

*Regular Papers***On obtaining localized bonding schemes from delocalized molecular-orbital wave functions****Vinzenz Bachler**

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Received: 7 August 1996 / Accepted: 18 March 1997

Abstract. A straightforward procedure is proposed for expanding a molecular orbital determinantal wave function into a set of determinantal wave functions composed of atomic orbitals localized at the atoms of a molecule. By employing this method, atomic orbital determinants and their weights can be derived for a molecule from the computed molecular-orbital wave function. The procedure permits the interpretation of a molecular orbital determinantal wave function in terms of bonding schemes related to the classic resonance structures used by organic chemists. By using the unrestricted molecular orbital determinant, bonding schemes and their weights are obtained for butadiene, the butadiene radical cation and the acrylonitrile radical anion. Their dominant bonding schemes are in accord with the relevant resonance structures for these molecules. For the butadiene radical cation and the acrylonitrile anion they are shown to be compatible with the accepted mechanisms of the electrochemical coupling reactions of butadiene and acrylonitrile.

Key words: Localization – Bonding schemes**1 Introduction**

Many molecular properties such as geometries, ionization potentials, dipole moments and the electronic charge distribution can be computed from the *ab initio* Hartree-Fock (HF) wave function [1]. This important one-determinantal wave function is composed of canonical molecular orbitals (MOs) delocalized over the whole molecule. For computing other properties such as electronic spectra or dissociation energies correlated wave functions are needed [2]. They can be linear combinations of determinantal wave functions composed of MOs, which are perhaps the most important theoretical tool of the organic chemist. Their shapes are the basis of the successful frontier orbital concept rationalizing a large body of chemistry [3]. Their symmetry properties are applied in symmetry rules and in correlation diagram methods. They led to compre-

hensive explanations of reaction mechanisms and the stereospecificity of chemical reactions [4].

The other classical theoretical concept is the manifold of resonance structures for a molecule as conceived by the organic chemist. They are an efficient notation of the accumulated knowledge about a molecule. By drawing lines in a resonance structure, one localizes spin-coupled electron pairs in bond regions or in lone pairs at the atoms of the molecule. Such localizations are not an *a priori* property of the HF wave function. In this function, spin-coupled electron pairs occupy MOs which are delocalized over the whole molecule. The HF wave function, however, is invariant with respect to a unitary transformation of the occupied MOs [5]. This property is applied for devising well-known unitary transformations which produce localized MOs [6]. In many cases they are localized in bond regions and in lone pairs, in a way compatible with the predominant resonance structure for a molecule [7].

A direct way of obtaining resonance structures for a molecule is to apply the valence bond (VB) theory [8]. In this classic approach, the exact wave function is a linear combination of determinantal wave functions composed of atomic orbitals (AOs) which are localized at the atoms [8]. Any AO determinant corresponds to one or several localization schemes of spin-coupled electron pairs. The linear combination coefficients in the expansion are determined variationally [8]. Large coefficients indicate determinants of important resonance structures characterizing the resonance hybrid for a molecule [9]. The merit of the VB approach is to provide a firm quantum mechanical basis for the resonance structures of organic chemistry [10]. In quantitative calculations however, a large number of resonance structures must be employed to expand the molecular wave function [11]. The construction of spin-adapted functions is a solvable but formidable task [12]. Due to the non-orthogonality of the AO determinantal wave functions [13], the Hamilton matrix elements are difficult to compute. Therefore, MO methods have surpassed VB approaches in the area of quantitative computations.

Nevertheless, VB approaches have experienced a renaissance in recent decades. Shaik and coworkers devel-

oped a correlation diagram method based on qualitative VB structures for reactants and products [14]. Their curve-crossing model is a qualitative scheme to discuss reaction mechanisms [14] and to estimate geometries of transition states [15]. Harcourt applied the VB approach to many topics in organic chemistry [16]. The diradical character of 1,3-dipoles has been estimated [17] and an application to the interesting problem of hypervalent organic compounds appeared [18]. Epiotis developed a qualitative approach which is a hybrid of the MO and VB method [19]. This procedure led to a fairly comprehensive rationalization of many areas of chemistry [19]. Malrieu et al. developed the effective VB hamiltonian method for conjugated hydrocarbons [20]. It is based on a Heisenberg spin operator acting on a set of covalent resonance structures for the π -electron systems [20]. This method is an efficient tool to describe ground and excited state properties of conjugated hydrocarbons [20]. Recently, Roth et al. carefully parametrized this π -electron procedure [21]. Moreover, they supplemented the scheme with a classical force field for the σ -electrons [21]. This hybrid technique led to accurate stabilization energies for a large number of π -radicals. Treboux et al. applied a geometry dependent Heisenberg Hamiltonian supplemented by a properly selected force field for the σ -electrons [22]. Properties of covalent excited states of rather large π -electron systems could be computed with good accuracy [22]. The Heisenberg Hamiltonian combined with a force field for the σ -electrons was used by Bernardi et al. to simulate bond breaking in organic reactions [23]. A fairly large number of parameters and high-level ab initio computations were used to parametrize the matrix representation of the Hamiltonian [23]. An application of this procedure led to a comprehensive rationalization of the photochemical transformations of ergosterol [24]. Several program packages are available for performing quantitative VB computations [25]. An efficient method is the spin-coupled VB procedure developed by Gerratt and his group [26]. The determinantal wave functions employed are composed of hybrid orbitals delocalized over the molecule [27]. Their use leads to rather compact VB expansions [26]. The spin-coupled VB method has been applied to many molecules and high-quality wave functions are obtained [28]. However, for medium-size or large molecules the computations are very time consuming. In contrast, rather large molecules can be treated by means of the ab initio HF method [29] or by methods which employ limited configuration interaction. Therefore, a scheme is desirable whereby resonance structures and their weights can be obtained from HF wave functions. Such a scheme implies that a relationship between MO and VB wave functions exists.

The expansion of MO wave functions into a set of VB functions was carried out for small molecules in the early days of quantum chemistry [30]. The first general scheme, however, was devised by Hiberty and Leforestier [31]. A one-determinantal wave function composed of delocalized MOs is expanded into a linear combination of determinantal wave functions made up of localized AOs [31]. By using the concept of half-determinants [31], an explicit formula for the expansion coefficients was obtained [32]. The procedure of Hiberty and Leforestier

involves several stages [31]. Firstly, the MO determinantal wave function is obtained by means of the HF method. Secondly, a linear independent set of relevant normalized VB functions which are spin eigenfunctions is constructed by means of Rumer's method [33]. Thirdly, the expansion coefficients and subsequently the weights of the VB functions in the MO wave function are determined. This expansion scheme has been applied to many chemical problems as summarized in a comprehensive review [34]. Important resonance structures for 1,3-dipoles and also their diradical character have been analysed [34]. The push-pull substitution in benzene was discussed in terms of calculated weights of resonance structures [34]. The localization of π -electrons in ring-annulated systems known as the Mills-Nixon effect could be rationalized [34]. The expansion of MO wave functions into AO determinants was also applied by Karafiloglou and Malrieu in their analysis of electron correlation effects [35]. The same formula for the expansion coefficients as in the procedure of Hiberty and Leforestier was applied [36]. This formula was discussed by Karafiloglou and Ohalessian in an interesting pedagogical paper [37]. It relates the expansion method to an early paper by Moffit [38]. The power of the expansion method is shown in the analysis of hydride transfer processes [39]. It is interesting to see how the weights of important resonance structures vary along the reaction coordinate [39]. Environmental effects on molecules were also studied by expanding the MO wave functions into resonance structures [40]. Recently, an alternative procedure based on the first-order density matrix was suggested for the expansion of an MO wave function into VB functions [41].

The above-mentioned applications show that expanding MO wave functions into resonance structures leads to useful chemical insights. In the following sections we introduce a simple procedure for expanding a determinantal wave function composed of MOs into determinantal wave functions made up of AOs. The procedure is in many ways related to the scheme of Hiberty and Leforestier [31]. Our method, however, uses a compact formula for obtaining the entire set of AO determinants contained in an MO wave function. We illustrate the procedure by finding important localized bonding schemes for the π -electron systems of butadiene, the butadiene radical cation and the acrylonitrile radical anion. The obtained bonding schemes accord with resonance structures which are considered as being relevant for describing the properties of these molecules.

2 Theoretical considerations

2.1 Expanding the MO wave function

Consider a closed- or open-shell doublet one-determinantal wave function. A wave function which is more general than the restricted one is the unrestricted Hartree-Fock (UHF) wave function [42]. This simple one-determinantal wave function does not describe a pure-spin state [43]. However, it provides different space parts for the α - and β -spin orbitals [42]. This flexibility permits electrons of different spin to become localized in

different spatial regions of the molecule. This property makes the UHF wave function more appropriate for our purposes than the restricted Hartree-Fock (RHF) determinant. In an open-shell doublet system, $m + 1$ α - and m

minantal wave functions composed of localized spin orbitals. We start out by representing the one-determinantal UHF MO wave function in a particular way shown below where

$$\Psi_{\text{UHF}} = \text{Det} \begin{vmatrix} \Psi_{1^{(1)}} & \Psi_{1^{(2)}} & \dots & \Psi_{1^{(n)}} \\ \bar{\Phi}_{1^{(1)}} & \bar{\Phi}_{1^{(2)}} & \dots & \bar{\Phi}_{1^{(n)}} \\ \vdots & \vdots & \vdots & \vdots \\ \Psi_{m^{(1)}} & \Psi_{m^{(2)}} & \dots & \Psi_{m^{(n)}} \\ \bar{\Phi}_{m^{(1)}} & \bar{\Phi}_{m^{(2)}} & \dots & \bar{\Phi}_{m^{(n)}} \\ \Psi_{m+1^{(1)}} & \Psi_{m+1^{(2)}} & \dots & \Psi_{m+1^{(n)}} \end{vmatrix} \quad n \times n$$

$$= \text{Det} \begin{vmatrix} a_{11} & a_{21} & \dots & a_{N1} & \circ & \circ & \dots & \circ \\ \circ & \circ & \dots & \circ & b_{11} & b_{21} & \dots & b_{N1} \\ \vdots & \vdots & & \vdots & \vdots & & & \vdots \\ a_{1m} & a_{2m} & \dots & a_{Nm} & \circ & \circ & \dots & \circ \\ \circ & \circ & \dots & \circ & b_{1m} & b_{2m} & \dots & b_{Nm} \\ a_{1m+1} & a_{2m+1} & \dots & a_{Nm+1} & \circ & \circ & \dots & \circ \end{vmatrix} \quad n \times 2N$$

$$\begin{pmatrix} \chi_1^{(1)} & \chi_1^{(2)} & \dots & \chi_1^{(n)} \\ \chi_2^{(1)} & \chi_2^{(2)} & \dots & \chi_2^{(n)} \\ \vdots & \vdots & \vdots & \vdots \\ \chi_{N^{(1)}} & \chi_{N^{(2)}} & \dots & \chi_{N^{(n)}} \\ \bar{\chi}_1^{(1)} & \bar{\chi}_1^{(2)} & \dots & \bar{\chi}_1^{(n)} \\ \bar{\chi}_2^{(1)} & \bar{\chi}_2^{(2)} & \dots & \bar{\chi}_2^{(n)} \\ \vdots & \vdots & \vdots & \vdots \\ \bar{\chi}_{N^{(1)}} & \bar{\chi}_{N^{(2)}} & \dots & \bar{\chi}_{N^{(n)}} \end{pmatrix} \quad 2N \times n \quad (2)$$

