TURTLE – A gradient VBSCF Program
Theory and Studies of Aromaticity

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The *Ab Initio* Valence Bond program TURTLE has been under development for about 12 years and is now becoming useful for the non-specialist computational chemist as is exemplified by its incorporation in the GAMESS-UK program. We describe here the principles of the matrix evaluation and orbital optimisation algorithms and the extensions required to use the Valence Bond wavefunctions in analytical (nuclear) gradient calculations. For the applications, the emphasis is on the selective use of restrictions on the orbitals in the Valence Bond wavefunctions, to investigate chemical concepts, in particular resonance in aromatic systems.

1. INTRODUCTION

Valence Bond theory has always struck a sympathetic chord in chemist's minds, because it can be linked so closely to the familiar Lewis structure. A bond is immediately translated in the wavefunction by two non-orthogonal orbitals on neighbouring atoms that are singlet coupled. An ionic structure may contain an atomic orbital, that is occupied twice, or alternatively two orbitals on the same atom. So it is simply possible to translate the assumed concept of the bonding in a molecule into a (small) set of structures. Alternatively, if the nature of the bonding is in question, the relative importance of the different structures may give insight. Vital for an unbiased wavefunction is the ability to optimise the wavefunction, both its orbitals and its structure coefficients. An efficient way to perform such an optimisation is implemented in the spin-coupled program and in its later incarnation the CASVB method [1,2]. These methods usually consider all spin-couplings and often a single set of singly occupied optimised orbitals.

In the development of the TURTLE program [3], we started by considering a multi-structure Valence Bond wavefunction and added the capability to optimise the orbitals. We tried to avoid putting restrictions on the way the wavefunction is built and to allow great flexibility in the choice of orbitals. For

instance if covalent and ionic structures are employed, the orbitals used in these structures may be identical, which just mimics the effect of orbital optimisations. Also all orbitals in an ionic structure, both doubly and singly occupied ones, may be chosen to be different from those in the covalent structure. This yields a very compact and accurate wavefunction (the Breathing Orbital Valence Bond method) [4,5] at the cost of a troublesome orbital optimisation, due to the near identity of the orbital spaces. The orbitals used may be fully optimised as in the spin-coupled approach, but they may also be restricted to a subspace of the full orbital space, e.g. just the one atom. This enhances the interpretability of the wavefunction considerably. Recently we added gradient capabilities to the program and integrated it into the GAMESS-UK [6] program.

We will describe the main features of our program and give examples of the use of the code for studying the aromaticity in various molecules.

2. WAVEFUNCTION OPTIMISATION

Our wavefunction is build as a linear combination of structures

$$\Phi = \sum_i C_i \Phi_i \tag{1}$$

Each structure is a spin-adapted linear combination of determinants. Both Rumer diagrams and Branching Diagrams may be chosen. If required, even individual determinants may be employed as building blocks. The coefficients in Eq. (1) are usually determined by solving the corresponding generalised eigenvalue problem

$$(\mathbf{H} - E\mathbf{S})\mathbf{C} = \mathbf{0} \tag{2}$$

Alternatively, they may be fixed from the outset. To the structures, weights can be attributed, which add up to one, using a formula given by Chirgwin and Coulson [7].

$$W_j = \sum_i c_i c_j S_{ij} \tag{3}$$

2.1 Orbital Optimisation

The orbital optimisation is based on the Generalised Brillouin Theorem [8] as extended to non-orthogonal wavefunctions [9,10]:

$$\langle \Phi_0 | H - E_0 | \Phi_{ij} \rangle = 0 \tag{4}$$

where Φ_{ij} is the singly excited state, a Brillouin state, obtained by applying the unnormalised excitation operator $C_{i\to j}$ to the wavefunction:

$$\Phi_{ij} = C_{i\to j}\Phi_0 \tag{5}$$

The excitation operator does not have to adhere to the unitary condition, as is the case for orthogonal orbitals. Each Brillouin matrix element (Eq. (4)) represents the stationary condition for the mixing of orbitals ϕ_i and ϕ_j according to $\phi_i \to \phi_i + \partial\phi_j$. The wavefunction consisting of Φ_0 and all singly excited states

$$\Phi = b_0\Phi_0 + \sum_{i,j} b_{ij}\Phi_{ij} \tag{6}$$

is obtained by solving the corresponding generalised eigenvalue problem, the Brillouin state interaction problem. One can employ the coefficients b_{ij} to determine improved orbitals according to

$$\phi_i \to \phi_i + b_{ij}\phi_j \tag{7}$$

For orthogonal orbitals this procedure is often called the SuperCI method.

When the new orbitals are determined, the Valence Bond function is re-determined using Eq. (2), and the procedure is repeated until convergence is obtained, i.e. all b_{ij}'s in Eq. (6) are zero and the Generalised Brillouin theorem (Eq. (4)) is satisfied.

The usual convergence acceleration/stabilisation tools may be employed in this orbital optimisation. For instance, we have implemented level shifting and DIIS [11].

The SuperCI itself is usually quite stable, but involves solving a non-orthogonal CI of a considerable dimension, with each Brillouin state containing the same number of determinants as the Valence Bond wavefunction, which is rather time consuming. The SuperCI matrix can be approximated by its first row (the Brillouin theorem elements) and the diagonal at a considerable time saving. Then the Brillouin state coefficients b_{ij} are estimated following

$$b_{ij} = -\frac{\langle \Phi_0 | H - E_0 | \Phi_{ij} \rangle}{\langle \Phi_{ij} | H - E_0 | \Phi_{ij} \rangle} \tag{8}$$

which is the non-orthogonal equivalent of the first-order Raleigh-Schrödinger perturbation expression [12]. This approach produces, for not so complicated wavefunctions, acceptable convergence behaviour, especially when convergence aids like DIIS are invoked.

3. EXPRESSIONS FOR THE ENERGY AND ITS DERIVATIVES [13-15]

The wavefunction consists of a linear combination of structures, which themselves are spin-adapted linear combinations of determinants:

$$\Psi = \sum_p C_p \Phi_p \tag{9}$$

According to Löwdin [16] the interaction between two determinants Φ_p and Φ_q is:

$$\langle \Phi_p | \hat{H} | \Phi_q \rangle = \sum_{ik} h_{ik} \mathbf{S}^{(i,k)} + \sum_{i<j,k<l} \{ \langle ij|kl\rangle - \langle ij|lk\rangle \} \mathbf{S}^{(i,j,k,l)} \tag{10}$$

The overlap is obtained by expanding along an arbitrary column (k):

$$\langle \Phi_p | \Phi_q \rangle = |\mathbf{S}| = \sum_i S_{ik} S^{(i,k)} \tag{11}$$

In these equations h_{ik} and S_{ik} are the one-electron matrix elements for orbital i and k $\langle \phi_i(1)|h(1)|\phi_k(1)\rangle$ and $\langle \phi_i(1)|\phi_k(1)\rangle$. The $<ij|kl>$ are the two-electron integrals $\langle \phi_i(1)\phi_j(2)|1/r_{12}|\phi_k(1)\phi_l(2)\rangle$. $\mathbf{S}_{ab}^{(i,k)}$ and $\mathbf{S}_{ab}^{(i,j,k,l)}$ are the first and second order cofactors of the overlap matrix, which are signed minors of it. The orbitals in Eqs. (10) and (11) are the orbitals occupied in the determinants Φ_p and Φ_q. So the indices i and j refer to the occupied orbitals in Φ_p, and the indices k and l to occupied orbitals in Φ_q. **S** is the overlap matrix between the occupied orbitals of Φ_p and Φ_q. More about cofactors and adjugates can be found in for example a book by Aitken [17]. The approach used to obtain the various cofactors will be discussed in the next paragraph.

Assuming a normalised wavefunction, we can now write the energy as

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_p \sum_q C_p C_q \left[\sum_{ik} h_{ik} \mathbf{S}_{pq}^{(i,k)} + \sum_{i<j,k<l} \{ \langle ij|kl\rangle - \langle ij|lk\rangle \} \mathbf{S}_{pq}^{(i,j,k,l)} \right] \tag{12}$$

By rearranging the summations and realising that $S_{pq}^{(i,k)}$ and $S_{pq}^{(i,j,k,l)}$ are sub-determinants of the determinant representing the overlap between Φ_p and Φ_q and that they are zero if the orbitals i,j and k,l do not appear in the respective determinants, we obtain

$$
\begin{aligned}
E &= \left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle \\
&= \left[\sum_{ik} h_{ik} \sum_p \sum_q \mathbf{S}_{pq}^{(i,k)} C_p C_q + \sum_{i<j,k<l} \left\{ \langle ij|kl\rangle - \langle ij|lk\rangle \right\} \sum_p \sum_q \mathbf{S}_{pq}^{(i,j,k,l)} C_p C_q \right]
\end{aligned}
\tag{13}
$$

or

$$
E = \langle \Phi | H | \Phi \rangle = \left[\sum_{ik} h_{ik} d_{ik} + \sum_{i<j,k<l} \left\{ \langle ij|kl\rangle - \langle ij|lk\rangle \right\} D_{ijkl} \right]
\tag{14}
$$

with the one and two electron reduced density matrices

$$
\begin{aligned}
d_{ik} &= \sum_p \sum_q \mathbf{S}_{pq}^{(i,k)} C_p C_q \\
D_{ijkl} &= \sum_p \sum_q \mathbf{S}_{pq}^{(i,j,k,l)} C_p C_q
\end{aligned}
\tag{15}
$$

This is of course the familiar expression from orthogonal MO theories. The complexity due to the non-orthogonality is now hidden in the cofactors in the reduced density matrices.

3.1 Hellmann-Feynman theorem

For exact wavefunctions, the Hellmann-Feynman [18,19] theorem states that the derivative of the energy with respect to a nuclear co-ordinate x equals the expectation value of the derivative of the Hamiltonian.

$$
\frac{dE}{dx} = \left\langle \Phi \left| \frac{\partial \hat{H}}{\partial x} \right| \Phi \right\rangle
\tag{16}
$$

When the wavefunction is expanded, using expansion parameters c, this theorem still holds if $\partial E/\partial c=0$, or when $\partial c/\partial x=0$. The first is the case for completely optimised wavefunctions and the second for wavefunctions where some, or all, of the coefficients are frozen. This can be seen when we write the derivative of E with respect to x as a sum of two terms:

$$\frac{dE(x)}{dx} = \frac{\partial E(x;c)}{\partial x} + \frac{\partial E(x;c)}{\partial c}\frac{\partial c}{\partial x} \tag{17}$$

The first term contains the direct dependence on x, the second the dependence on x through c. When $\partial E/\partial c=0$ (optimised), or $\partial c/\partial x=0$ (frozen coefficients) the second part disappears:

$$\frac{dE(x)}{dx} = \frac{\partial E(x;c)}{\partial x} \tag{18}$$

Therefore, the dependence on the coefficients does not enter the gradient expression; not for fixed orbitals, which is the classical Valence Bond approach and not for optimised orbitals, irrespective of whether they are completely optimised or if they are restricted to extend only over the atomic orbitals of one atom. If the wavefunction used in the orbital optimisation differs, additional work is required. This would apply to a multi-reference singles and doubles VB (cf. [20,21]). Then we would require a yet unimplemented coupled-VBSCF procedure. Note that the option to fix the orbitals is not available in orthogonal (MO) methods, due to the orthonormality restriction.

