926.
- Weinhold, F. (1999). Chemical bonding as a superposition phenomenon. *Journal of Chemical Education*, 76, 1141-1146.
- Weinhold, F. (2001). A new twist on molecular shape. *Nature*, 411, 539-541.
- Weinhold, F. & Landis, C.R. (2001). Natural bond orbitals and extensions of localized bonding concepts. *Chemistry Education: Research and Practice in Europe (CERAPIE)* 2, 91-104.  
[[http://www.uoi.gr/conf\\_sem/cerapie](http://www.uoi.gr/conf_sem/cerapie)]