β -spin orbitals are occupied by α - and β -electrons, respectively. The odd number of electrons is given by $n = 2m + 1$. In a singlet state, the number of α and β -spin orbitals is equal. However, their space parts may be different. Using the linear combination of atomic orbitals (LCAO) approximation, we expand the α - and β -spin orbitals into sets of N atomic spin orbitals χ_μ and $\bar{\chi}_\mu$, respectively. For a doublet state, we write

$$\Psi_i(j) = \sum_{\mu=1}^N a_{\mu i} \chi_\mu(j) \quad i = 1, 2 \dots m + 1, \quad (1a)$$

$$\bar{\Phi}_i(j) = \sum_{\mu=1}^N b_{\mu i} \bar{\chi}_\mu(j) \quad i = 1, 2 \dots m. \quad (1b)$$

By convention, electron j has α spin in ψ_i and χ_μ . The β spin functions in $\bar{\phi}_i$ and $\bar{\chi}_\mu$ are represented by a bar. The coefficients $a_{\mu i}$ and $b_{\mu i}$ in Eq. (1a, b) designate the LCAO coefficients for the MOs ψ_i and ϕ_i , respectively. The one-determinantal UHF wave function comprises molecular spin orbitals delocalized over the molecule. Our aim is to interpret this wave function in terms of localized bonding schemes where electrons are localized in bond regions and in lone pairs at the atoms of a molecule. Thus, the wave function for a localized bonding scheme should be composed of atomic spin orbitals localized at the atoms. In the following we expand a delocalized MO determinantal wave function into a sequence of deter-

The left-hand side of Eq. (2) represents the UHF MO wave function composed of delocalized molecular spin orbitals. It is a determinant of a square matrix of dimension n where n is the number of electrons. This square matrix is represented on the right-hand side of Eq. (2) as a product of two rectangular matrices. The first matrix contains the LCAO coefficients of all occupied MOs and zero entries. It comprises n rows and $2N$ columns where N is the number of AOs in the molecule. The second matrix comprises atomic-spin orbitals grouped according to α - and β -spin. It is made up of $2N$ rows and n columns. The forms of the rectangular matrices ensure that their multiplication produces the quadratic matrix on the left-hand side of Eq. (2). The doublet UHF wave function is also obtained by forming the determinant on the right-hand side of Eq. (2). This is represented by the short-hand notation

$$\Psi_{\text{UHF}} = \text{Det}[C(n \times 2N) \chi(2N \times n)] \quad (3)$$

The matrices $C(n \times 2N)$ and $\chi(2N \times n)$ symbolize the first and the second matrix on the right-hand side of Eq. (2), respectively.

In Eq. (2), the UHF wave function is represented as a determinant of the product of two rectangular matrices. This form permits us to employ the general multiplication rule for determinants known as the Binet-Cauchy theorem [44]. Baba et al. [45] used this theorem to

interpret configuration interaction (CI) calculations in terms of reference functions. Hohlneicher and Börsch-Pulm [46] developed a procedure for interpreting a CI calculation for a molecule in terms of Platt's perimeter model [47]. The perimeter electronic states serve as reference functions [46]. The Binet-Cauchy theorem is applied to expand the electronic states into the set of perimeter electronic states [46]. Balint-Kurti and Karplus [48] expressed Hamilton matrix elements over non-orthogonal Slater determinants in terms of orthogonal Slater determinants. This key transformation, used in a VB calculation, resembles an application of the Binet-Cauchy theorem [48]. To the best of our knowledge, however, this theorem was not explicitly applied to interpret determinantal MO wave functions in terms of atomic spin orbital determinants. Using the Binet-Cauchy theorem [44], we can write

$$\Psi_{\text{UHF}} = \text{Det} \begin{vmatrix} \Psi_{1^{(1)}} & \Psi_{1^{(2)}} & \dots & \Psi_{1^{(n)}} \\ \bar{\Phi}_{1^{(1)}} & \bar{\Phi}_{1^{(2)}} & \dots & \bar{\Phi}_{1^{(n)}} \\ \vdots & \vdots & \vdots & \vdots \\ \bar{\Phi}_{m^{(1)}} & \bar{\Phi}_{m^{(2)}} & \dots & \bar{\Phi}_{m^{(n)}} \\ \Psi_{m+1^{(1)}} & \Psi_{m+1^{(2)}} & \dots & \Psi_{m+1^{(n)}} \end{vmatrix} = \sum_{1 \leq k_1 < k_2 < \dots < k_n \leq 2N} \text{Det} \begin{vmatrix} c_{1k_1} & c_{1k_2} & \dots & c_{1k_n} \\ \vdots & \vdots & \vdots & \vdots \\ c_{nk_1} & c_{nk_2} & \dots & c_{nk_n} \end{vmatrix} \cdot \text{Det} \begin{vmatrix} \chi_{k_1^{(1)}} & \chi_{k_1^{(2)}} & \dots & \chi_{k_1^{(n)}} \\ \chi_{k_2^{(1)}} & \chi_{k_2^{(2)}} & \dots & \chi_{k_2^{(n)}} \\ \vdots & \vdots & \vdots & \vdots \\ \chi_{k_n^{(1)}} & \chi_{k_n^{(2)}} & \dots & \chi_{k_n^{(n)}} \end{vmatrix} \quad (4)$$

Thus, the UHF wave function is expanded into a sum. Any sum member is a product of two determinants formed from $n \times n$ matrices (see Eq. 4). The first determinant contains a selection of LCAO coefficients as obtained from a standard UHF calculation. The second determinant represents a one-determinantal wave function composed of localized atomic spin orbitals. The summation is performed over groups of indices. Any group represents n indices k_1, k_2, \dots, k_n , where n is the number of electrons. Any k_i can assume a value between 1 and $2N$, where N is the number of AOs in the molecule. The n indices k_1, k_2, \dots, k_n , however, are ordered in magnitude as indicated below the summation sign (see Eq. 4). Any index group designates a definite column selection of the rectangular coefficient matrix and a row selection of the rectangular atomic spin orbital matrix of Eq. (2). These selections determine the coefficient and atomic spin orbital determinants of Eq. (4). Equation (4) is a straightforward device for expanding a one-determinantal UHF MO wave function into a linear combination of AO determinantal wave functions. The linear combination coefficients are the coefficient determinants in Eq. (4). They contain LCAO coefficients which transform AOs into MOs. However, an infinite number of LCAO coefficient sets exists all related by unitary transformations. The transformations

leading from canonical to localized MOs are well known [6]. Those unitary transformations leave the MO determinant invariant [5], but the coefficient determinants in Eq. (4) are also invariant (see Appendix). Thus, expanding the MO determinant into a sequence of AO determinants by means of Eq. (4) is unique. This expansion has been the basis for the electron correlation analysis performed by Karafiloglou and Malrieu [35] and of the expansion technique developed by Hiberty and Leforestier [31]. Their coefficient formula [31, 36] for a definite AO determinant is a coefficient determinant of Eq. (4). They obtained it, however, in a different way by employing the concept of half determinants [31]. Hiberty and Leforestier expand the MO wave function into VB functions [31]. In a first step, a linear independent set of VB functions which are spin eigenfunctions is constructed [31]. Subsequently, the linear combination coefficients


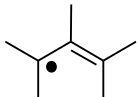
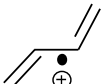



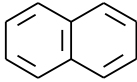
for these spin eigenfunctions are calculated and their weights in the expansion are determined [31]. The advantage of Eq. (4) is that it represents a systematic way to obtain the entire set of AO determinants. Their spin multiplicity agrees with that of the expanded MO wave function. Thus, from a doublet UHF wave function, only doublet AO determinants are generated. For all improper spin multiplicities, the coefficient determinants of Eq. (4) vanish [49]. However, neither the UHF MO determinant nor the obtained AO determinants are in general spin eigenfunctions. Moreover, the AO determinants are not exactly normalized to unity. Nevertheless, they correspond to localized bonding schemes of correct spin multiplicity. Therefore, the Binet-Cauchy theorem leads to a compact tool for analysing a delocalized MO wave function in terms of strictly local bonding schemes.

We can apply the well-known conditions for a vanishing of determinants to the coefficient determinants in Eq. (4). This leads to the number N_D of AO determinants which are contained in the MO determinant. N_D is given by

$$N_D = \binom{N}{n_\alpha} \binom{N}{n_\beta} = \left(\frac{N!}{n_\alpha!(N-n_\alpha)!} \right) \left(\frac{N!}{n_\beta!(N-n_\beta)!} \right) \quad (5)$$

Here, n_α and n_β are the number of α - and β -electrons, respectively. This formula for N_D was previously obtained and applied for partitioning the electron correlation energy in molecules [50]. N_D is represented in Table 1 for the π -electron systems of various molecules. Thus, 4 AO determinants evolve from a one-determinantal MO wave function containing the two π -electrons of ethylene. From the π -electron system of butadiene 36 AO determinants are obtained. Table 1 illustrates the well-known fact that N_D is rather large even for medium size π -electron systems like benzene and naphthalene [51]. This sheer number of AO determinants makes the complete expansion of MO determinants a formidable problem. Often, however, the electrons in a molecule can be partitioned into groups of chemically active and inactive electrons. They may refer to a characteristic functional group and the remaining part of a molecule, respectively. A technique has been devised where only the components of the MO wave function for the chemically active electrons are expanded into localized AO determinants [52]. The components for the inactive electrons, however, remain delocalized [52].