3.2 Gradient expression

The only restriction for the gradient evaluation is that the wavefunction has to be normalised, i.e.

$$\langle \Phi | \Phi \rangle = 1 \quad or \quad \left[\langle \Phi | \Phi \rangle - 1 = 0 \right] \tag{19}$$

To take this restriction into account, the Lagrange multiplier formalism is employed. We devise a Lagrangian by adding the restriction multiplied by a Lagrange multiplier λ.

$$L = E - \lambda [S - 1] = \left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle - \lambda \left[\langle \Phi | \Phi \rangle - 1 \right] \tag{20}$$

The Lagrange multiplier λ is determined by requiring that the derivatives of the Lagrangian with respect to all optimised variables like the structure coefficients C_k are zero:

$$\frac{\partial L}{\partial C_k} = \frac{\partial}{\partial C_k} \left[\sum_{ij} C_i C_j H_{ij} - \lambda \left[\sum_{ij} C_i C_j S_{ij} - 1 \right] \right] = 2 \sum_i C_i \left\{ H_{ik} - \lambda S_{ik} \right\} = 0 \tag{21}$$

This is clearly equivalent to the secular equations

$$\sum_i C_i \left\{ H_{ik} - E S_{ik} \right\} = 0 \tag{22}$$

Thus λ equals the energy E. Similarly one can derive the expression involving the orbital coefficients, which involves the generalised Brillouin theorem (Eq. (4)) which again yields $\lambda = \lambda$.

The required energy derivative is

$$\frac{\partial E}{\partial x} = \frac{\partial L}{\partial x} = \frac{\partial}{\partial x} \left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle - E \frac{\partial}{\partial x} \langle \Phi | \Phi \rangle \tag{23}$$

Another way to see that E is the required Lagrange multiplier is by taking the derivative of the energy expression for an unnormalised wavefunction:

$$\frac{\partial}{\partial x} \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\langle \Phi | \Phi \rangle \frac{\partial}{\partial x} \langle \Phi | \hat{H} | \Phi \rangle - \langle \Phi | \hat{H} | \Phi \rangle \frac{\partial}{\partial x} \langle \Phi | \Phi \rangle}{\langle \Phi | \Phi \rangle^2} \tag{24}$$

Now add normalisation of Φ so that $\langle \Phi | \Phi \rangle = 1$, and use:

$$E = \langle \Phi | \hat{H} | \Phi \rangle \tag{25}$$

and obtain:

$$\frac{\partial E}{\partial x} = \frac{\partial}{\partial x} \left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle - E \frac{\partial}{\partial x} \langle \Phi | \Phi \rangle \tag{26}$$

Eq. (26) gives the final expression for the derivative of the energy. The derivatives of the energy (Eq. (14)) and the norm of the wavefunction have to be evaluated, using partial differentiation, since both one- and two-electron integrals and the density matrices (through the cofactors) may change with the geometry:

$$\begin{aligned} \frac{\partial \langle \Phi | H | \Phi \rangle}{\partial x} = & \left[\sum_{ik} \frac{\partial h_{ik}}{\partial x} . d_{ik} + \sum_{i<j,k<l} \left[\frac{\partial \langle ij | kl \rangle}{\partial x} - \frac{\partial \langle ij | lk \rangle}{\partial x} \right] D_{ijkl} \right] \\ & + \left[\sum_{ik} h_{ik} \frac{\partial d_{ik}}{\partial x} + \sum_{i<j,k<l} \left\{ \langle ij | kl \rangle - \langle ij | lk \rangle \right\} \frac{\partial}{\partial x} D_{ijkl} \right] \end{aligned} \tag{27}$$

This equation has two parts. The first part contains derivatives of the one and two electron integrals. These are supplied by any standard gradient package and also appear in gradient expressions for orthogonal MO methods. The other part contains the derivatives of the density matrices, more specifically the derivatives of the first and second order cofactors. These are absent in the orthogonal methods by virtue of the fact that all cofactors are either 1 or 0. The orthonormality of the wavefunction is handled by the orthonormality restrictions, which in their turn give rise to Lagrange multipliers. We will gather all terms involving derivatives of the overlap in the derivatives expression into a matrix **L**, which can take the place of the Lagrange multiplier matrix of MO based gradient packages.

3.3 Density matrices and Cofactors

As a cofactor is itself a determinant, we may just consider the determinant of an overlap matrix. A determinant can be expressed as a sum of products of its matrix elements. The derivative of a product of matrix elements is obtained by taking the derivative of one matrix element and multiplying this by the product of the other matrix elements. This has to be done for all the matrix elements in the product, and the results have to be added. Another way to look at a determinant is by expanding it in its first order cofactors (cf. Eq. (11)) :

$$|\mathbf{S}| = \sum_{i}^{N} s_{ik} S^{(i,k)} \tag{28}$$

Now the determinant is a linear combination of matrix elements of a row (or column) times the corresponding cofactors. The weight of a certain matrix element in the determinant is given by its first order cofactor. The derivative must be the sum of the derivatives of the matrix elements times their cofactors, like shown in the next equation:

$$\frac{d|\mathbf{S}|}{dx} = \sum_{rs} \frac{ds_{rs}}{dx} \mathbf{S}^{(r,s)} \tag{29}$$

Because cofactors are sub-determinants, one can immediately write down their derivatives. The first order cofactors of first order cofactors are second order cofactors, and first order cofactors of second order cofactors introduce third order cofactors.

$$\frac{d\mathbf{S}^{(i,k)}}{dx} = (sign)\sum_{rs} \frac{dS_{rs}}{dx}\mathbf{S}^{(i,r,k,s)}$$
$$\frac{d\mathbf{S}^{(i,j,k,l)}}{dx} = (sign)\sum_{rs} \frac{dS_{pq}}{dx}\mathbf{S}^{(i,j,r,k,l,s)} \tag{30}$$

In these equations there is also a sign involved, which depends on the relative positions of the original indices i,j,k and l with respect to r and s. The first indices refer to the original overlap matrix, while r and s should refer to the matrix where row i (and j) and column k (and l) have been removed. To keep the equations simple we will omit this sign in our equations†.

Thus the derivatives of the density matrix elements are

$$\frac{\partial d_{ik}}{\partial x} = \sum_{rs} \frac{ds_{rs}}{dx}\sum_{p}\sum_{q} \mathbf{S}_{pq}^{(i,r,k,s)} C_p C_q = \sum_{rs} \frac{ds_{rs}}{dx} d_{irks}$$
$$\frac{\partial D_{ijkl}}{\partial x} = \sum_{rs} \frac{ds_{rs}}{dx}\sum_{p}\sum_{q} \mathbf{S}^{(i,j,r,k,l,s)} C_p C_q = \sum_{rs} \frac{ds_{rs}}{dx} d_{ijrkls} \tag{31}$$

Thus, we now need also a third order reduced density matrix, which involves the corresponding third order cofactors.

Eq. (28) can now be used to derive the expression for the derivative of the norm of the wavefunction, which is also required in Eq. (26).

$$\frac{\partial\langle\Phi|\Phi\rangle}{\partial x} = \sum_{p}\sum_{q} C_p C_q \frac{d|\mathbf{S}_{pq}|}{dx} = \sum_{rs} \frac{ds_{rs}}{dx}\sum_{p}\sum_{q} C_p C_q \mathbf{S}_{pq}^{(r,s)} = \sum_{rs} \frac{ds_{rs}}{dx} d_{rs} \tag{32}$$

Combining Eqs. (27), (31) and (32) the final expression for the derivative of the energy with respect to say a geometrical parameter is

$$\frac{\partial\langle\Phi|H|\Phi\rangle}{\partial x} = \left[\sum_{ik} \frac{\partial h_{ik}}{\partial x}.d_{ik} + \sum_{i<j,k<l}\left[\frac{\partial\langle ij|kl\rangle}{\partial x} - \frac{\partial\langle ij|lk\rangle}{\partial x}\right]D_{ijkl}\right] - \sum_{ik} \frac{\partial s_{ik}}{\partial x}.L_{ik} \tag{33}$$

---

† The sign depends on the relative position of the rows and the columns, which are removed. For instance, if $r<i$, the sign is unchanged when removing r, but if r lies beyond i the sign should reflect, that r actually should be moved 1 place back and therefore a -1 is produced cf. [22].

with

$$L_{ik} = E_0 . d_{ik} - \sum_{rs} h_{rs} d_{risk} - \sum_{r<j,s<l} \left\{ \langle rj|sl\rangle - \langle rj|ls\rangle \right\} D_{rjislk} \tag{34}$$

This expression is very similar to those in the normal orthogonal case. We may therefore use any general gradient package. Our VB program generates the density matrices and the matrix **L**, which is used instead of the Lagrange multiplier matrix of for instance a MCSCF function.

3.4 Cofactors [23,24]

For the calculation of cofactors we use algorithms based on work by Löwdin [16], and Prosser and Hagstrom [25,26]. An overview of the theory of determinants, cofactors, adjugates and compound matrices can be found in a book by Aitken [17]. The symmetry and possible orthogonality in the orbital spaces give rise to a block-structure in the overlap matrices. This structure is exploited [22,27] to minimise the size of the matrices in the **L-d-R** decomposition, described below, an n^3 process for each matrix.

The calculation of the first order cofactors is simplified by performing an **L-d-R** decomposition of the overlap matrix. **L** and **R** are lower and upper diagonal matrices respectively. They have ones on the diagonal and therefore their determinant is one as well. **L** and **R** are chosen in such a way, that when **S** is pre-multiplied by **L** and post-multiplied by **R** the result is a diagonal matrix **d**.

$$\mathbf{d} = \mathbf{L} \cdot \mathbf{S} \cdot \mathbf{R}$$

$$|\mathbf{L}| = |\mathbf{R}| = 1 \tag{35}$$

$$\mathbf{S} = \mathbf{L}^{-1} \cdot \mathbf{d} \cdot \mathbf{R}^{-1}$$

Because the determinants of **L** and **R** are one, the determinant of **S** equals the determinant of **d**.

$$|\mathbf{S}| = |\mathbf{d}| = \prod_{i=1}^{N} d_{ii} \tag{36}$$

Now the adjugate matrix of **S**, which contains the first order cofactors can be calculated using [17] and Eq. (38)

$$adj(\mathbf{S}) = adj(\mathbf{L}^{-1} \cdot \mathbf{d} \cdot \mathbf{R}^{-1}) = adj(\mathbf{R}^{-1}) \cdot adj(\mathbf{d}) \cdot adj(\mathbf{L}^{-1}) = \mathbf{R} \cdot adj(\mathbf{d}) \cdot \mathbf{L} \tag{37}$$

The nullity of the overlap-matrix **S**, is its dimension minus its rank, so the nullity of **S** corresponds to the number of zero diagonal elements in **d**. Nullity above 0, implies a singular **S**-matrix. The algorithm depends on the nullity.

3.4.1 Nullity 0

Using the fact that the inverse of a diagonal matrix is a diagonal matrix with inverse elements, and that the adjugate of a matrix is directly related to its inverse

$$adj(d) = |d|.d^{-1} \tag{38}$$

the complete first order cofactor matrix can be calculated using Eq. (37) at a cost of $\sim n^3$ operations per overlap matrix, where n is the number of electrons. For the higher order cofactors we use the Jacobi ratio theorem to express higher order adjugates in terms of the compound matrices of the first order adjugate

$$adj^{(k)}(\mathbf{A}) = |\mathbf{A}|^{1-k}\left(adj(\mathbf{A})\right)^{(k)} \tag{39}$$

The kth order compound matrix $B^{(k)}$ is a matrix with the kth order minors (k^{th} order sub-determinants) as elements. So the kth order adjugate can be expressed in terms of the kth order compound matrix of the first order adjugate.

The 2nd order cofactors cost 2 multiplications each, at a total cost of $2.n^4$, no more than the cost of multiplying them by the two-electron integrals. Similarly, 3rd order cofactors take $6.n^6$ in total.

3.4.2 Nullity 1

Now the first order adjugate of the matrix **d** contains only 1 nonzero element, simplifying the application of Eq. (37). The Jacobi ratio theorem cannot be used straightaway for the higher order cofactors, when the overlap matrix is singular, since its determinant is zero. However, we can make use of the fact that determinants and thus cofactors, which are sub-determinants, are linear in their elements. If we change a matrix element of **S** as [13,28]

$$S_{pq}(t) = S_{pq} + t \tag{40}$$

then the determinant of **S** changes as:

$$|\mathbf{S}(t)| = |\mathbf{S}| + t\mathbf{S}^{(p,q)} \tag{41}$$

The changes in the cofactors are similar.

$$
\begin{aligned}
\mathbf{S}(t)^{(i,l)} &= \mathbf{S}^{(i,l)} + (sign)t\mathbf{S}^{(i,p,l,q)} \\
\mathbf{S}(t)^{(i,j,l,m)} &= \mathbf{S}^{(i,j,l,m)} + (sign)t\mathbf{S}^{(i,j,p,l,m,q)} \\
\mathbf{S}(t)^{(i,j,k,l,m,n)} &= \mathbf{S}^{(i,j,k,l,m,n)} + (sign)t\mathbf{S}^{(i,j,k,p,l,m,n,q)} \\
&\ldots
\end{aligned}
\tag{42}
$$

This procedure can be used to eliminate the singularities by changing the zero (diagonal) element of **d** after an **L-d-R** decomposition. The sign in these equations depends, like in the derivation of the derivatives of cofactors, on the ordering of p and q with respect to i,j,k,l,m and n. However, in a standard **L-d-R** decomposition the singularity is moved to the last position of **d** and the sign is just plus.

To obtain the nth order cofactors for a singular matrix, with nullity 1 we have to interpolate between two values of t, i.e. t= +1 and t= -1. The nth order cofactors of $\mathbf{S}(t)$ for t=1 and t=-1 are added to obtain the nth order cofactors of **S**

$$
adj^{(n)}(\mathbf{S}) = \frac{1}{2}\left(adj^{(n)}(\mathbf{S}(1)) + adj^{(n)}(\mathbf{S}(-1))\right) \tag{43}
$$

3.4.3 Nullity 2

When the nullity equals 2, all first order cofactors are eliminated. For the higher order adjugate matrices, two parameters have to be introduced and we need four points to interpolate and obtain

$$
adj^{(n)}(\mathbf{S}) = \frac{1}{4}\begin{bmatrix} adj^{(n)}(\mathbf{S}(1,1)) + adj^{(n)}(\mathbf{S}(1,-1)) \\ +adj^{(n)}(\mathbf{S}(-1,1)) + adj^{(n)}(\mathbf{S}(-1,-1)) \end{bmatrix} \tag{44}
$$

3.4.4 Nullity k

When the nullity is k there are also k parameters. The interpolated expression for the adjugate has now 2^k terms and we have to evaluate determinants of order n, where n is the order of the adjugates we require. When $n<k$ all cofactors are zero.

A special case is when k equals n, i.e. the nullity equals the order of the adjugates. Then one can extend an algorithm by Prosser and Hagstrom [25,26].

Writing **S** as $\mathbf{L}^{-1}\cdot\mathbf{d}\cdot\mathbf{R}^{-1}$ the adjugate of **S** is

$$
\begin{aligned}
adj^{(n)}(\mathbf{S}) &= adj^{(n)}\left(\mathbf{L}^{-1}\cdot\mathbf{d}\cdot\mathbf{R}^{-1}\right) \\
&= adj^{(n)}\left(\mathbf{R}^{-1}\right)\cdot adj^{(n)}(\mathbf{d})\cdot adj^{(n)}\left(\mathbf{L}^{-1}\right)
\end{aligned}
\tag{45}
$$

The determinants of **L** and **R** are one, and we can introduce the nth order compound matrices of **R** and **L**.

$$adj^{(n)}\left(\mathbf{R}^{-1}\right)\cdot adj^{(n)}(\mathbf{d})\cdot adj^{(n)}\left(\mathbf{L}^{-1}\right)=\mathbf{R}^{(n)}\cdot adj^{(n)}(\mathbf{d})\cdot\mathbf{L}^{(n)} \tag{46}$$

The nullity equals n, and therefore the nth order adjugate of **d** has only one non-zero element. Now only one row of $\mathbf{R}^{(n)}$ and one column of $\mathbf{L}^{(n)}$ remain in the product, and the nth order adjugate of **S** reduces to the product of this row and column multiplied by the only element of the nth order adjugate of **d**.

4. PROGRAM

The formalisms derived above were implemented in the *Ab Initio* Valence Bond program TURTLE [3]. The logo for the program is shown in Fig. 1. This is the logo for the parallel version, as is obvious from the number of turtles depicted.

Currently the program has been parallellised using MPI[29,30], following the scheme in Fig. 2. This implies parallellising over 99% of the program, since contrary to MO programs, the matrix elements, both those needed when calculating the wavefunction and those required in the SuperCI, dominate completely. In the present implementation, a speedup of 54 is obtained when using 64 processors[31]. An implementation using Global Arrays[32-34] is in progress. In this implementation, the integral transformation and all calculations of density matrices are parallellised.

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Fig. 1. TURTLE logo. The logo was originally developed by J. Verbeek.

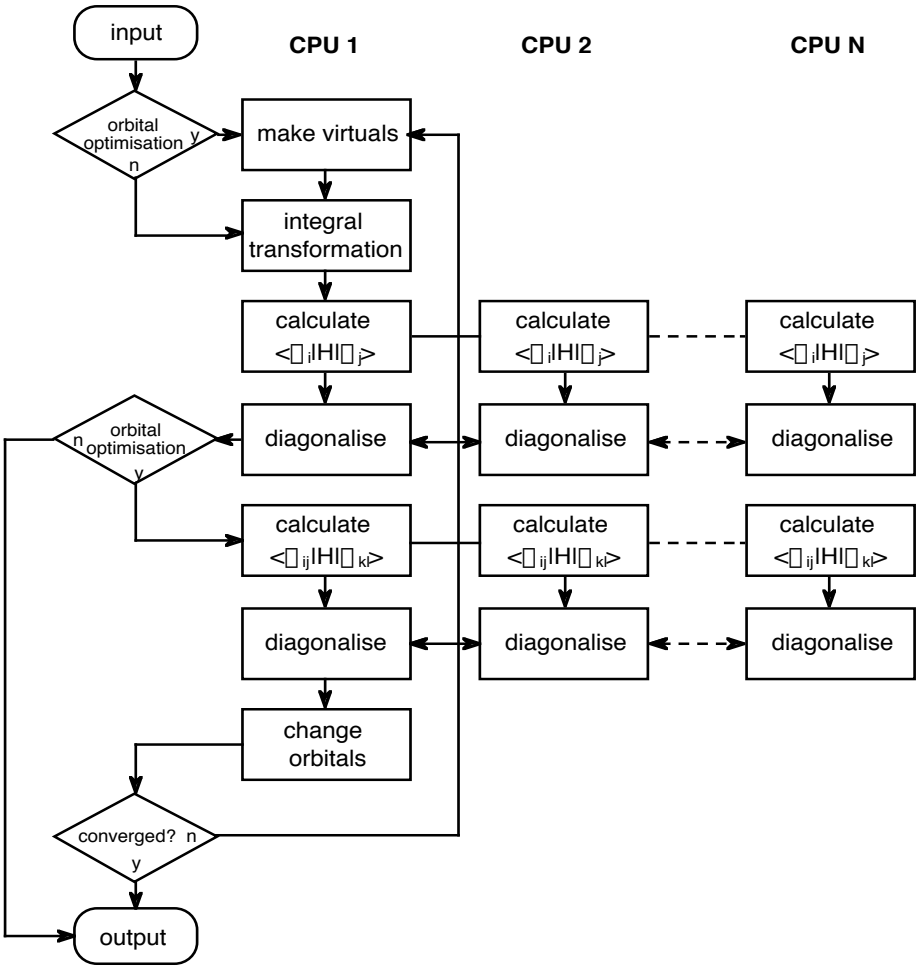

Fig. 2. The structure of the parallellised version of TURTLE.

5. APPLICATIONS

The concept of aromaticity has been intriguing chemists for years. An overview of the discussion about aromaticity and the various experimentally measurable effects can be found in textbooks as Garratt's [35], a paper by Von Schleyer and Jiao [36], and in a review by Wiberg [37].