Table 1. The number of atomic spin orbital determinants (N_D) which are contained in a molecular orbital (MO) determinantal wave function. Only the π -electrons are considered. N_D is calculated by means of Eq. (5)

Molecule	N	n_α	n_β	N_D
	2	1	1	4
	3	2	1	9
	4	2	1	24
	4	2	2	36
	4	3	2	24
	6	3	3	400
	10	5	5	63504

2.2 The weights of AO determinants in the expansion

In the previous section we introduced a simple scheme for expanding an MO-determinantal wave function into a sequence of AO determinantal wave functions. Any AO determinant localizes electrons in a specific way into bond regions or at the atoms of the molecule. These localizations lead to bonding schemes which are the basis of the resonance structures used by organic chemists. Our aim is to obtain localized bonding schemes which characterize a molecule. Therefore, we must derive weights for the AO determinants contained in the MO wave function. We can write the expansion in Eq. (4) symbolically as

$$\Psi^{\text{mo}} = \sum_i^{N_D} c_i \Psi_i^{\text{ao}} \quad (6)$$

Here, Ψ^{mo} may be the UHF wave function composed of canonical MOs and the Ψ_i^{ao} are the AO determinants evolving from Ψ^{mo} . The number N_D of AO determinants with non-vanishing coefficients in Eq. (6) is given by Eq. (5). Wave function Ψ^{mo} is normalized and the probability of finding all electrons in space is unity. Using Eq. (6), we can write

$$\begin{aligned} \langle \Psi^{\text{mo}} | \Psi^{\text{mo}} \rangle &= 1 = \sum_i^{N_D} \sum_j^{N_D} c_i c_j \langle \Psi_i^{\text{ao}} | \Psi_j^{\text{ao}} \rangle \\ &= \sum_i^{N_D} (c_i^2 \langle \Psi_i^{\text{ao}} | \Psi_i^{\text{ao}} \rangle + \sum_{j \neq i}^{N_D} c_i c_j \langle \Psi_i^{\text{ao}} | \Psi_j^{\text{ao}} \rangle) \quad (7) \end{aligned}$$

The AO determinants form a set of non-orthogonal many-electron functions [53]. Hence, overlap integrals between AO determinants appear in Eq. (7). The unit probability can be partitioned into contributions w_i given by

$$w_i = c_i^2 \langle \Psi_i^{\text{ao}} | \Psi_i^{\text{ao}} \rangle + \sum_{j \neq i}^{N_D} c_i c_j \langle \Psi_i^{\text{ao}} | \Psi_j^{\text{ao}} \rangle \quad (8)$$

Their meaning becomes evident from the following reasoning. Let us remove from the expansion in Eq. (6) one Ψ_i^{ao} . This changes the unit probability of finding all electrons in space by w_i . Thus, w_i is the weight of the AO determinant Ψ_i^{ao} in the probability of finding all electrons in space. This weight definition (Eq. 8) has been employed extensively in the past [54]. Its application requires the computation of overlap integrals between non-orthogonal AO determinants. The non-orthogonality also implies that the squares of all coefficients in Eq. (6) do not add up to unity. In our applications we have used Eq. (6), but only an approximate weight definition was employed. Using the expansion in Eq. (6), we can write for the normalization condition

$$\begin{aligned} \langle \Psi^{\text{mo}} | \Psi^{\text{mo}} \rangle &= 1 \\ &= \sum_i^{N_D} \sum_j^{N_D} c_i c_j \delta_{ij} \langle \Psi_i^{\text{ao}} | \Psi_j^{\text{ao}} \rangle \quad (9) \end{aligned}$$

Thus, instead of considering all different overlap integrals as in Eq. (7), we use an average normalization integral. Equation (9) implies that it should be equal to

$$\langle \overline{\Psi^{\text{ao}}} | \overline{\Psi^{\text{ao}}} \rangle = \frac{1}{\sum_k^{N_D} c_k^2} . \quad (10)$$

Consequently, the weight w_i of an AO determinant Ψ_i^{ao} in the expansion (Eq. 6) is given by

$$w_i = \frac{c_i^2}{\sum_k^{N_D} c_k^2} . \quad (11)$$

This simple weight formula has been suggested [55] and applied [56] in the past.

Moreover, it is easy to see that a significant weight w_i is also compatible with a large energy increment E_i of the molecular electronic energy. The electronic UHF energy is the expectation value of a UHF MO determinant over the electronic Hamiltonian H . Using the expansion in Eq. (6), we can write

$$E_{\text{UHF}} = \sum_i^{N_D} \sum_j^{N_D} c_i c_j \langle \Psi_i^{\text{ao}} | H | \Psi_j^{\text{ao}} \rangle = \sum_i^{N_D} E_i . \quad (12)$$

Hamilton matrix elements over non-orthogonal AO determinants appear in Eq. (12) and an energy increment E_i is given by

$$E_i = c_i^2 \langle \Psi_i^{\text{ao}} | H | \Psi_i^{\text{ao}} \rangle + c_i \sum_{j \neq i}^{N_D} c_j \langle \Psi_i^{\text{ao}} | H | \Psi_j^{\text{ao}} \rangle . \quad (13)$$

Thus, a large expansion coefficient c_i leads to a large weight, but also to a significant contribution of the diagonal and the off-diagonal matrix elements in E_i . Therefore, the meaning of a weight w_i is twofold. Firstly, w_i indicates how strongly Ψ_i^{ao} contributes to the unit probability of finding the electrons in space. Secondly, a large w_i shows also that the electronic energy is likely to contribute significantly to the electronic energy of a molecule.

3 Applications

3.1 Computational procedures employed

All MO calculations were performed by means of the Open VMS version of the Gaussian 92 suite of ab initio programs [57] implemented on an AlphaDec-Station. We are mainly interested in semiquantitative results. Therefore, the standard STO-3G minimal basis sets [58] were employed primarily. Doublet, but also singlet ground state molecules were treated by means of the UHF method [42]. To obtain a UHF wave function for a singlet ground state molecule, it is mandatory to start the self-consistent field (SCF) iterations with orbitals breaking the spatial symmetry of the closed-shell MOs. We employed the "mix" option implemented in the guess link of the Gaussian 92 [57]. This option linearly combines the restricted guess frontier orbitals into symmetry broken HOMO+LUMO and HOMO-

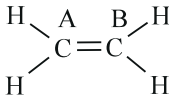
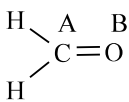
LUMO linear combinations. They serve as α and β guess HOMOs, respectively, in the UHF iteration process [57].

3.2 The π -bonds of ethylene and formaldehyde

In Sect. 2 we devised a simple procedure for obtaining localized bonding schemes for a molecule from a one-determinantal MO wave function composed of delocalized MOs. Here, we apply the expansion technique to the simple π -bond systems of ethylene and formaldehyde. We are interested in how the procedure describes purely covalent and polar π -bonds respectively.

We performed an RHF calculation for the ethylene molecule by means of the STO-3G minimal basis sets [58] at the experimental geometry [59]. We are only interested in the π -bond. Therefore, an MO determinant for the two π -electrons was expanded. Hence, the LCAO coefficients in Eqs. (2–4) are the coefficients for the π -MO of ethylene. According to Eq. (5), the expansion in Eq. (4) produces four singlet AO determinants (see Table 1) and any AO determinant is a wave function for a localized bonding scheme. Thus, two covalent and two ionic schemes evolve from the expansion. They are symbolized in the first row of Table 2. Their weights were computed by means of Eq. (8) and Eq. (11) where the Eq. (8) considers explicitly the non-orthogonality of the AO determinants. The two sets of weights are identical for ethylene and they are recorded in the second column of Table 2. The structural formula of ethylene, as written by the organic chemist, corresponds to the two covalent bonding schemes of Table 2. They appear with a total weight of 0.5. Due to the non-polarity of the bond, the two ionic forms evolve with equal weights. Their values of 0.25, however, are far too large. This is a well-known artefact of the RHF one-determinantal MO wave function [60]. It permits electrons of opposite spin to become too close to the atoms. Therefore, the ionic bonding schemes appear with weights that are too large. When correlated wave functions are expanded, a decrease and an increase of the ionic and covalent weights, respectively [61], is found. An analysis of these correlation effects led to transferable scaling factors. These convert RHF weights into almost exact weights [62]. Expansions of exact π -MO wave functions into AO determinants has been investigated by Lepetit et al. [63]. The π -MO wave functions were eigenfunctions of the Hubbard or of the Parise-Parr-Pople Hamiltonian [63]. The expansions led to a set of exact coefficients \bar{C}_I which measure the contribution of AO determinant I to the exact π -MO wave function. The authors showed that an exponential relationship holds between the coefficients for the exact wave function and the coefficients obtained from expanding the simple RHF MO determinant [63]. This led to a simple recipe for converting RHF coefficients \bar{C}_I into almost exact coefficients C_I [64]. Only the energies for the AO determinants and one variational parameter are needed [64]. The corrected wave function gave energies which comprised a large part of the correlation energy [64]. The procedure was further enhanced by introducing variational parameters for

Table 2. Covalent and ionic weights for the π -bonds of ethylene and formaldehyde. They are computed by means of Eq. (11). The weights in parentheses are obtained from Eq. (8) which accounts for the non-orthogonality of AO determinants. A UHF-MO determinant leads to weights which emphasize characteristically one covalent AO determinant. This arises from the spin polarization inherent in the UHF method

	\uparrow A — B	\downarrow A — B	\ominus + A — B	+ \ominus A — B	Molecule
RHF	0.2500 (0.2500)	0.2500 (0.2500)	0.2500 (0.2500)	0.2500 (0.2500)	
UHF	0.0287 (0.0482)	0.6898 (0.6090)	0.1407 (0.1714)	0.1407 (0.1714)	
RHF	0.2473 (0.2482)	0.2473 (0.2482)	0.2011 (0.2092)	0.3043 (0.2944)	
UHF	0.6559 (0.5871)	0.0349 (0.0535)	0.1224 (0.1496)	0.1868 (0.2098)	

individual atom pairs [65]. The improvement of an RHF MO wave function is in essence a diminishing of the coefficients for AO determinants which describe ionic charge separations in a molecule. It was shown that this lowering depends on a combination of properties for individual bonds [65]. This led to a procedure without variational parameters where only bond properties and the geometry of the molecule are needed [65]. The local character of the electron correlation problem is also exploited in the electron correlation treatment based on the local approach [66].

Large ionic weights may also be avoided by applying the UHF wave function. This simple one-determinantal wave function provides different molecular orbitals for α - and β -electrons [42]. Thus, α - and β -electrons can localize in different parts of the molecule. Therefore, ionic bonding schemes with spin-coupled electron pairs at the atoms, may evolve from the UHF wave function with small weights. The greater flexibility of the UHF wave function as compared to the RHF wave function may lead to the result that E_{UHF} is lower than E_{RHF} even for singlet ground states. Such a lowering was first found for the RHF wave function of a one-dimensional electron gas model [67]. There is always a spin-density wave solution with lower energy than the RHF energy [67]. UHF solutions with lower energy than the RHF solution are well known for singlet ground states of linear polyenes [68] and for conjugated molecules [69]. This lower energy can lead to UHF molecular orbitals not symmetry adapted to the full molecular point group. This deficiency is known as the symmetry dilemma [70]. The prospect that E_{UHF} is lower than E_{RHF} initiated the development of instability conditions for the RHF wave function [71]. Their importance for understanding organic reaction mechanisms has been comprehensively outlined [72].

We performed an UHF calculation for the singlet ground state of ethylene at the experimental geometry [59] and by using the STO-3G basis set [58]. E_{UHF} was lower than E_{RHF} by the small amount of 3.02 kcal/mol. The obtained UHF MOs are not symmetry-adapted in the D_{2h} point group. In general, an UHF wave function is not eigenfunction to the total spin operator S^2 . A singlet UHF wave function is primarily contaminated by a triplet component [73]. For pure singlet and triplet wave functions the S^2 expectation values should be 0.0 and 2.0,

respectively. We computed for the ethylene UHF wave function a value of 0.3058. Hence, the UHF wave function is a reasonable approximation for a singlet wave function. This is also supported by the UHF and RHF Mulliken charges which are almost identical. We also computed singlet UHF wave functions by means of the more extensive basis sets 4-31G [74] and 6-311G** [75]. The numerical values for E_{UHF} and E_{RHF} are very close when these basis sets are used. Moreover, the RHF and the UHF wave functions are almost identical and the latter is only weakly symmetry-broken. In general, the existence of a UHF solution with lower energy than the RHF solution depends on the interatomic distances in a molecular system [76]. Such UHF solutions seem to be less frequent when large basis sets are employed [77].