There is still much dispute about what aromaticity really is. As a consequence of induced ring currents in aromatic π-systems [38,39] the magnetic properties of aromatic compounds differ with respect to those of non-conjugated alkenes. Hence, magnetic properties [36] (large anisotropy of the magnetic susceptibility [ΔΔ], exalted magnetic susceptibility [Δ], deshielded ring protons and negative Nucleus Independent Chemical Shift (NICS) [40]) are also frequently used as aromaticity criteria. There are many other criteria, for instance based on geometric criteria [41-43]. The anomalous magnetic properties and bond equalisation all result from the cyclic electron delocalisation, with which aromaticity is associated.

The theoretical models start with Kekulé's [44] description of benzene, as having two structures. Later Hückel [45,46] discovered his [4*n*+2] and [4*n*] rules, and was able to account for the stability of benzene ([4*n*+2]) and the instability of cyclobutadiene and cyclo-octatetraene (both [4*n*]). The [4*n*+2] compounds were called aromatic after benzene, while the [*4n*] compounds were given the designation anti-aromatic.

A natural way to study aromaticity would be to make use of the concept of two structures, as introduced by Kekulé. The first to use this view were Pauling and Wheland [47]. They used an approximate form of the valence bond (VB) method developed by Heitler and London [48], for describing the aromaticity of benzene.

Classical VB calculations using fixed orbitals and containing all possible covalent and ionic structures for the π-system were done by Norbeck and Gallup [49] and by Tantardini *et al.* [50]. They both used π-orbitals from an SCF calculation. The resonance energy used by them is the energy difference between benzene (described with all the structures) and 1,3,5-cyclohexatriene (described with a subset of structures) at a certain geometry. In these calculations, high resonance energies of -61.4 and -67.4 kcal/mol are obtained for benzene.

More recently, Mo and Wu [51] used this type of description for benzene and cyclobutadiene as well. They also optimised the geometries of these molecules and of the ones with localised bonds. In their calculation of resonance- and stabilisation energies, they took another set of structures for the description of the cyclohexatriene, which leads again to a different definition of the resonance energy.

The first calculations on benzene using optimised orbitals were done by Cooper *et al.* [52], using their spin-coupled VB method [20]. A review [53] has appeared with an overview of their work on aromatic and anti-aromatic compounds.

Resonating Generalised Valence Bond (GVB) calculations were performed on cyclobutadiene by Voter and Goddard [54]. They find a resonance energy of -22 kcal/mol for this molecule. According to them its geometry cannot easily be predicted, and is determined by the interaction between resonance and bond strain.

In the last 15 years new theories about aromaticity appeared. Since the discovery of the Hückel rules, aromaticity was considered as an effect of the interacting π-electrons. Shaik, Hiberty and co-workers [55-61] challenged that view, and stated that the σ-system of benzene favours a distorted geometry with localised bonds, and that the π-system forces the molecule to be symmetric. Glendening *et al.* [62] on the other hand conclude from their calculations on benzene with localised bonds that the interaction between the two Kekulé structures is necessary for the molecule to have a symmetric geometry.

In classical Valence Bond theory, a bond is simply defined as a singlet coupled orbital (electron) pair. Thus, a single bond is obtained using:

$$(Bond)_{12} = \left(|\phi_1\bar{\phi}_2| - |\bar{\phi}_1\phi_2|\right)/\sqrt{2} \equiv (12) \tag{47}$$

Then a total wavefunction is obtained by multiplying these units together and proper antisymmetrisation, thus

$$\Phi = (12)(34)(56)(78)\cdots \tag{48}$$

This resembles the GVB picture of chemical bonding as promoted by Goddard *et al.* [63]. However, in contrast to this, here we have no orthogonality imposed and the number of structures is, in principle, unlimited.

Ionic structures are most easily represented, as are lone pairs, by a doubly occupied orbital or, by two orbitals on one atom located in the same region [4], which is a more balanced picture. Finally, not all bonds have to be designated explicitly. Instead, one might define an orthogonal core, which contains these doubly occupied orbitals.

Thus, the simplest wavefunction describing say three bonds using the Valence Bond model in addition to an orthogonal core is given by

$$\Phi = |(core)(12)(34)(56)| \tag{49}$$

The wavefunction in Eq. (49) could be the wavefunction for a simple molecule, allowing for three bond dissociating, or it could be one of the structures of benzene. The wavefunction for benzene, containing two Kekulé structures for the π-system, is pictorially given in Fig. 3 and in formula by :

$$\Phi = c_1|(\phi_{core})(12)(34)(56)| + c_2|(\phi_{core})(23)(45)(61)| \tag{50}$$

The spin-space for the π-space of benzene is completed by adding the three Dewar structures shown in Fig. 4.

The wavefunction in Eq. (50) does describe the resonance between the two Kekulé structures through the interaction between the two structures.

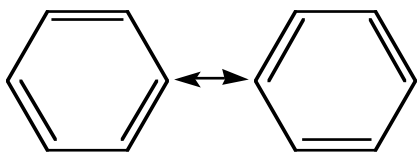

Fig. 3. The two Kekulé structures of benzene

Thus one can study the 'hypothetical' situation without resonance by just including one of the structures in the wavefunction, so as to assess the importance of resonance.

There is still freedom in the choice of "atomic" orbitals used in Eq. (50). For instance, one can use fixed atomic orbitals, which eliminates the (sometimes costly) orbital optimisation. One can also use fully optimised, potentially delocalised orbitals in the spin-coupled / Coulson-Fischer sense. Finally, one can use "real atomic" orbitals by limiting each orbital to its own atom. This often gives a clearer physical picture of chemical bonding. It generates for instance optimal hybrids [9,10].

Since a restriction is applied to the wavefunction, the energy goes up and the bond-strength is diminished. This is used in assessing the effects of the strengths of the bonds in cyclobutadiene. The orbitals may also be restricted to extend just over a part of the molecule [64], inhibiting delocalisation.

The applications we present are all related to the concepts of aromaticity, resonance and delocalisation.

5.1 The importance of resonance - benzene and cyclobutadiene[24,65-67]

Our VB program TURTLE [3] allows for both a more extensive and a more restrictive description of benzene and cyclobutadiene than was available in the previous studies. We included full orbital and full geometry optimisation. Two orbital models were used. The first has p-like (p_{π}) orbitals strictly localised on the carbon atoms. This corresponds to the classical Heitler-London model [48], but with optimal orbitals. The second uses delocalised fully optimised [68] p_{π} orbitals, which include tails to neighbouring atoms.

The main difference between them is that the delocalisation of the orbitals mimics the effects of ionic structures, giving stronger bonds in the molecule. This allows us to study the effect of the bond-strength in the π-system on the geometry. The local orbitals allow a description closer to the Pauling picture [47], since the orbitals lack freedom.

Since we can assign bonds at will, we may distinguish four molecules, some of which are not real in a chemical sense. First there is benzene which we described using just the two Kekulé structures (Fig. 3). The three Dewar structures (Fig. 4) were not taken into account.

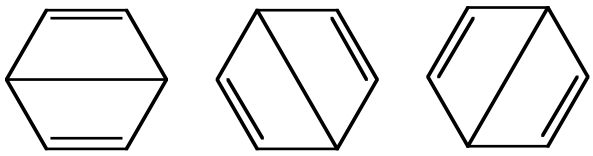

Fig. 4. The three Dewar Structures of benzene

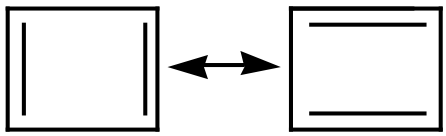

Fig. 5. The two resonance structures for cyclobutadiene

Earlier calculations [52,69] showed that they have a weight of about 6-7% each. Because these weights are relatively small, compared to the total weight of the Kekulé structures of about 80%, and since they obscure the view of the resonance, they were left out.

Next, we have cyclobutadiene, which is described using two structures as well (Fig. 5), though the two are not expected to have equal weight in the wavefunction.

Strictly adhering to the Pauling definition [47], the resonance energy (E_{res}) of an aromatic hydrocarbon is obtained as the difference between the total VB energy and the energy of the most stable structure ($E_{res}=E_{tot}-E_{lowest}$).

The energy difference between the two-structure calculation and a one-structure calculation at the same geometry with optimal orbitals but lacking resonance/π-electron delocalisation gives the vertical resonance energy (VRE) [70].

Finally, we can just use one structure, which for C_6H_6 gives the elusive cyclohexatriene (D_{3h} symmetry) (fig. 6). Of course, for cyclobutadiene, nothing out of the ordinary is observed and the normal 1,3-cyclobutadiene results. The difference in energy with the two-structure calculation gives the theoretical resonance energy (TRE) [51].

The energy of the hypothetical cyclohexatriene was previously estimated by Dewar *et al.* using experimental data by taking three times the C=C and C-C increment [71].

For all the compounds, orbitals and geometries were optimised using a 6-31G basis set [72].

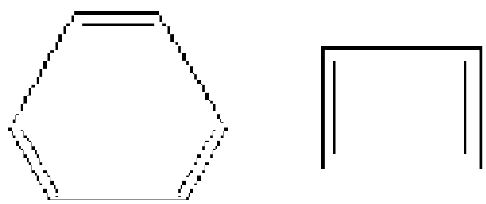

Fig. 6. 1,3,5-cyclohexatriene and 1,3-cyclobutadiene

5.1.1 Benzene and Cyclohexatriene

The benzene calculations using delocalised orbitals yielded a symmetric structure with a C-C bond length of 1.399 Å, in excellent, be it fortuitous, agreement with the experimental value (1.399Å [73]). In the calculations where orbitals were restricted to the atoms, the C-C bonds were weakened and correspondingly they lengthened to 1.426 Å. This elongation was also found when the local approximation was applied to the π-system of ethene [67]. The cyclohexatriene calculations (1 structure), resulted in a D_{3h} geometry, with C-C bond lengths of 1.433 and 1.369 Å, in reasonable agreement with linear 1,3,5–hexatriene (1.458 and 1.368 Å [74]). If the π-orbitals are restricted to the atoms the effect is only noticeable on the single bonds, which elongate to 1.509 Å, whereas the double bonds even contract very slightly to 1.368 Å.

This suggests, that in the delocalised calculation the formal single bonds still have some double bond character, as they have in 1,3,5-hexatriene. They lose this in the purely localised calculation.

This throws some doubt on the clear interpretability of the delocalised calculation. However if a two-structure calculation is performed at the optimised geometry of cyclohexatriene, the weights according to Eq. (3) of the structures are quite similar in both models, viz. 0.74/0.26 for the delocalised calculations vs. 0.79/0.21 for the strictly localised ones.

In Table 1 we collect all resonance energies. The values for both the VRE and TRE are considerably lower than most previously reported values (range -5 to -95 kcal/mol [51,75-77]). We note that in previous calculations the 1,3,5-cyclohexatrienes (D_{6h} and D_{3h}) were accessed with non-optimised orbitals [76], or with pre-determined ethene π-orbitals [77]. Note the large difference between the Pauling resonance energy and the vertical resonance energy for the delocalised orbitals, whereas there is no difference for strictly localised orbitals. Obviously just for benzene, the extra freedom offered by the delocalisation is utilised to the full. If anything, the other resonance energies are remarkably similar, showing that the resonance persists even in cyclohexatriene. The two-structure calculation on cyclohexatriene does not represent a true minimum. It lies just 1.2 kcal/mol (delocalised orbitals) above benzene and will revert to that geometry if the geometry is relaxed.

Table 1

Resonance energies for benzene and cyclohexatriene

Molecule	Benzene		Cyclohexatriene	
model	delocalised	localised	delocalised	localised
Pauling Resonance Energy	-19.8	-25.4	-8.4	-7.7
Vertical Resonance Energy	-9.6	-25.1	-6.2	-7.7
Theoretical Resonance Energy	-7.4	-11.3		

The calculations show that the resonance energy is the driving force behind the symmetrisation of benzene (cf. [62]). Indeed benzene is easy to distort to e.g. a cyclohexatriene geometry [61]. This, however, should not be construed to be an indication of the unimportance of resonance but, on the contrary, to be taken as a sign of its persistence (cf. [69]).

Some of the previous calculations in the literature stressed the importance of ionic configurations. They are indeed needed for a proper description of the bonding when localised orbitals are used, as shown by the poor bond lengths obtained without. The calculations with ionic structures also give huge resonance energies, due to the large number of ionic structures used in the description of benzene. It is our feeling that the only reasonable definition for the resonance of benzene is the interaction between two Kekulé structures. Inclusion of the full set of ionic structures makes it difficult to obtain a balanced description of both cyclohexatriene and benzene. Different choices can be made for the description of cyclohexatriene as well (cf. [51] and [49]). The application of the spin coupled method[53], where the orbitals are optimised, gives essentially the same result (-20.0 kcal/mol) for the resonance energy as our calculations using delocalised orbitals. The only difference is that the Dewar structures of Fig. 4 were also present in the spin-coupled wavefunction.

5.1.2 Cyclobutadiene

A calculation using the delocalised orbital model yields a rectangular structure as expected [78], both with the two-structure and with the one-structure calculation. The bond lengths are 1.552 Å and 1.367 Å for the two-structure calculation and hardly different for the one-structure calculation. The resonance energy is quite small (-0.98 kcal/mol).

However when the π-bond strength is diminished, when using strictly localised orbitals, a molecule with equal C-C bondlengths (1.465 Å) is obtained. Now the resonance energy is quite large (Pauling E_{res}= -17.66 kcal/mol). So is the stabilisation energy of -7.85 kcal/mol with respect to the 1-structure calculation, which obviously still yields a rectangular structure with bond lengths of 1.556 and 1.395 Å. The π-bonds are relatively weak in this system, due to the use of strictly localised orbitals. Thus, the square geometry can be explained by a preference of the σ-system for equal bond lengths.

In order to see if it possible to neutralise this effect of the σ-system we performed a second calculation which used localised orbitals for the σ-system as well as for the π-system. In this calculation one perfect-pairing structure was used for the C—C bonds of the σ-system. All orbitals were localised on the C—H fragments. Doubly occupied orbitals were used for the C—H bonds, and strictly localised singly occupied orbitals for the C—C bonds. This calculation again yields a rectangular geometry with a much lower resonance energy. The

bond lengths are also longer than for calculations with only localised π-bonds, which shows that the bonds are indeed weaker.

We may conclude that the relative strengths of the σ- and the π-bonds determine the geometry of cyclobutadiene. For relatively weak σ-bonds, the resonance, together with the π-bonds, prevails to yield a square geometry. With stronger σ-bonds or weaker π-bonds the, expected, rectangular structure is produced.

5.1.3 Concluding remarks on the importance of resonance

Of the views expressed in the literature, we find two of them to be partly compatible with our findings. The model developed by Shaik, Hiberty and co-workers [55-61] states that the σ-system prefers equal bond lengths, while the π-system prefers alternating bond lengths. The resonance of the π-system is also a symmetrising influence.

The viewpoint expressed by Glendening *et al.* [62] is that the resonance between the structures is the key factor for delocalisation. We find this as well. When there is no resonance in cyclobutadiene (and benzene), the molecule becomes asymmetric. Just resonance is not enough, however. Both benzene and square cyclobutadiene have large resonance energies.

Finally, we have to disagree with Zilberg and Haas[79]. They state that the geometric distortion of cyclobutadiene is a fundamental property of [4n]-electron ring systems. We were able to generate a square symmetric system just by weakening the π-bonds. Voter and Goddard[54] correctly suggest that the geometry of cyclobutadiene is a result of a balance between bond strain and resonance.

We can therefore now conclude that there are three contributions that determine the geometry of benzene and cyclobutadiene. The first contribution is that of the σ-system which prefers equal bond lengths. The other two contributing factors are the π-bonds and the π-resonance. The π-bonds by themselves give rise to two states with a minimum at one of the geometries with alternating bond lengths. The resonance provides interaction between the two states and stabilises the symmetric structure.

5.2 Aromaticity of bent benzene rings [69]

An interesting question [80] is: “What happens when the benzene ring is bent from its planar structure?” Will it still be aromatic? The only experimental way to get insight into the possible behaviour of bent benzene molecules is by attaching bridges over the ring that put the ring under strain. Examples of such molecules are [n]meta- and [n]paracyclophane molecules, the number n denoting the length of the carbon chain that is attached to the benzene ring. The only way to study bent benzene molecules, without the disturbing influence of

the bridges, is to use theoretical methods, where the Born-Oppenheimer approximation [81] allows one to freeze the molecular geometry.

For the description of the bent benzene, the flat benzene ring was the starting point. For this system, there is a clear σ π separation. There is a clear distinction between the doubly occupied orbitals for the σ-core and the 6 non-orthogonal p-orbitals for the π-system.

The π-system is described by all five Rumer structures, which is the complete spin-space (i.e. Fig. 3 and Fig. 4). This allows a smooth transition from benzene, where the 2 Kekulé structures are most important, to the highly bent Dewar benzene, where only one of the Dewar structures (Fig 4) is important. All the orbitals, doubly occupied and singly occupied are fully optimised. For each bent structure, the orbitals from the preceding less bent structure were used as initial guess. This and the choice of wavefunction ensure that an aromatic "π-system" can be identified, even when no symmetry separation exists. All orbitals were completely optimised so we have a wavefunction of the spin-coupled type. This is the type of wavefunction used by Cooper *et al.* [52] in their study of benzene.

To obtain geometries, 10-orbital 10-electron complete active space self-consistent field (CASSCF) [82-84] calculations were performed with the GAMESS-UK program [6]. The occupied orbital order in an SCF for flat benzene is σ,2σ,2π. In the bent molecule, there is no clear distinction between σ- and π-orbitals and we want to include all the π-orbitals in the CAS-space. Thus, 10 orbitals in the active space are required. Obviously, the 5 structure VB wavefunction would have been a preferable choice to use in the geometry optimisation. However, at that time, the VB gradients were not yet available. The energies of the VBSCF at the CASSCF geometries followed the CASSCF curve closely.

The geometry of the molecule at each point was optimised for a fixed bending angle ϕ (Fig. 7), while all the other geometrical parameters were free.

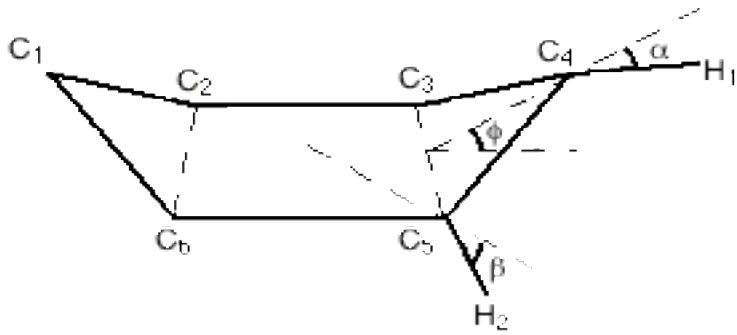

Fig. 7. Important geometrical parameters: ϕ is the angle between the plane of the displaced carbon atom 4 with carbon 3 and 5 and the plane of the 4 lower carbon atoms.

C_{2v} symmetry has been used throughout. Calculations were performed for α from 0º to 90º with a step-size of 5º. All calculations were performed using the 6-31G basis set [72].

The carbon-carbon bond lengths remain very similar, with differences of less than 0.03 Å, up to a bending angle (α) of 55º. The end-CH (β) bending increases up to 40º at α=55º, thus maintaining the π-system as much as possible. Beyond α=55º, the end-CH turns upwards (β=-1º at α=60º), signalling the end of the aromatic ring. At that angle the equivalence between the C-C bonds is gone as well. There is a drastic change in the geometry between 55º and 60º, where the molecule attains the shape of Dewar benzene. The barrier in the potential energy curves is also here.

The clearest picture of the bonding is given by considering the weights of the Rumer structures (Eq. (3), Fig. 8). The weights for equivalent structures are added; So the weights of the two Kekulé structures are summed and the weights of two of the Dewar structures are summed. It is clear that at low angles the two Kekulé structures are the most important ones. They make up for more than 70 % of the wavefunction, up to 55º. Then one Dewar structure takes over completely and the molecule has become Dewar benzene.

The energies of the individual structures behave more smoothly. They are continuously rising (except for the bonding Dewar structure beyond 60º), though there is sudden change at 60º because of the change in geometry.

The resonance energy (Pauling definition [47]) is -20.30 kcal/mol for flat benzene and it decreases to -17.39 kcal/mol at 55º. Thus, we still have an aromatic molecule at 55º. After 55º one Dewar structure dominates the wavefunction and the resonance energy decreases to -0.10 kcal/mol; the aromaticity is gone.