We computed the STO-3G UHF weights for the localized bonding schemes of ethylene by means of Eqs. (8) and (11). Both sets of weights are recorded in Table 2. When Eq. (11) is used, the second covalent scheme evolves with the large weight of 0.6898. Thus, the bonding scheme written by the organic chemist is derived with a weight of about 70 %. Weights for the two ionic and the remaining covalent scheme are significantly smaller, namely 0.1407 and 0.0287, respectively (see Table 2). The weights obtained by means of Eq. (8) lead to the same qualitative results (see Table 2). Thus, the UHF wave function favours the covalent but disfavors the ionic bonding schemes (see Table 2). This finding is in line with the spin localization capabilities of the UHF procedure. There, two electrons of the same spin enjoy a binding exchange interaction [78]. It brings electrons of same spin close together at the atoms. Electrons of opposite spin, however, experience only a coulomb repulsion [78]. Therefore, spin-coupled electron pairs prefer different atoms (covalent) but avoid a localization at one atom (ionic).

An RHF wave function for formaldehyde was obtained by using the experimental geometry [79] and the minimal STO-3G basis set [58]. Again, bonding schemes and their weights were computed by means of Eqs. (8) and (11). Both sets of weights are almost identical and they are recorded in the fourth row in Table 2. As for ethylene, covalent and ionic bonding schemes evolve with similar weights. The ionic weights describe correctly the polarity of the carbonyl group but their values are too large.

We derived a UHF wave function for the singlet ground state of formaldehyde at the experimental geometry [79] and by using the STO-3G basis set [58]. E_{UHF} was lower than E_{RHF} by only 2.88 kcal/mol. The expectation value over S^2 is 0.2781, indicating only a small triplet contamination of the singlet ground state wave function. Again, RHF and UHF Mulliken charges are almost identical. Both findings support the notion that the UHF wave function is sufficient for describing the singlet ground state of formaldehyde. We also attempted to obtain singlet ground state UHF wave functions by means of the 4-31G [74] and the 6-311G** [75] basis sets. For the 4-31G basis set we derived a UHF energy which was lower than the RHF energy by a very small amount. However, all UHF computations converged to the RHF solution when the 6-311G** basis set was employed. Weights obtained from the STO-3G singlet UHF wave function for formaldehyde were computed by means of Eqs. (8) and (11). Both sets of values are recorded in the last row of Table 2. The weights from Eq. (11) indicate that one covalent bonding scheme appears with a weight of about 66 %. The two ionic bonding schemes evolve with significantly smaller weights. Their relative magnitude is in line with the polarity of the carbonyl group. Weights obtained from Eq. (8) show also the dominance of one covalent bonding scheme and the correct polarity of the bond (see Table 2). Thus, our expansion classifies the carbonyl π -bond as a covalent π -bond which is slightly polarized. This finding is in line with the wealth of chemical experience. Our results support the notion that the UHF wave function is more appropriate than the RHF wave function for obtaining bonding schemes and their weights.

3.3 The π -electron system of butadiene

3.3.1 Preferred local spin occupations

Butadiene is characterized by two weakly interacting π -bonds. Encouraged by the results for the single π -bonds of ethylene and formaldehyde, we applied the expansion technique to the more complicated case of butadiene. We computed the UHF wave function for the singlet ground state of butadiene at the experimental geometry [80] and by using the STO-3G basis set [58]. The energy E_{UHF} was lower than E_{RHF} by 11.52 kcal/mol. The S^2 expectation value for the UHF wave function was 0.7432. This result indicates significant triplet and higher spin contaminations for the singlet ground state. However, the computed UHF and RHF Mulliken charges [81] are almost identical. For the terminal carbon atoms net charges of -0.125 (UHF) and -0.130 (RHF) are obtained. Charges of -0.058 (UHF) and -0.058 (RHF) occur at the central carbon atoms. Thus, in spite of spin contaminations, the UHF MO determinant seems to be appropriate for spin independent properties of the singlet ground state. The symmetry-broken character of the UHF wave function persisted when the larger basis sets, 4-31G [74] and 6-311G** [75], were applied.

We are interested in bonding schemes for the π -electron system and we expanded a UHF MO determinant for the four π -electrons. Thus, only LCAO-coefficients

of the occupied α and β π -MOs occur in Eqs. (2) and (4). In accord with Eq. (5), 36 AO determinants (see Table 1) evolve from the UHF MO determinant with non-vanishing coefficients. We obtained all AO determinants in the sequence of decreasing weights. Numbers in the first column of Table 3 designate the position of the AO determinant in this sequence. In the second column, occupations of localized spin AOs are displayed. They are indicated by the diagonal of the corresponding AO determinant. Their weights are computed by means of Eq. (11) and are recorded in the fourth row. The purely covalent determinant 1 with complete spin alternation evolves with a weight of 0.5220. It is followed by the monoionic determinants 2 to 5. They describe electron occupations where one carbon atom carries a positive and another one a negative charge (see Table 3). The

Table 3. Localized bonding schemes and their weights as they evolve from the UHF MO determinant for the singlet ground state of butadiene. Entries in the first column indicate the position of the scheme in a weight-ordered sequence of all schemes. The weight for AO determinant 1 is partitioned into the weights for two bonding schemes (see Sect. 3.3.2). AO determinants 1–5 emerge with a weight of about 85%. Notice the large weight for the covalent scheme of about 50%. Schemes below the *double line* supplement the schemes above the line. Bonding schemes above and below the *double line* are interrelated by spin inversion

No.	Occupation	Bonding scheme	Weight
1			0.52197
2			0.08129
3			0.08129
4			0.08036
5			0.08036
<hr/>			
11			0.01251
12			0.01251
27			0.00038
18			0.00219
19			0.00219
20			0.00216
21			0.00216

first five determinants evolve from the expansion with a total weight of about 85 %. Determinants below the double line have an equivalent meaning to the determinants above the line. They emerge, however, with significantly smaller weights (see Table 3).

The weights in Table 3 illustrate a characteristic feature of the UHF method. A binding exchange interaction between electrons of the same spin occurs which is absent for electrons of different spin [78]. The coulomb repulsion, however, operates also for electrons of different spin [78]. This spin polarization permits electrons of the same spin to become localized at the atoms and it disfavours spin-coupled electron pairs at the atoms. Therefore, ionic bonding schemes evolve from the UHF MO determinant with smaller weights than from an RHF MO determinant. In butadiene, α -electrons are localized at the atoms C_1 and C_3 . The β -electrons are concentrated at C_2 and C_4 . Hence, determinant 1 appears with a large weight, but the equivalent determinant 27 arises with a very small weight (see Table 3).

3.3.2 Spin occupations and bonding schemes

The UHF MO determinant for the π -electrons of butadiene contains the leading AO determinant 1 with a large weight of 0.5220 (see Table 3). It describes a covalent occupation of all four π -AOs with electrons. Their spin quantum numbers alternate along the carbon chain. Our aim is to obtain localized bonding schemes for the π -electron system of butadiene. A line in a bonding scheme or in an organic resonance structure symbolizes a bond formed by two electrons of different spin quantum numbers. Simple spin pairing shows that AO determinant 1 contributes at least to two bonding schemes. The first is the formula of butadiene with two terminal double bonds. The second describes a singlet 1,4-biradical with a central double bond. Therefore, the weight of AO determinant 1 should be partitioned into contributions for the two bonding schemes. Such a partitioning is not necessary in the expansion technique of Hiberty and Leforestier [31]. In this procedure the MO-determinant is expanded into the set of VB-functions [31]. They are linear combinations of AO determinants formed in such a way that the resulting VB function is eigenfunction to the total spin operator S^2 [82]. This property ensures that any VB function describes a definite spin-pairing scheme [83]. Thus, to determine weights for different resonance structures means obtaining weights for VB functions which are a priori different.

We expanded into the set of simple AO determinants and their weights in a MO determinant are also related to bond properties of a molecule. Maynau et al. [84] showed that a linear relationship exists between the length of a bond A—B in a polyene and the probability of finding a singlet-spin arrangement between the atoms A and B. This probability depends linearly on the probability of finding a spin alternation between A and B in the set of AO determinants [85]. This probability is the sum of squares of those coefficients in Eq. (6) which refer to covalent AO determinants with a spin alternation between A and B. Thus, the weight for AO deter-

minant 1 is determined by the number of bonds and by their properties in the above two bonding schemes. Therefore, the weight should be partitioned in a way reflecting the number and the bond strengths of the π -bonds in the two bonding schemes. The first scheme comprises the two terminal π -bonds of butadiene. The second scheme is for the 1,4-biradical with two weakly interacting radical centres and a central π -bond. Therefore, its weight should be dominated by the strength of the central π -bond. The local character of the AO determinant implies that all bonds contribute separately to the weight. These notions suggest the first condition for a weight partitioning, namely $2p + p' = 0.5220$. Here, p and p' are weight contributions for a terminal and the central π -bond, respectively. The terminal π -bond is much stronger than the central π -bond. This is indicated by their different bond lengths [80], but also by their rotational barriers which are 56.1 kcal/mol [86] and 6.9 kcal/mol [87], respectively. We suggest that a weight partitioning should be in line with the ratio of these barriers. This leads to the second condition, $p/p' = 8.1$, for the weight partitioning. By combining the two conditions, we separated the weight for AO determinant 1 into a weight for the butadiene formula and a weight for the 1,4-biradical scheme. Their values are given in the third column of Table 3. The same type of partitioning can be done for the weight of the AO determinant 27. However, this weight is very small (see Table 3). We attributed it solely to the bonding scheme with two terminal π -bonds.

3.3.3 A characteristic set of localized bonding schemes

Table 3 leads to a representation of butadiene in terms of localized bonding schemes as shown in Fig. 1. We obtained them by adding the weights of equivalent bonding schemes of Table 3. The schemes of Fig. 1 evolve from the UHF MO determinant with a total weight of about 85 %. The leading covalent bonding scheme should be supplemented by four ionic bonding schemes (see Fig. 1). The obtained set of bonding schemes accords with the resonance structures conceived

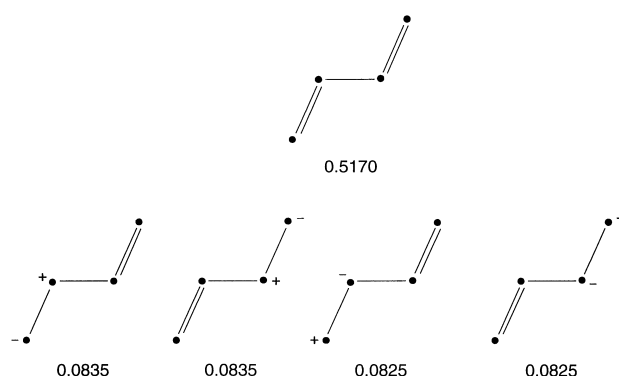


Fig. 1. Localized bonding schemes and their weights for a proper description of the π -electron system of butadiene. The bonding schemes are obtained from the singlet ground state UHF determinant with a total weight of about 85 %. They accord with the resonance structure description [88] used by organic chemists

as important for butadiene [88]. The expansion also produces AO determinants where electrons of a spin-coupled electron pair are localized at non-adjacent carbon atoms. They describe the 1,4- and 1,3-biradical character of the singlet ground state of butadiene. In Table 4, we have displayed the relevant bonding schemes and their computed weights. Above the double line bonding schemes with larger weights are recorded. Below the line equivalent schemes with significantly smaller weights are given (see Table 4). Both groups are related by spin inversion. We have added up all weights for equivalent bonding schemes of Table 4. For the 1,4 biradical, we also considered the weight in Table 3. This leads to a description of the 1,4- and 1,3-biradical

Table 4. Localized bonding schemes for the 1,4- and 1,3-diradical character of butadiene. Schemes and their weights are obtained from the UHF MO determinant for the singlet ground state. Numbers in the first column designate the position of the scheme in a weight-ordered sequence of all schemes. Schemes above the *double line* emerge with larger weights than the schemes below the *double line*. Both groups of bonding schemes are related by spin inversion

No.	Occupation	Bonding scheme	Weight
6			0.02386
7			0.02386
22			0.00109
14			0.00372
15			0.00372
16			0.00367
17			0.00367
<hr/>			
34			0.00003
35			0.00003
36			$0.18 \cdot 10^{-5}$
28			0.00015
29			0.00015
30			0.00015
31			0.00015

character as given in Fig. 2. All schemes for the 1,4- and the 1,3-biradical character appear with total weights of about 8.0 % and 1.5 % , respectively. Thus, in accord with chemical experience, the diradical character of the singlet ground state of butadiene is only small. The 1,4-diradical character is slightly more pronounced than the 1,3-diradical character. Localization procedures, based on unitary transformations of the occupied MOs, can also lead to bonding schemes compatible with the structural formula [7]. The diradical character of a closed-shell singlet ground state, however, is obscured by these localization techniques. In the expansion technique, however, it emerges naturally from the local properties of the AO determinants.

3.3.4 The π -electron delocalization in butadiene

Above, we showed that the UHF π -electron MO determinant of butadiene contains the covalent and the four ionic bonding schemes with a total weight of 85 % (see Fig. 1). In Table 5 we have represented four double ionic bonding schemes. They can be formed by shifting the electron pairs of the terminal π -bonds onto the

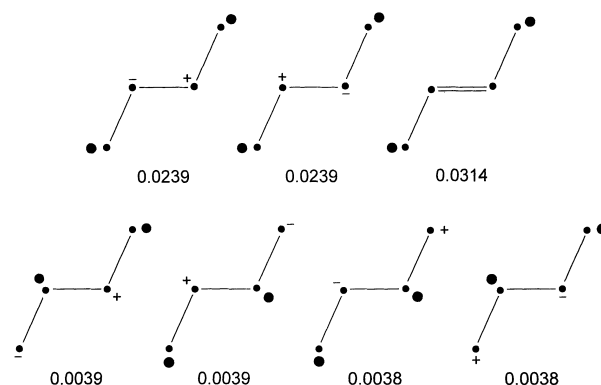


Fig. 2. Localized bonding schemes representing the 1,4- and 1,3-diradical character of butadiene. They are derived from the UHF MO determinant for the singlet ground state. Only a weak diradical character is indicated. The 1,4-diradical schemes appear with a weight of about 8.0 % whereas the 1,3-diradical schemes occur with 1.5 % . Thus, the 1,4-diradical character of butadiene should be slightly more pronounced

Table 5. Four purely ionic bonding schemes compatible with the two localized terminal π -bonds of butadiene. They evolve from the UHF MO determinant with a total weight of about 5.3%

No.	Occupation	Bonding scheme	Weight
8			0.01404
9			0.01404
10			0.01266
13			0.01237

carbon atoms of the bonds. The bonding schemes evolve from the UHF MO determinant with a total weight of about 5 percent (see Table 5). The schemes of Fig. 1 and Table 5 are compatible with two non-interacting terminal π -bonds. They are contained in the UHF MO determinant with a total weight of about 90 %. An energy increment for a bonding scheme should be proportional to its weight. Consequently, 90 % of the total π -electron energy of butadiene originates from a localization of the π -electrons into the two terminal π -bonds. By lifting the localization, the π -electrons become delocalized over the whole set of AOs. The resulting energy gain has been defined as the delocalization energy [89]. Thus, about 10 % of the π -electron energy should be delocalization energy. Our analysis is restricted to the π -electrons. Hence, a comparison with the delocalization energy obtained by the Hückel method is legitimate. This classic method leads to a total energy of 4.472β for butadiene. If the energy of two isolated ethylene molecules [89] is subtracted, we obtain the value of 0.472β for the delocalization energy [89]. This energy represents 10.6 % of the total energy of butadiene which is close to our value of 10 %. This finding supports the notion that the obtained bonding schemes and their weights are reasonable for a description of butadiene.

The first and comprehensive analysis of delocalized π -systems in terms of localized MOs has been performed by England and Ruedenberg [90]. The delocalization energy of a conjugated closed-shell π -electron molecule was defined as the difference between two quantities [91]. The first quantity is the sum over all energies of the occupied π -MOs of the molecule multiplied by 2 [91]. The second quantity is the π -MO energy of an isolated ethylene multiplied by the number of π -electrons of the molecule [91]. The sum over all energies of the occupied MOs, however, is invariant under unitary transformations leading to localized MOs [5, 6]. Thus, canonical or localized orbitals can be used for a computation of the delocalization energy [90]. The delocalization energy stabilizes a π -electron system and it should be negative. The delocalization energy is negative provided all energies of the occupied π -orbitals of the molecule are lower than the π -orbital energy of ethylene. England and Ruedenberg showed that this condition holds for the energies of the localized MOs [92]. In general, this condition is not valid for the delocalized HF-MOs [93]. Thus, localized MOs served to elucidate the stabilizing character of the delocalization. Their form also provides a rationalization for the origin of the resonance energy [90]. Localized MOs can be formed by requiring that the electrons occupying these orbitals maximize their self-repulsion energy [94]. This leads to MOs for delocalized π -electron systems which are maximally localized. However, in spite of this property, they are still more delocalized than in ethylene. Thus, the stabilizing delocalization occurs because the maximally localized π -orbitals of a conjugated π -system are still more delocalized than the π -orbital of the reference molecule ethylene [95]. This notion is illustrated by the forms of the localized occupied π -MOs of butadiene. One doubly occupied π -MO is represented in Fig. 3 [96]. It consists of two π -lobes having a positive and negative sign, respectively.

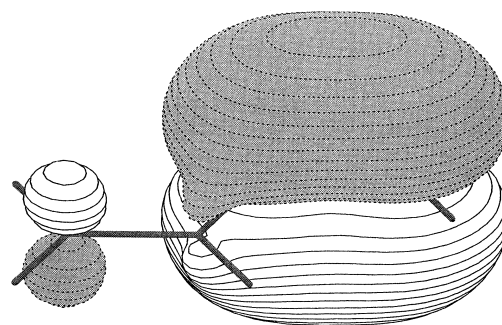


Fig. 3. Form of one localized occupied π -orbital of *trans*-butadiene. The orbital was obtained by means of the minimal STO-3G basis set. A space contour line of 0.025 is shown. The lobe, characterizing a terminal π -bond, is also partially localized in the central carbon bond region. This lobe extension illustrates the tendency of the π -electrons of a terminal π -bond to become delocalized

The positive lobe is mainly localized in the region of one terminal π -bond (see Fig. 3). However, small functional values appear also in the bond region of the central carbon bond (see Fig. 3). Thus, the two π -electrons of the terminal π -bond have also a tendency to become localized in the central bond region. This tendency induces the π -electron delocalization in butadiene. All bonding schemes of Fig. 1 locate π -electrons into the bond regions of the two terminal π -bonds. The large overall weight (85 %) shows that this type of localization dominates. The diradical bonding schemes of Fig. 2 cannot be attributed to the two terminal π -bonds. They describe the delocalization of the π -electron system. The upper three bonding schemes of Fig. 2 have the largest weights. They locate two π -electrons into the central bond region (see Fig. 2). Thus, the π -electrons of butadiene prefer the terminal π -bonds (Fig. 1) and their delocalization (Fig. 2) proceeds predominantly via the central carbon bond. These conclusions are indicated by the weights of the localized AO determinants but also by the form of the positive π -lobe of the localized MO (see Fig. 3). Therefore, the form of the localized π -MOs and the applied expansion technique explain similarly the π -electron delocalization in butadiene.

3.3.5 Comparison with other expansion work

In Sect. 3.3.1 we obtained for the π -electron system of butadiene a set of AO determinants and their weights from the UHF MO determinant. Hiberty and Ohanessian investigated butadiene by expanding the RHF MO determinant for the π -electrons into a linear independent set of VB functions [97]. These functions are normalized linear combinations of AO determinants and they are spin eigenfunctions. Thus, the expansion set differs from our set of simple AO determinants. Moreover, these authors applied a weight formula where the overlap between the non-orthogonal AO determinants is explicitly considered [97]. Our applied weight formula (Eq. 11), however, neglects the non-orthogonality (see Sect. 2.2). Hiberty and Ohanessian improved their RHF weights by considering electron correlation [62]. This increased and decreased the covalent and ionic RHF weights, respectively [62].

Table 6. Comparison of the UHF weights and the full configuration interaction (CI) weights [98] for the bonding schemes of butadiene. The UHF weights are obtained from UHF π -MO determinant computed for the singlet ground state. Numbers in the first column indicate equivalent bonding schemes whose weights were added to obtain the total weight. The inherent spin polarization of the UHF wave function leads to large weights for the covalent bonding scheme. The UHF weights reflect correctly the sequence of the exact full CI weights

No.	Bonding scheme	UHF	Full CI
1, 11, 12, 27	●=●-●=●	0.5170	0.508
2, 3, 18, 19	⊖ + ●-●=●	0.1670	0.166
4, 5, 20, 21	+ ●-⊖=●	0.1650	0.159
1, 22, 36	●-●=●-●	0.0315	0.058
6, 7, 34, 35	● + ⊖ ●	0.0478	0.032
8, 9	+ ⊖ + ⊖	0.0280	0.031
10	⊖ + + ⊖	0.0127	0.010
13	+ ⊖ ⊖ +	0.0124	0.009
24, 26	+ ●=●-⊖	0.0032	0.006

In the fourth column of Table 6, VB function weights for butadiene are recorded. They were obtained from a π -electron wave function computed by complete π -space CI [98]. In the third column our derived weights are given. We obtained them by superimposing bonding schemes of Tables 3 and 4 which resemble the VB functions of Table III in [62]. Thus, the covalent VB function is simulated by superimposing all bonding schemes which describe two terminal covalent bonds. These are the schemes 1, 11, 12 and 27 recorded in the first column of Table 6. To obtain the overall weight we added up all weights of the component bonding schemes. We performed this procedure for all nine resonance structures given in Table III of [62]. Table 6 shows that the UHF and the full CI weights almost coincide for the leading covalent bonding scheme and the important monoionic schemes of Fig. 1. This is also valid for the resonance structures with smaller weights. A deviation is found for the 1,4-diradical structures. The full π CI weights favour the purely covalent structure. Our weights, however, prefer the monoionic bonding schemes (see Table 6). Nevertheless, the overall agreement exemplified in Table 6 supports the notion that expanding an UHF MO determinant into simple AO determinants is a tool to derive bonding schemes and their weights which are chemically meaningful.