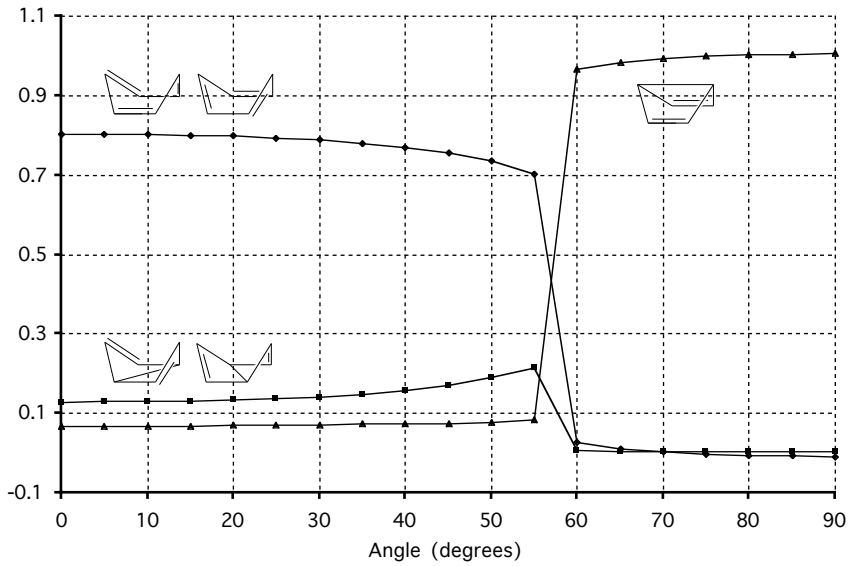

Fig. 8. Structure weights in bent benzene

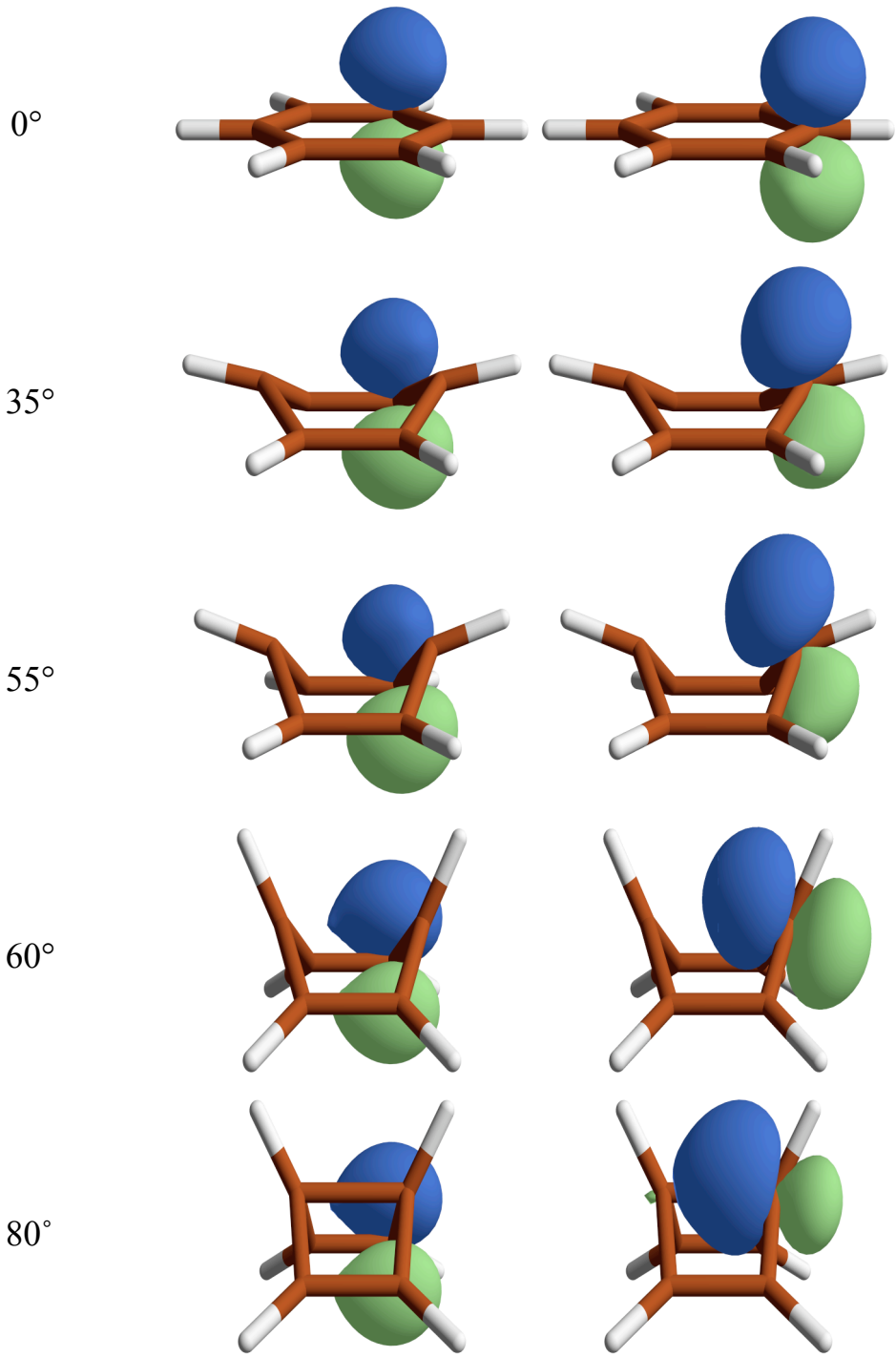

Fig. 9. π like orbitals on carbon atoms 3 and 4 for some important bending angles. The orbitals on the other atoms may be obtained by mirror-symmetry. The pictures were produced with the help of Molden **[85]**

Orbital pictures for the different bending angles are shown in Fig. 9. The pictures show iso-surfaces with an absolute value of 0.1. The different signs are shown by the dark and light grey-shades, and the orbitals extend to neighbouring atoms, reflecting the delocalised model employed. They show that the orbitals try to adapt to the form of the molecule and to maintain bonds for the Kekulé structures. At 60º the p-like orbitals on carbon atom 1 and 4 rotate to form a bond between those two atoms. So. first of all, the overlaps are maximised for the bonds in the Kekulé structures. Then the orbitals on the two carbon-atoms, which are bent out of plane (atom 1 and 4) rotate to form a bond in the Dewar structure with correspondingly much larger overlap.

The orbitals in bent benzene try to adapt to the bent ring as much as possible while still keeping large overlaps for the Kekulé structures. This also has to do with the geometry of the molecule, especially the hydrogen atoms attached to the carbon atoms 1 and 4. First, they are bent down making it possible for the p-orbitals on the carbons to stay perpendicular to the plane of the other 4 carbon atoms. In the Dewar form, they are bent up and the p-orbitals are again perpendicular to the plane of the hydrogen. So the geometry and the bonds adapt to each other.

If now the geometry would be forced to inhibit the aromatic system, as is the case in the experimental systems, where bridges are attached to bend the molecule, the aromaticity disappears at much lower angles. Test calculations [86], where the angle Φ is reversed to simulate this situation, indicate that then the aromaticity is only maintained up to 30º.

5.3 Aromaticity of Pyrene and its Cyclopentafused Congeners [65,87]

Polycyclic aromatic hydrocarbons (PAH's) with external cyclopentafused five-membered rings, such as the cyclopentafused pyrene derivatives (Fig. 10), belong to the class of non-alternant polycyclic aromatic hydrocarbons.

Several qualitative models, e.g. Platt's ring perimeter model [88], Clar's model [89] and Randi¶'s conjugated circuits model [90-92] have either been or are frequently used for the rationalisation of their properties. All these qualitative models rationalise the properties of aromatic and anti-aromatic hydrocarbons in terms of the Hückel [4n+2] and [4n] rules. The extra stability of a PAH, due to π-electron delocalisation, can also be determined, computationally or experimentally, by either considering homodesmotic relationships [36] or by the reaction enthalpy of the reaction of the PAH towards suitable chosen reference compounds [93].

In a related study on the cyclopentafused pyrenes [94] in which regular *ab initio* methods were used (RHF/6-31G* and B3LYP/6-31G*), we found that the magnetic properties suggested that the aromatic character decreases upon cyclopentafusion. The aromatic stabilisation energies were unaffected, though.

These effects prompted us to study the effect of cyclopentafusion in the cyclopentafused pyrene series on the interaction between the different Kekulé resonance structures and thus on the resonance energy.

All geometries of **1-7** were optimised at the RHF/6-31G level. Structures **1-6** are really flat but **7** was found to be bowl-shaped [94]. In a treatment of the conjugated system in this geometry, the π orbitals cannot easily be excluded, as the strict σ π separation is destroyed.

The deviation from the planar form of **7** is rather small. Since an aromatic structure is not easily destroyed by bending (cf. Section (5.2), [69]), the VB results obtained for the planar transition state are expected not to deviate much from those of bowl-shaped **7**. Of course, the calculation on planar **7** is computationally much cheaper.

The σ-core was taken from a preceding RHF/6-31G calculation. The π-system was described by strictly atomic non-orthogonal p-orbitals, which were optimised for benzene. Test calculations on cyclopenta[*cd*]pyrene (**2**) indicated that the structure energies and weights change only marginally upon optimisation of the p-orbitals.

For pyrene (**1**) 1430 covalent structures can be generated. Only six of those have all π-bonds along the σ-bonds. These six structures are the Kekulé resonance structures of pyrene. In the case of *tetra*cyclopenta[*cd,fg,jk,mn*]-pyrene (**7**), 208012 covalent structures can be generated. Only ten Kekulé resonance structures exist for this molecule. It is expected that only the Kekulé resonance structures are important in the description of these molecules and that the other structures can be ignored at a considerable saving in time and gain in interpretability.

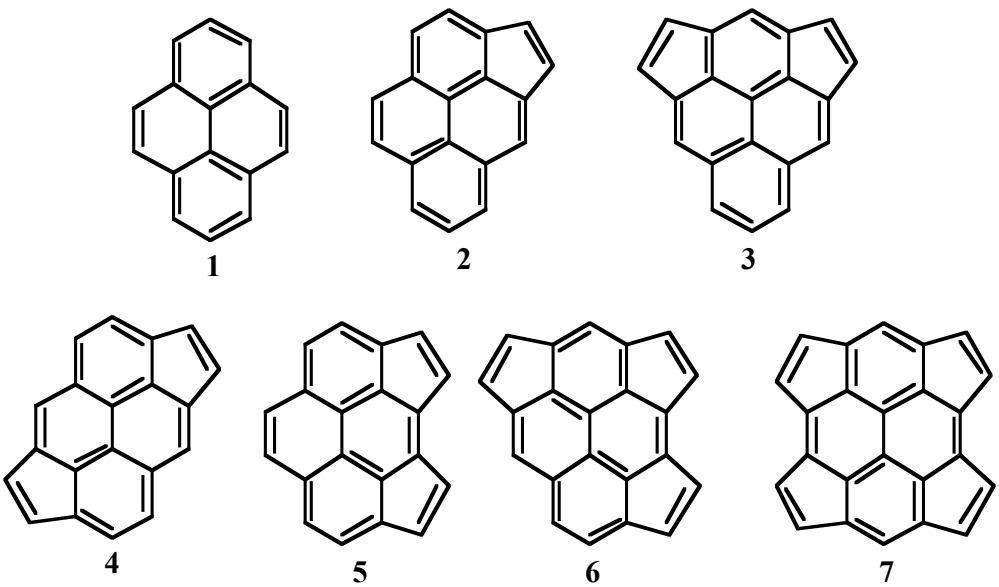

Fig. 10. The structures of **1-7**.