3.3.6 The expansion using an extended basis set

Above, we have expanded the UHF MO determinant for the π -electron system of butadiene into a set of AO determinants. They are composed of π -AOs represented by the minimal STO-3G basis set [58]. However, Eq. (2) and the expansion in Eq. (4) hold also for extended basis

sets. In those instances, the χ in Eqs. (2) and (4) refer to groups of Gaussians. They are determined by the contraction scheme of the primitive Gaussian basis set. In this section we expand again a symmetry-broken UHF MO determinant for the π -electrons of butadiene, but we use the extended 4-31G basis set [74]. Thus, any π -AO consists of two functions χ which refer to the inner and outer part of the π -AO. They are represented by three and one primitive Gaussian [74], respectively. The expansion produced 784 AO determinants with non-vanishing expansion coefficients. We obtained them in a weight-ordered sequence. A selection of important AO determinants and their weights is recorded in Table 7. The first 16 covalent AO determinants describe a complete spin alternation. The AO determinant 1 locates the four π -electrons exclusively into the inner parts (i) of the π -AOs. It occurs with the largest weight of all covalent AO determinants. In contrast AO determinant 16 attributes all π -electrons to the outer parts (o). It appears with the smallest weight of all covalent AO determinants. The AO determinants 7 and 8 evolve with intermediate weights. They describe a partial occupation of inner and outer parts of the π -AOs. Thus, the π -electrons have a tendency to occupy the inner parts of the π -AOs. The same principle governs also the weights of the monoionic AO determinants 17–80. Covalent and monoionic AO determinants evolve from the expansion with a total weight of 44 % and 36 %, respectively. These findings accord qualitatively with the minimal basis set weights given in Table 3. Using the extended basis set, we also obtained AO determinants which attribute all four π -electrons to only one carbon atom. The weights for those AO determinants, however, are almost zero. A vanishing of weights for unrealistic electron occupations was found previously in a similar analysis [99]. In this work the 4-31G basis was used to expand the MO determinant for 1,3-dipoles into a set of VB structures [99].

Another way of using extended basis sets for expanding MO determinants would be the employment of specific minimal valence sets. They are constructed to simulate molecular properties computed with the extended basis sets. One option is the employment of orthogonal polarized AOs [100]. They span a vector space containing the occupied MOs obtained with the extended basis set [100]. Moreover, they are designed to resemble the AOs of the free atoms [100]. Another choice is the use of orthogonal natural AOs [101]. They are formed by requiring that their occupation numbers nearly sum up to the total number of electrons [101]. Another minimal valence set are the modified AOs [102] which are orthogonal at the atoms but which are non-orthogonal when located at different atoms [102]. They are obtained by requiring that the difference between the sum of their occupation numbers and the number of electrons is minimized [102].

3.4 Localized bonding schemes for the π -electron system of the butadiene radical cation

In the butadiene radical cation three π -electrons are distributed over four π -AOs. The manifold of bonding schemes represents various localization patterns of the

Table 7. A selection of covalent and monoionic AO determinants and their weights for butadiene. They were obtained by means of the extended 4-31G basis set and the symmetry-broken UHF wave function was expanded. The expansion produced 16 covalent AO determinants. The largest weight is found for AO determinant 1 where all inner parts (i) of the π -AOs are occupied. The smallest weight is derived for the AO determinant 16 where only outer π -orbital parts are (o) occupied. A partial occupation of inner and outer parts leads to intermediate weights as for AO determinants 7 and 8. The same principles govern also the weights of all 64 monoionic AO determinants. Covalent and monoionic AO determinants appear with a total weight of 44% and 36%, respectively

No.	C_1		C_2		C_3		C_4		Weight
	i	o	i	o	i	o	i	o	
1	↑		↓		↑		↓		0.03353
•				•					•
•				•					•
•				•					•
7	↑		↓		↑		↓		0.02733
8		↑		↓		↑		↓	0.02733
•				•					•
•				•					•
•				•					•
16		↑		↓		↑		↓	0.02186
<hr/> <hr/>									
17	↑		↓		↑↓				0.00800
18			↑↓		↑		↓		0.00800
•				•					•
•				•					•
•				•					•
79		↑		↓		↑↓			0.00345
80			↑↓		↑		↓		0.00345

unpaired electron, the positive charge and the remaining two π -electrons. In the following we expand the UHF π -electron MO determinantal wave function into the set of AO determinants. Our aim is to obtain localized bonding schemes which describe the butadiene radical cation.

We optimized the geometry of the butadiene radical cation at the UHF/STO-3G level. Bond lengths of 1.4049 Å and 1.4100 Å were calculated for the terminal and the central carbon bonds, respectively. Thus, the pronounced bond-length alternation of butadiene is diminished in the butadiene radical cation. The S^2 expect-

tation value for the UHF wave function was 0.9750. Hence, the wave function describes a doublet state (0.7500) weakly contaminated by a higher quartet component. We employed a UHF MO determinant for the three π -electrons to obtain the AO determinants. Thus, the coefficients in Eq. (4) are π -MO LCAO coefficients obtained by the UHF method.

The expansion produced 24 AO determinants with non-vanishing coefficients (see Table 1). The most important AO determinants and their weights are recorded in Table 8. Numbers in the first column designate their position in the weight-ordered sequence of AO determinants. The second column displays the spin occupation as indicated by the diagonal of the corresponding AO determinant. Weights for the AO determinants are computed by means of Eq. (11) and they are given in the last column. In column three spin occupations are converted into bonding schemes. The AO determinants 3 and 6 give rise to two bonding schemes with different spin pairings. One pairing leads to a bonding scheme with a terminal, the other to a

Table 8. Relevant bonding schemes for the butadiene radical cation and their computed weights. The UHF π -MO determinant for the doublet ground state were expanded. Numbers in the first column indicate the position of the AO determinant in a weight-ordered-sequence. AO determinants 1–6 evolve with a total weight of about 83%. They are supplemented by the AO determinants below the *double line*. AO determinants above and below the *double line* are interrelated by spin inversion

No.	Occupation	Bonding scheme	Weight
1	↑ ↓ ↑	• - + - = •	0.21880
2	↑ ↓ ↑	= • - + •	0.21877
3	↑ ↓ ↑	+ • = • 0.04903 + • = • 0.04903	0.09805
4	↑ ↓ ↑	+ - + •	0.09804
5	↑ ↓ ↑	• + - +	0.09803
6	↑ ↓ ↑	= • • + 0.04901 • = • + 0.04901	0.09802
<hr/> <hr/>			
12	↑ ↑ ↓	• - = • - +	0.00825
13	↓ ↑ ↑	+ • = • •	0.00825
16	↓ ↑ ↑	= • - + •	0.00666
17	↑ ↑ ↓	• + • = •	0.00666

scheme with a central π -bond (see Table 8). Their weights were obtained by a partitioning of the weights of the corresponding AO determinants 3 and 6. In analogy to butadiene (Sect. 3.3.2), the partitioning was guided by the bond strength of the terminal and the central π -bonds. The UHF method and the STO-3G basis set produced almost equal rotational barriers of about 50 kcal/mol for the terminal and the central carbon bonds. This finding suggests that half of the weights of AO determinants 3 and 6 should be attributed to any of the corresponding bonding schemes (see Table 8). The bonding schemes above the double line in Table 8 evolve from the expansion with a total weight of about 83%. The leading schemes 1 and 2 locate the unpaired spin at one terminal carbon atom. The other terminal carbon is involved in a covalent π -bond (see Table 8). Below the double line schemes are recorded with rather small weights. They are related to the schemes above the line by spin inversion. For example, scheme 17 is derived from scheme 1 by inverting the spins in the covalent π -bond (see Table 8). In scheme 1, complete spin alternation between α - and β -spins exists. In scheme 17, however, α -spins are at C_1 and C_3 (see Table 8) and complete spin alternation is absent. Due to the concept of maximal spin alternation [103], an electron system with complete spin pairing should be energetically more favourable than a system with only partial pairing [103]. This concept led to a comprehensive rationalization of magnetic and structural properties of conjugated hydrocarbons [103]. The weights for the AO determinants 1 and 17 (see Table 8) illustrate the operation of this concept. It is further exemplified by the AO determinant pairs 2–16 and by the AO determinant pairs 3–13 and 6–12 (see Table 8).

Bonding schemes relevant for a description of the butadiene radical cation are depicted in Fig. 4. Their weights are derived from Table 8 by adding the weights of equivalent schemes above and below the double line. The butadiene radical cation should be described by eight bonding schemes (see Fig. 4). They evolve from the UHF MO determinant with a total weight of about 86%. The leading schemes locate the unpaired electron at a terminal carbon atom. The positive charge prefers

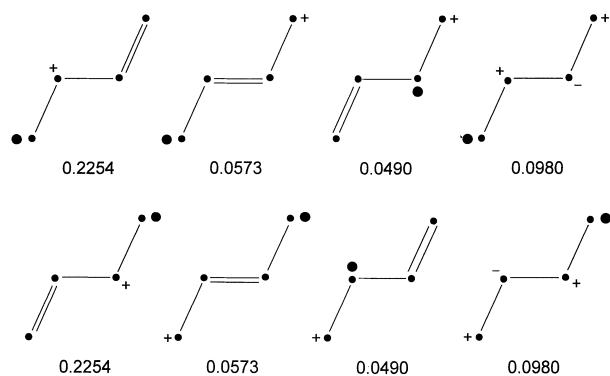


Fig. 4. Relevant bonding schemes of the butadiene radical cation and the computed weights. All bonding schemes make up a weight of about 86%. The UHF π -MO determinant for the doublet ground state was expanded. The unpaired electron prefers the terminal carbon atoms. The positive charge is delocalized in an allyl cation fashion

the adjacent or the other terminal carbon atom. Thus, stabilization of the positive charge is accomplished as in the allyl cation.