In the spirit of Pauling [95], only the Kekulé resonance structures were considered

To identify the most important resonance interactions between Kekulé resonance structures and thus the most aromatic subsystems the total resonance energy had to be partitioned. Therefore the **H** matrix was transformed to an orthogonal basis using Löwdin-orthogonalisation [96], yielding $\mathbf{H}^{\square}$. The total energy can then be partitioned in the weighted diagonal contributions of the structures and the weighted resonance contributions between them

$$E = \sum_i \sum_j c_i c_j H_{ij}^{\square} = \sum_i c_i c_i H_{ii}^{\square} + \sum_i \sum_{j>i} 2 c_i c_j H_{ij}^{\square} = E_{diag}^{m} + E_{res}^{m} \tag{51}$$

where c_i is the coefficient of structure i in the wavefunction.

The sum of the resonance contributions (E_{res}^{m}) is again another measure of the resonance energy, namely with respect to the weighted mean value of the energy of all structures. This mean resonance energy is thus more negative (stabilising) than the Pauling resonance energy (E_{res}). In Table 2 we give the total energies and resonance energies of the 7 compounds. The E_{res}^{m} values for **1–7** follow the same trend as the E_{res} values.

The contribution to E_{res}^{m} of a particular interaction between two structures is twice the weighted resonance contribution ($2c_i c_j H_{ij}^{\square}$). The differences between a pair of Kekulé resonance structures elucidate the conjugated circuit in which the $\square$ electrons are delocalised by resonance as shown in Fig. 11.

Table 2

Total energies of compounds 1-7 (a.u.) and resonance energies (kcal/mol).

Compound[a]	RHF	VB	E_{res} [b]	E_{res}^{m} [b]
1 (6)	-611.555550	-611.286631	-62.3	-100.9
2 (6)	-687.242053	-686.940798	-58.5	-101.1
3 (6)	-762.918242	-762.584880	-62.2	-101.8
4 (7)	-762.922606	-762.592661	-54.5	-101.5
5 (7)	-762.925727	-762.595225	-56.4	-101.8
6 (8)	-838.595341	-838.236025	-58.6	-102.7
7 (10)	-914.259921	-913.873884	-62.5	-104.2

[a]The number of Kekulé resonance structures is indicated between parentheses.

[b]For comparison the resonance energies of benzene, calculated with local p-orbitals (6-31G basis set) and two structures, are E_{res} = -25.4 kcal/mol (Table 1) and E_{res}^{m} = -44.2 kcal/mol.

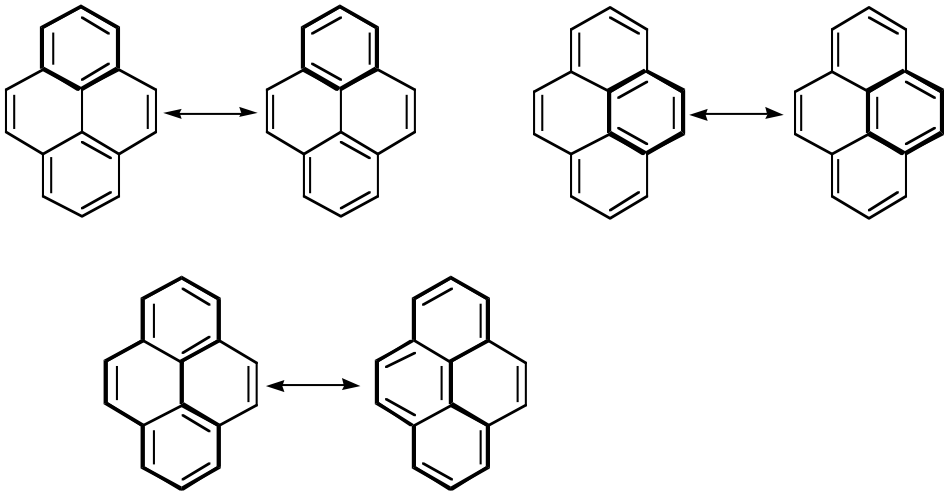

Fig. 11. Resonance between the structures leading to benzene-like resonance in the top six π electron, central six π electron and 14 π electron conjugated circuits, respectively.

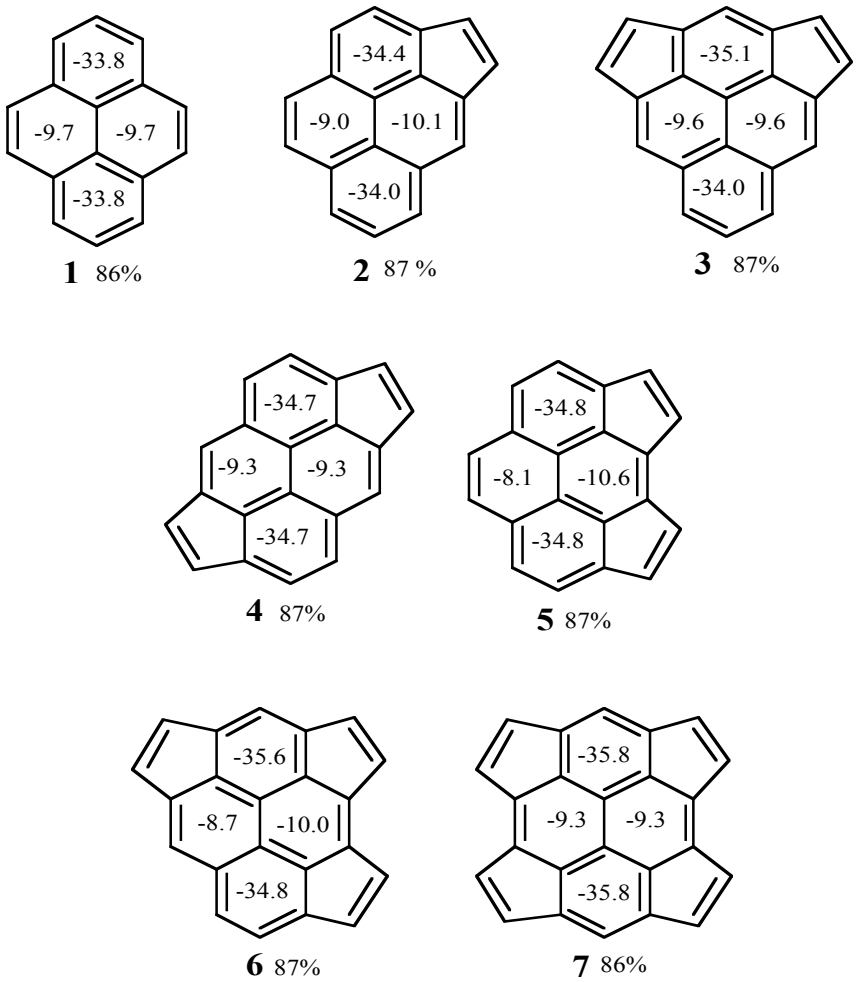

Fig. 12. Contributions of the individual rings to the resonance energy.

Using this method, the resonance energy was divided over the rings. The result is displayed in Fig. 12. The percentages below each structure give the amount of resonance energy accounted for by just the rings indicated. The remainder is resonance in 10/12/14/.. rings.

The partitioning of the resonance energy shows large contributions to the mean resonance energy (E_{res}^{m}) from the resonance interactions in the top and bottom six-membered rings. The right and left central six-membered rings contribute less than a third to the resonance energy.

In a previous study, it was shown that the aromatic stabilisation energies of the compounds **1-7** are all nearly equal [94] *i.e.* cyclopentafusion has no effect on the resonance energy. This conclusion is confirmed by the VB calculations. The resonance energy (both E_{res} and E_{res}^{m}) of the compounds **1-7** are all of the same magnitude (Fig. 12 and Table 2).

More generally, upon the addition of externally fused five-membered rings, the weights and energies of the pyrene sub-structures are only marginally affected. The contributions of the different conjugated circuits to E_{res}^{m} show for all compounds the same trends; the six π-electron (benzene-like) conjugated circuits in the top and bottom six-membered rings have the highest contribution to E_{res}^{m}, independently of cyclopentafusion. Hence, all compounds should be seen as substituted pyrene derivatives.

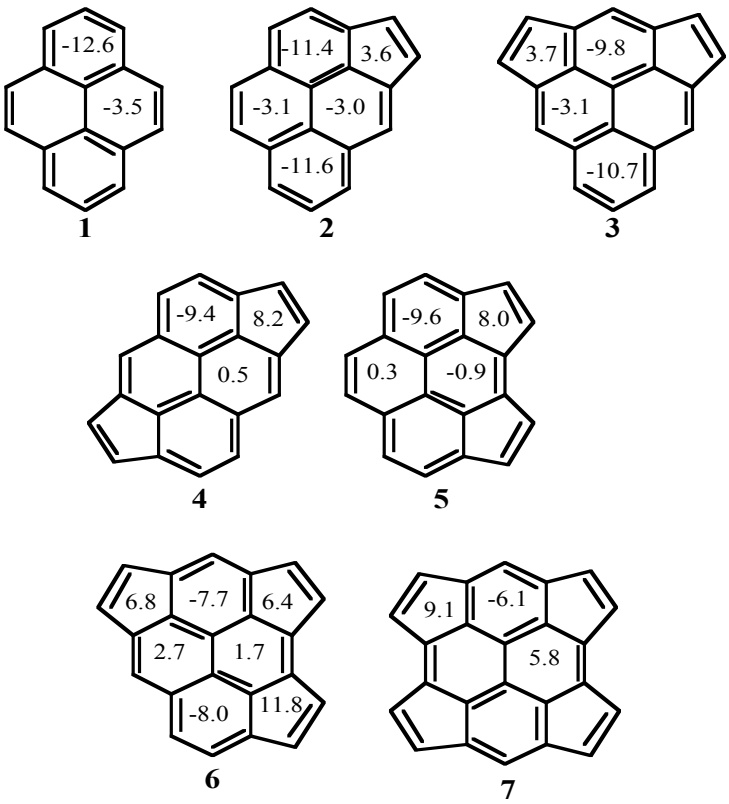

Fig.13. The NICS values of the individual rings.