3.4.1 Localized bonding schemes

and the electrochemical coupling reaction of butadiene

In the previous section we obtained for the π -electron system of the butadiene radical cation a set of localized bonding schemes and their weights. Here, we test the relevance of our theoretical results by relating the dominant bonding schemes to the reactivity of the butadiene radical cation. Schäfer and Steckhan [104] performed electrochemical experiments with butadiene. A graphite anode was used to electrolyse a water–methanol mixture in the presence of butadiene [104]. The positively charged anode oxidized butadiene and the butadiene radical cation was produced in the vicinity of the anode [104]. The high radical cation concentration led to its dimerization, a prototype reaction known as anodic coupling [105]. The coupling yielded three isomeric dimethoxy octadienes in a current yield of about 15% [104]. The observed octadienes (a), (b) and (c) are represented in Fig. 5. The dotted lines symbolize newly formed σ carbon bonds (see Fig. 5). The observed products are consistent with the relevant bonding schemes represented in Fig. 4. New bonds are formed between the terminal carbon atoms carrying the unpaired electrons. The 2 and 6 positions of the octadiene double bonds are in accord with the schemes of Fig. 4. In addition to carbon bond formation, nucleophilic substitutions by two methoxy groups occur. The positions of attack agree with the preferred localization of the

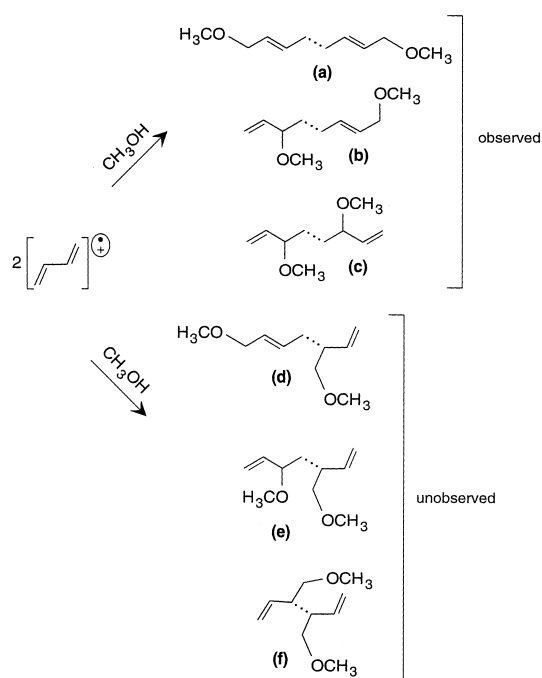


Fig. 5. The electrochemical reactions of the butadiene radical cation. Only the octadienes (a), (b) and (c) are observed. Bond formations and nucleophilic substitutions by the CH_3O group correspond to the localized bonding schemes of Fig. 4

positive charges in the bonding schemes of Fig. 4. Also of interest are the heptadienes (d), (e) and the hexadiene (f) (see Fig. 5) unobserved in the experiment. Their formation would imply that a bonding scheme has a large weight where the unpaired spin is localized at an inner carbon atom. Such schemes, however, appear in Fig. 4 only with small weights. Consequently, products (d), (e) and (f) are unfavourable also by theory. Thus, the electrochemical dimerization of the butadiene radical cation is satisfactorily rationalized by the dominant bonding schemes represented in Fig. 4.

3.5 Localized bonding schemes for the π -electron system of the acrylonitrile radical anion

The large electron affinity of acrylonitrile is attributed to the π -electron withdrawing property of the nitrile group. This molecule easily accepts an electron and the radical anion is formed. This species is a key precursor in chemical reactions leading to large-scale formation of products important for the fibre industry. In this doublet open-shell molecule, five π -electrons are distributed over four π -AOs. In the following, localized bonding schemes and their weights are obtained for the acrylonitrile radical anion.

We optimized the geometry of the acrylonitrile radical anion at UHF/3-21G level of theory. For the $\text{H}_2\text{C}=\text{CHCN}$ carbon double bond length, a value of 1.4276 Å was obtained which is rather long for a double bond. For the single carbon bond $\text{H}_2\text{CHC}-\text{CN}$ the small bond distance of 1.3785 Å was derived. The carbon nitrogen triple bond length of the nitrile group turned out to be 1.1671 Å. Thus, the double (single) bond in the acrylonitrile radical anion has a significant single (double) bond character. To obtain localized bonding schemes, we employed a doublet UHF MO determinantal wave function for the five π electrons situated in five π -MOs. This wave function was calculated at the optimized geometry, but the minimal STO-3G basis set [58] was used. This minimal basis UHF wave function led to an S^2 expectation value of 0.8323. Hence, the doublet state (0.7500) is only slightly contaminated by the quartet spin component.

In accord with Eq. (5), 24 AO determinants evolve from Eq. (4) (see Table 1). The most prominent AO determinants and their weights are recorded in Table 9. Again, entries in the first column number the position of the AO determinants in a weight-ordered sequence. Their weights are recorded in the last column. The second and third columns show the local spin occupations and the resulting bonding schemes, respectively. Any of the AO determinants 3 and 5 give rise to two bonding schemes. They differ by their location of the π -bonds. Their weights should be derived by a weight partitioning for the corresponding AO determinant. However, we considered only the bonding schemes with a strong π -bond as indicated by their computed bond distances. Thus, the weight of AO determinant 3 is solely attributed to the bonding scheme with a π bond in the CN group (see Table 9). The weight for AO determinant 5 contributes only to the weight for the bonding scheme with the $\text{CH}_2\text{CH}-\text{CN}$ carbon π -bond (see Table 9).

Bonding schemes above and below the double line are interrelated by spin inversion (see Table 9). We see, bonding schemes 1–7 evolve from the expansion with a total weight of about 78 %. Schemes 1 and 2 alone contribute about 40 % (see Table 9). Based on Table 9, we recorded in Fig. 6 three bonding schemes which evolve from the UHF MO determinant with a total weight of about 57 percent. The bonding schemes in Fig. 6 lead to several conclusions. In the acrylonitrile radical anion the unpaired electron prefers the terminal

Table 9. Localized bonding schemes and their weights for the acrylonitrile radical anion. They are obtained from the UHF π -MO determinant for the five π -electrons. The scheme numbers are the position of the scheme in a weight-ordered sequence of all schemes. Bonding schemes 1–7 evolve from the determinant with a total weight of about 78%. The schemes above and below the *double line* are related by spin inversion

No.	Occupation	Bonding scheme	Weight
1	$\uparrow \uparrow \downarrow \uparrow$ ●—●—●=NI	$\bullet - \bullet - \bullet \equiv \text{NI}$ ●—●—●=NI	0.21997
2	$\uparrow \uparrow \downarrow \uparrow \downarrow$ ●—●—●=NI	$\bullet - \bullet - \bullet + \bullet - \bullet$ ●—●—●=NI	0.196460
3	$\uparrow \downarrow \uparrow \downarrow \uparrow$ ●—●—●=NI	$\bullet - \bullet \bullet - \bullet \equiv \text{NI}$ ●—●—●=NI	0.08595
4	$\uparrow \downarrow \uparrow \downarrow \uparrow$ ●—●—●=NI	$\bullet = \bullet - \bullet - \bullet \equiv \text{NI}$ ●—●—●=NI	0.07754
5	$\uparrow \downarrow \uparrow \downarrow \uparrow$ ●—●—●=NI	$\bullet - \bullet = \bullet = \bullet - \bullet$ ●—●—●=NI	0.06925
6	$\uparrow \downarrow \uparrow \downarrow \uparrow$ ●—●—●=NI	$\bullet - \bullet \bullet + \bullet - \bullet$ ●—●—●=NI	0.06461
7	$\uparrow \uparrow \downarrow \uparrow \downarrow$ ●—●—●=NI	$\bullet - \bullet - \bullet + \bullet$ ●—●—●=NI	0.06341
<hr/>			
8	$\uparrow \uparrow \downarrow \uparrow \downarrow$ ●—●—●=NI	$\bullet - \bullet - \bullet \equiv \text{NI}$ ●—●—●=NI	0.05663
13	$\uparrow \downarrow \uparrow \downarrow \uparrow$ ●—●—●=NI	$\bullet - \bullet \bullet - \bullet \equiv \text{NI}$ ●—●—●=NI	0.01862
19	$\downarrow \uparrow \uparrow \downarrow \uparrow$ ●—●—●=NI	$\bullet = \bullet - \bullet = \bullet - \bullet$ ●—●—●=NI	0.00176
9	$\uparrow \uparrow \downarrow \uparrow \downarrow$ ●—●—●=NI	$\bullet - \bullet = \bullet = \bullet - \bullet$ ●—●—●=NI	0.03132
<hr/>			
		$\bullet - \bullet - \bullet \equiv \text{NI}$	0.2766
		$\bullet - \bullet - \bullet + \bullet = \bullet - \bullet$	0.1965
		$\bullet = \bullet - \bullet = \bullet - \bullet$	0.1006

Fig. 6. Relevant bonding schemes for a description of the acrylonitrile radical anion. They are contained in the UHF π -MO determinant with a total weight of about 57 %. Spin density is mainly localized at the terminal carbon atom. The negative charge prefers the adjacent carbon atom. A small charge delocalizing power of the nitrile group is indicated by the rightmost scheme and its small weight

carbon atom. The negative charge favours the carbon atom adjacent to the nitrile group. Thus, the nitrile group stabilizes the negative charge only to a minor extent by π -electron delocalization. Significant delocalization would imply that the first and the third bonding scheme of Fig. 6 appear with similar weights. The lack of delocalization is indicated by their different weights (see Fig. 6). The bonding schemes of Fig. 6 also provide a rationalization for the bond lengths. The terminal C—C bond is, in all three schemes, a single bond (see Fig. 6). Therefore, the $\text{H}_2\text{C}=\text{CHCN}$ carbon double bond has a significant single-bond character. In contrast, the $\text{H}_2\text{CHC}-\text{CN}$ single bond should possess a weak double-bond character (see Fig. 6). Thus, the leading bonding schemes are in accord with the computed bond lengths (see above). In the following section we show that they are also compatible with the chemical properties of the acrylonitrile radical anion.

3.5.1 Localized bonding schemes and the electrochemical coupling reaction of acrylonitrile

Adipodinitrile is an important starting material for the technical production of fibres. A classic technological process leading to adipodinitrile is the electrochemical dimerization of acrylonitrile known as hydrodimerization. The accepted mechanism [106] of this large-scale process is represented in Fig. 7. Acrylonitrile is electro-lyzed in aqueous solution at a graphite cathode. In the first step (a), an electron is transferred from the cathode to the acrylonitrile in the presence of a water molecule. This reduction leads to the acrylonitrile radical anion. The radical anion, however, reacts immediately with a

proton provided by an adjacent water molecule. The kinetically controlled step is a protonation at the nitrogen [107]. Finally, step (a) leads to the neutral 2-cyano ethyl radical which is thermodynamically more stable [107]. In the second step (b), a further electron is accepted from the cathode and the closed-shell 2-cyano ethyl carbanion is produced. In step (c) the negatively charged carbanion undergoes a nucleophilic substitution reaction with a neutral acrylonitrile molecule. This coupling reaction produces the four-membered carbon chain. In the final step (d), a protonation occurs and the adipodinitrile is formed.

Thus, the hydrodimerization is initiated by the slow step (a) followed by the fast step (b). We recognize that steps (a) and (b) are in accord with the leading localized bonding schemes for the acrylonitrile radical anion as depicted in Fig. 6. The protonation step (a) leads finally to a product where the carbon atom adjacent to the nitrile group is protonated. The leading bonding scheme locates the negative charge at this carbon atom (see Fig. 6). It indicates also that step (a) localizes the unpaired electron at the terminal carbon atom. This conclusion is in line with the fast electron transfer step (b). Here, the second electron is captured by the unpaired electron at the terminal carbon atom. A carbanion is formed where the negative charge is localized at the terminal carbon atom. Only such a carbanion can enter the nucleophilic substitution reaction of step (c) leading to the four-membered carbon chain. Thus, the accepted mechanism of the hydrodimerization of acrylonitrile is compatible with the theoretically obtained localized bonding schemes.

4 Conclusion

In this paper we suggested an effective procedure for expanding a determinantal wave function composed of delocalized MOs into a sequence of determinantal wave functions made up of AOs. A characteristic feature of the procedure is that only AO determinants appear which have the same spin multiplicity as the MO determinant. The AOs are localized at the atoms of the molecule. Therefore, the expansion technique leads to an interpretation of the MO wave function in terms of localized bonding schemes. We applied the method to obtain bonding schemes and their weights for the molecules butadiene, the butadiene radical cation and the acrylonitrile radical anion. For the doublet open-shell molecules we expanded a UHF MO determinant. However, we employed a UHF MO determinant also for the singlet ground state of butadiene. Covalent and ionic bonding schemes evolved from this wave function with large and small weights, respectively. In contrast, expanding an RHF MO determinant led to similar weights for the covalent and ionic bonding schemes [60]. Thus, the overionicity, plaguing RHF expansions, seems to be avoided by the employment of the UHF MO determinant. In all cases the predominant bonding schemes are consistent with chemical intuition or experiments. The results support the notion that relevant bonding schemes can be obtained from ab initio UHF calculations. In spite of the great impact of the MO method in the field of computational chemistry, resonance structures are still a classic theoretical device in

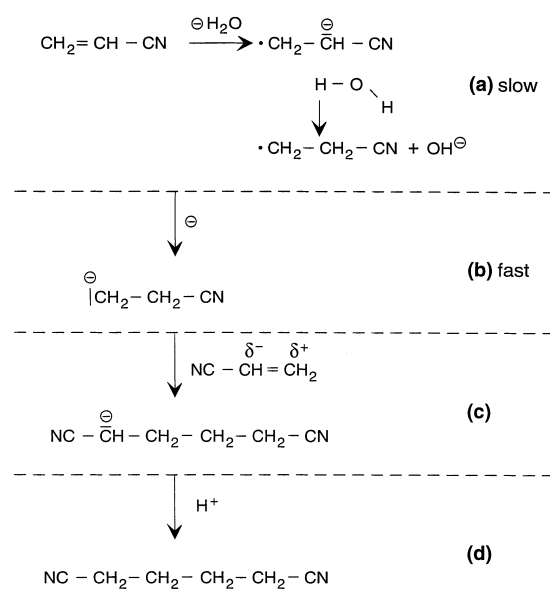


Fig. 7. Accepted mechanism for the anodic dimerization of acrylonitrile leading to adipodinitrile. Two electrons are needed in the reaction sequence. The slow rate determining process is the formation of the radical anion and the reaction with a water proton (step a). Subsequently, the fast step (b) leads to a closed-shell anion starting a nucleophilic dimerization (step c). Steps (a) and (b) are in accord with the leading localized bonding schemes of Fig. 6

organic chemistry. The suggested procedure may provide theoretical access to localized bonding schemes which are closely related to resonance structures.

Acknowledgements. The author acknowledges several discussions and helpful comments made by Drs. P. Schuchmann, A. Korkin and F. Mark. Several suggestions by Prof. v. Sonntag are gratefully appreciated. Valuable remarks and the correspondence with Prof. P. Hiberty are gratefully acknowledged.

Appendix

Equation (4) represents a theoretical device for expanding an MO determinantal wave function into a sequence

$$\Psi_{\text{UHF}} = \text{Det} \begin{pmatrix} \lambda_{1(1)}\lambda_{1(2)} & \dots & \lambda_{1(n)} \\ \vdots & & \vdots \\ \lambda_{m+1(1)}\lambda_{m+1(2)} & \dots & \lambda_{m+1(n)} \\ \bar{\lambda}'_{1(1)}\bar{\lambda}'_{1(2)} & \dots & \bar{\lambda}'_{1(n)} \\ \vdots & & \vdots \\ \bar{\lambda}'_{m(1)}\bar{\lambda}'_{m(2)} & \dots & \bar{\lambda}'_{m(n)} \end{pmatrix} = \text{Det} \begin{pmatrix} l_{11} & \dots & l_{N1} & 0 & \dots & 0 \\ \vdots & & \vdots & \vdots & & \vdots \\ l_{1m+1} & \dots & l_{Nm+1} & 0 & \dots & 0 \\ 0 & \dots & 0 & l'_{11} & \dots & l'_{N1} \\ \vdots & & \vdots & \vdots & & \vdots \\ 0 & \dots & 0 & l'_{1m} & \dots & l'_{Nm} \end{pmatrix} \begin{pmatrix} \chi_{1(1)} & \dots & \chi_{1(n)} \\ \vdots & & \vdots \\ \chi_{N(1)} & \dots & \chi_{N(n)} \\ \bar{\chi}_{1(1)} & \dots & \bar{\chi}_{1(n)} \\ \vdots & & \vdots \\ \bar{\chi}_{N(1)} & \dots & \bar{\chi}_{N(n)} \end{pmatrix} \quad (1b)$$

$L(n, 2N)$
 $\chi(2N, n)$

of AO determinants. The expansion coefficients are determinants formed from the LCAO coefficients transforming AOs into MOs. However, an infinite number of LCAO coefficient sets exists. They are all related by unitary transformations operating on the subspace of the occupied MOs. Unitary transformations leading from canonical MOs ϕ_i to localized orbitals λ_i are well known [6]. They leave the MO determinant invariant [5]. Here, we show that the expansion coefficients occurring in Eq. (4) are also left invariant.

Consider an UHF-MO determinant Ψ_{UHF} for n electrons. They are situated in $m+1$ α -spin orbitals λ_i ($i = 1, m+1$) and m β -spin orbitals λ'_j ($j = 1, m$). We assume that λ_i and λ'_j are localized MOs and we expand them into a set of N atomic orbitals χ_μ ($\mu = 1, N$).

$$\lambda'_1\lambda'_2\dots\lambda'_{m+1} = \chi_1\chi_2\dots\chi_N \begin{pmatrix} l_{11} & \dots & l_{1m+1} \\ l_{21} & \dots & l_{2m+1} \\ \vdots & & \vdots \\ l_{N1} & \dots & l_{Nm+1} \end{pmatrix}, \quad (1a)$$

The LCAO coefficients $l_{\mu i}$ and $l'_{\mu j}$ transform the AOs χ_μ into the localized α - and β -MOs, respectively. By interchanging rows and columns, we can bring Ψ_{UHF} into half-determinant form [46]. Using Eq. (1), we write Ψ_{UHF} in the form

The rectangular matrix L comprises n rows and $2N$ columns. Correspondingly, matrix χ consists of $2N$ rows and n columns. We can apply the Binet-Cauchy theorem [44] to expand Ψ_{UHF}

$$\Psi_{\text{UHF}} = \sum_{1 \leq k_1 < k_2 < \dots < k_n \leq 2N} \text{Det} \begin{pmatrix} L_{1k_1} & L_{1k_2} & \dots & L_{1k_n} \\ \vdots & \vdots & & \vdots \\ L_{nk_1} & L_{nk_2} & \dots & L_{nk_n} \end{pmatrix} \cdot \text{Det} \begin{pmatrix} \chi_{k_1(1)} & \chi_{k_1(2)} & \dots & \chi_{k_1(n)} \\ \chi_{k_2(1)} & \chi_{k_2(2)} & \dots & \chi_{k_2(n)} \\ \vdots & \vdots & & \vdots \\ \chi_{k_n(1)} & \chi_{k_n(2)} & \dots & \chi_{k_n(n)} \end{pmatrix} \quad (3)$$

L_i
 χ_i

Any coefficient L_i is a determinant formed from a quadratic (n,n) -matrix being a definite column selection of the rectangular matrix L (see Eq. (2)). Any AO determinant χ_i is a row selection of the rectangular

matrix χ (see Eq. (2)). We can obtain localized α -MOs λ_i from the UHF MOs by a unitary transformation which linearly combines the occupied canonical α -MOs ϕ_i ($i = 1, m+1$). An equivalent transformation can be applied for the localized β -MOs λ'_j ($j = 1, m$). These transformations, combined with the LCAO expansions for the canonical MOs ϕ_i and ϕ'_j , determine the LCAO coefficients for the localized MOs λ_i and λ'_j

$$\underbrace{\begin{pmatrix} l_{11} & \dots & l_{1m+1} \\ l_{21} & \dots & l_{2m+1} \\ \vdots & & \vdots \\ l_{N1} & \dots & l_{Nm+1} \end{pmatrix}}_{l(N, m+1)} = \underbrace{\begin{pmatrix} c_{11} & \dots & c_{1m+1} \\ c_{21} & \dots & c_{2m+1} \\ \vdots & & \vdots \\ c_{N1} & \dots & c_{Nm+1} \end{pmatrix}}_{c(N, m+1)} \underbrace{\begin{pmatrix} u_{11} & \dots & u_{1m+1} \\ \vdots & & \vdots \\ u_{m+11} & \dots & u_{m+1m+1} \end{pmatrix}}_{u(m+1, m+1)}, \quad (4a)$$

$$\underbrace{\begin{pmatrix} l'_{11} & \dots & l'_{1m} \\ l'_{21} & \dots & l'_{2m} \\ \vdots & & \vdots \\ l'_{N1} & \dots & l'_{Nm} \end{pmatrix}}_{l'(N, m)} = \underbrace{\begin{pmatrix} c'_{11} & \dots & c'_{1m} \\ c'_{21} & \dots & c'_{2m} \\ \vdots & & \vdots \\ c'_{N1} & \dots & c'_{Nm} \end{pmatrix}}_{c'(N, m)} \underbrace{\begin{pmatrix} u'_{11} & \dots & u'_{1m} \\ \vdots & & \vdots \\ u'_{m1} & \dots & u'_{mm} \end{pmatrix}}_{u'(m, m)}. \quad (4b)$$

Here, the rectangular matrices c and c' contain the canonical LCAO coefficients for the occupied α - and β -MOs, respectively. The transposed matrices l^t and l'^t occur in the matrix L of Eq. (2). By using Eq. (4a) and Eq. (4b), we can write for L

$$L(n, 2N) = \begin{pmatrix} l^t & 0 \\ 0 & l'^t \end{pmatrix} = \underbrace{\begin{pmatrix} u^t & 0 \\ 0 & u'^t \end{pmatrix}}_{U(n, n)} \underbrace{\begin{pmatrix} c^t & 0 \\ 0 & c'^t \end{pmatrix}}_{C(n, 2N)}. \quad (5)$$

All matrices in Eq. (5) have a characteristic block form. The numbers of rows and columns are indicated below the matrices. Any determinant L_i , representing the expansion coefficient in Eq. (3), is a definite column selection of the rectangular matrix $L(n, 2N)$. Using Eq. (5), we write for L_i

$$L_i = \text{Det} \begin{pmatrix} u^t & 0 \\ 0 & u'^t \end{pmatrix} \cdot \text{Det} \begin{pmatrix} c_{1k_1} & c_{1k_2} & \dots & c_{1k_n} \\ \vdots & \vdots & & \vdots \\ c_{nk_1} & c_{nk_2} & \dots & c_{nk_n} \end{pmatrix}. \quad (6)$$

$U(n, n) \qquad C(n, n)$

Here, the quadratic matrix $C(n, n)$ is an ordered column selection from the rectangular matrix $C(n, 2N)$ of Eq. (5). It contains the canonical LCAO coefficients of the occupied α - and β -MOs. The submatrices u and u' in Eq. (6) are unitary. This property and the block form in Eq. (6) imply that the first determinant at the right-hand side of Eq. (6) is $+1$ and -1 . Hence, we can write

$$L_i = f \text{Det } C(n, n) \quad f = 1 \text{ or } -1. \quad (7)$$

Thus, unitary transformations, relating localized and canonical MOs, do not affect the expansion coefficients L_i . They are solely determined by the LCAO coefficients for the canonical MOs. Therefore, expanding an MO determinant into a sequence of AO determinants is unique.

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