Nucleus Independent Chemical Shift (NICS) values in the ring centres [40] were calculated using the Direct IGLO [39,97] program, at the RHF/6-31G geometry using the IGLO-III basis set. The chemical shift shielding tensor is given as a sum of the diamagnetic and paramagnetic part by the IGLO program.

The NICS values calculated at the ring centres for the compounds **1-7** are depicted in Fig.13. Large negative NICS values are found for the top and bottom six-membered rings. The NICS values for these rings are shifted 10 ppm upfield with respect to the NICS values of the central six-membered rings, which is in line with the resonance criterion, derived above.

Upon addition of externally fused five-membered rings, the NICS values at the ring centres suggest a reduction of the aromatic character in this series. The resonance criterion (both E_{res} and E_{res}^{m}), however, does not suggest that the aromatic character of **1-7** decreases.

This apparent discrepancy might be understood by realising that the diamagnetic contribution of the chemical shielding tensor perpendicular to the molecular framework ($\mathrm{NICS}_{\square}^{d}$) is indicative for the induced ring currents. Unfortunately, the paramagnetic contribution, which is zero in benzene due to symmetry, is included in the NICS values and the relation between dia- and paramagnetic contributions is gauge dependent. Thus, the NICS values can only be used for comparing the aromatic character of similar rings.

5.4 The enhanced acidity of carboxylic acids and enols relative to alcohols [98-100]

In this early application of the TURTLE program, the ability to restrict the wavefunction is used to ascertain the relative importance of π-electron delocalisation and induction to the enhanced acidity of carboxylic acids and enols compared to alcohols. These generic classes of molecules are represented by formic acid, vinyl alcohol and ethanol respectively.

The enhanced acidity of carboxylic acids and enols relative to alcohols has long been attributed to the stabilisation of the carboxylate and enolate anions by delocalisation of their π electrons (see **1** and **2** below). Alkoxide anions, as saturated systems, are not subject to resonance stabilisation.

The parent acids and alcohols, on the other hand, are not expected to display any significant mesomeric stabilisation, because this would involve the participation of some rather unreasonable Lewis structures with separated positive and negative charges. As a consequence, the π-delocalisation in **1** and **2** is a factor that lowers the deprotonation energy of carboxylic acids and enols, thus reinforcing their acidity, according to standard organic-chemistry textbooks.

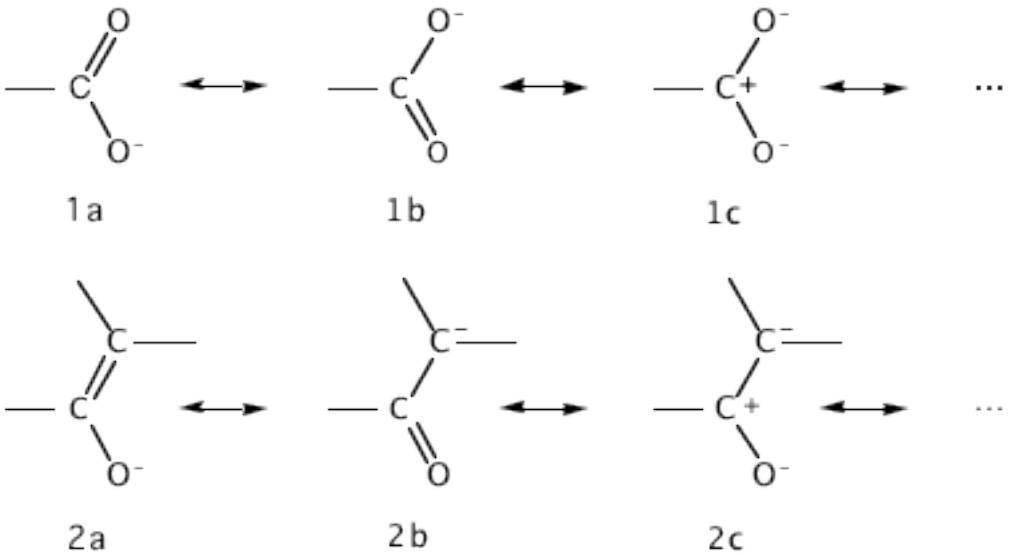

Fig. 14. Resonance structures for carboxylic acids and enols

Since the molecules are planar, there is a strict separation between the σ- and the π-system. In the calculations, the σ-system was handled with the usual delocalised orbitals. For the π-system two different models were defined.

In the localised VB the orbitals are only allowed to extend over part of the molecule. For instance, for an enolate anion, the basic wavefunction would have a doubly occupied σ-orbital, localised only on the oxygen atom and a doubly occupied π-orbital extending over both carbon atoms. Thus, while describing structure **2a** in Fig. 14, a single determinant is still employed. Since the orbitals are completely optimised, the π-system can partly counteract the charge separation.

The delocalised model entails a normal Hartree-Fock calculation, allowing a complete delocalisation of both the σ- and π-systems, and thus describing the complete delocalisation of the π-system.

In both models inductive effects are included, so one can calculate the energetic effect of π-delocalisation in a direct way. The calculations were performed at three different levels of theory, with an increasing degree of electron correlation. For instance one might allow left-right correlation in the σ-bond in the localised model and perform a corresponding CASSCF in the delocalised one. The results were found to be insensitive to the degree of electron correlation, so we present only the results of the simplest level here. It should be noted that in all cases inductive effects are fully operational, irrespective of the degree of localisation.

The calculations were performed with a standard 6-31G* basis set [101] augmented by diffuse p-functions [102]. The geometry optimisations of the delocalised states were carried out through a standard gradient technique with the GAUSSIAN92 program [103].

Table 3
Delocalisation energies of the deprotonated anions and their parent acids.

Anions	ΔE (kcal/mol)	*Acids*	ΔE (kcal/mol)
$HCOO^-$	40.2	HCOOH	17.5
CH_2CHO^-	34.9	CH_2CHOH	13.6
$CH_3CH_2O^-$	14.6	CH_3CH_2OH	6.6

Because no gradient routines were available at that time for the VB calculations, the geometries of the localised states were partly optimised by hand.

From a consideration of the optimised geometries, it could be concluded that both the acids and the deprotonated anions are subject to some π-electron delocalisation. In accord with chemical intuition, the effect of delocalisation is more important in the carboxylate and enolate anions than in the other species. However, the geometry changes that the acids undergo under deprotonation are only partly explained by π delocalisation.

The delocalisation energy (ΔE_{deloc}) of the parent acids and their anions is defined as the energy difference between the localised wavefunction, Φ_{loc}, and the delocalised ground state, Φ_{del} in their optimal geometry, i.e. the adiabatic delocalisation energy [104]

$$\Delta E_{deloc} = E_{\Phi_{loc}} - E_{\Phi_{deloc}} \tag{52}$$

The energetic effects of π-delocalisation as calculated through Eq. (52) are summarised in Table 3.

The results show that the carboxylate and enolate anions have the largest delocalisation energies among the six species, in accordance with the principles of resonance theory. This is because none of these anions can possibly be described by a single Lewis structure. For example, the carboxylate anion, with its symmetrical geometry, requires besides structure **1a** at least the contribution of **1b**. This also applies to the enolate anion, but with an important difference: **1a** and **1b** are degenerate structures, a factor that is expected to maximise the resonance energy, while the structures **2a** and **2b** are not equivalent and have different energies. Accordingly, the delocalisation energy is expected to be smaller in the enolate anion than in the carboxylate anion, which is indeed found to be the case (see Table 3).

As expected, because the parent acids of these two anions can be reasonably well described by a single Lewis structure, they have much smaller delocalisation energies. In ethanol and its deprotonated anion, for which no resonance between low-lying Lewis structures may be expected, the delocalisation energy is relatively small.

As delocalisation reinforces acidity only if it stabilises the anion more than the parent acid, the contribution of delocalisation to the acidity is best defined as the difference of the two delocalisation energies: ($\Delta\Delta E = \Delta E$(anion) – ΔE(acid)), Using this criterion, it appears that delocalisation contributes rather little (8 kcal/mol) to the acidity of ethanol, as expected from chemical intuition. In contrast, delocalisation contributes as much as 21–23 kcal/mol to the acidity of formic acid and of vinyl alcohol. Perhaps surprisingly, the $\Delta\Delta E$ values are the same for the two species, while one might have expected resonance effects to be more important in formic acid, for which the mesomeric description of its anion involves two equivalent structures. The explanation probably lies in the polar nature of the C–O bond, which results in a large contribution of structure **1c** to the anion. Since an ionic structure of the same type is also important in the undissociated acid, the nature of the π electronic system changes less than expected from acid to anion, so that the change in delocalisation energy remains relatively moderate. To push this reasoning to the limit: if the C–O bonds were entirely ionic, there would have been no resonance at all.

This does not mean that enols and carboxylic acids have comparable acidities, since inductive effects may also contribute to the acidities. In that respect, it is useful to compare the $\Delta\Delta E$ values obtained with the total acidity enhancements of formic acid and vinyl alcohol with respect to ethanol. The experimental gas-phase acidities of formic acid and ethanol are known to be 345 and 376 kcal/mol, respectively [105]. The acidity of vinyl alcohol has been accurately calculated by Streitwieser *et al.* [106], who predicted a value of 359.5 kcal/mol. So, the acidities of formic acid and vinyl alcohol are reinforced by 31 and 16.5 kcal/mol, respectively, relative to ethanol. The calculations indicate that delocalisation contributes 23, 21 and 8 kcal/mol, respectively, to the acidities of formic acid, vinyl alcohol and ethanol. Delocalisation therefore reinforces the acidities of the two former species by 15 and 13 kcal/mol, respectively, compared to ethanol. This is 48% and 78% of the total acidity enhancement, which is the major part of the acidity enhancement in vinyl alcohol. Delocalisation and inductive effects are found to be of equal importance to formic acid.

The calculations support the traditional view by showing that delocalisation is an important factor responsible for the enhanced acidity of carboxylic acids and enols relative to alcohols.

The same methodology was applied to the study of the role of conjugation in the stability and rotational barriers of formamide and thioformamide [100]. Here it was found that resonance accounts for roughly one-half of the rotational barrier of formamide and for two-thirds in the case of thioformamide.

CONCLUSION

We have given an account of some of the inner workings of the gradient VBSCF program TURTLE. The program is especially conceived to allow the optimisation of wavefunctions of arbitrary form. This feature is exploited in the study of resonance and delocalisation phenomena.

For instance it allows the complete optimisation, orbitals and geometry, of benzene (D_{6h} symmetry), which is described by two resonating structures and of the fictional molecule cyclohexatriene (D_{3h} symmetry), whose wave function consist of just one of the structures. A comparison of the results gives a better insight in the nature and the persistence of resonance.

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