

G. Geudtner · Z. Gómez-Sandoval · F. Janetzko  
P. Calaminici

## First principle $\sigma$ - $\pi$ energy separation

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**Abstract** A scheme for the  $\sigma$ - $\pi$  separation of the total energy at the Kohn-Sham density functional theory (KS-DFT) level is presented. Several six-, five- and four-membered ring systems were investigated with this scheme. Normal mode coordinate distortions were investigated. The character of the  $\sigma$  and the  $\pi$  energy with respect to bond equalization and bond alternation was studied. The influence of the core–core repulsion energy term on the results is discussed.

### 1 Introduction

Hückel [1] introduced the  $\sigma$ - $\pi$  separation as one of the fundamental concepts into quantum chemistry. He distinguished two types of orbitals, namely on one hand orbitals symmetric with respect to a reflection in the molecular plane ( $\sigma$  orbitals) and on the other hand orbitals antisymmetric to such a plane ( $\pi$  orbitals). In spite of the crude approximations of the Hückel molecular orbital (MO) method (e.g. the  $\sigma$  electrons were not treated explicitly and only nearest-neighbor interactions were taken into account), it could explain the reactivity and the special stability of benzene in a very simple way and gave therefore the first consistent description of benzene. Furthermore, based on this method the chemical behavior of a whole class of molecules could be predicted and the experimental verification of these predictions demonstrated impressingly the usefulness of the concept. The idea of the  $\sigma$ - $\pi$  separation had therefore a large influence on chemical thinking and on the interpretation of experimental findings and led for example to the famous Woodward-Hoffmann rules for concerted reactions [2, 3]. Due to this large impact, the original idea of Hückel was developed further as the development of elec-

tronic structure theory evolved. Several methods for the  $\sigma$ - $\pi$  separation were developed, which extend the concept from valence electron to all-electron  $\sigma$ - $\pi$  energy separation and which were recently reviewed [4, 5]. These methods gave evidence for a  $\sigma$ - $\pi$  interplay in the distortivity of delocalized electronic systems as an important result. This is in contrast to the usual idea that the delocalized  $\pi$  electrons are the driving force for the equal bond lengths in such systems.

However, in the generalization of the  $\sigma$ - $\pi$  energy separation concept two problems occur. The first one is the separation of the nuclear repulsion energy term. While the usual full incorporation of this term into the  $\sigma$  energy leads to an unbalanced partition of the energy [4], Shaik et al. [6] used only distortion coordinates for the  $\sigma$ - $\pi$  separation along which the nuclear repulsion energy stayed constant. Although the latter approach led to the important result that the  $\pi$  electrons e.g. in benzene have a distortive character, it is restricted due to the constrain of constant nuclear repulsion energy. A solution for this problem was suggested by Jug and Köster [7] who divided the molecule into neutral subsystems. They separated the nuclear charge  $Z_A$  of an atom  $A$  into a  $\sigma$  and a  $\pi$  part according to the number of  $\sigma$  and  $\pi$  electrons  $n_A^\sigma$  and  $n_A^\pi$  assigned to  $A$ . This is always possible if the total number of  $\pi$  electrons of the system is known. This model was successfully applied to a number of five- and six-membered ring systems and the distortive character of the  $\pi$  energy was found in all cases. Furthermore, it could be shown that in the cyclobutadiene molecule both energy contributions favored a distortion to a structure with two C–C single and two double bonds while in the cyclobutadiene dication the  $\sigma$  and the  $\pi$  contributions stabilized the squared  $D_{4h}$  structure with equal C–C bond lengths.

The second challenge for the generalization of the  $\sigma$ - $\pi$  energy separation concept is the inclusion of the correlation energy, since the correlated wave function is of multi-determinantal nature. Here, the Kohn-Sham density functional theory (KS-DFT) method [8] offers an alternative approach since the correlation effects are included in the one-determinant ansatz via the correlation functional. Recently, a  $\sigma$ - $\pi$  energy separation including the separation of the nuclear

This manuscript is dedicated to the celebration of the 65th birthday of Professor Karl Jug.

G. Geudtner · Z. Gómez-Sandoval · F. Janetzko · P. Calaminici (✉)  
Departamento de Química, CINVESTAV,  
Avenida Instituto Politécnico Nacional 2508,  
(A.P. 14-740) México D.F. 07000, México  
E-mail: pcalamin@mail.cinvestav.mx

charges as described above has been implemented in the KS-DFT program deMon2k [9] and it was successfully applied to benzene [10].

The purpose of this paper is to study the  $\sigma$ - $\pi$  interplay in different molecules having a delocalized electronic system with the DFT based  $\sigma$ - $\pi$  energy separation scheme. The computational details are given in the next section. After a detailed description of the  $\sigma$ - $\pi$  energy separation on the basis of the KS-DFT in Sect. 3, the choice of distortions and resonance coordinates for the investigation of selected six-, five- and four-membered ring systems is presented in Sect. 4. In Sects. 5 and 6, we discuss our results for the six- and five-membered systems, respectively, and compare them with the results of a previous SINDO1 study [7]. Our results of the investigation of cyclobutadiene and the cyclobutadiene dication are presented in Sect. 7 and again a comparison with the corresponding SINDO1 results is performed. Additionally, we extended the investigation to the dianionic molecule, which was not studied previously.

## 2 Computational details

The linear combination of Gaussian-type orbitals Kohn-Sham density functional theory (LCGTO-KS-DFT) method as implemented in the program deMon [9] was used to carry out all geometry optimizations and harmonic vibrational frequency calculations.

The calculations were performed using the local exchange-correlation contributions proposed by Vosko et al. [11] as well as with the non-local B-LYP exchange-correlation functional [12, 13]. Since no qualitative differences were observed using local and non-local approximations, only the results of the  $\sigma$  and  $\pi$  energies obtained with the B-LYP functional will be presented. The double zeta plus valence polarization (DZVP) basis, together with the A2 auxiliary function set [14] was employed.

A quasi-Newton method in internal redundant coordinates with analytic energy gradients was used for the structure optimization [15]. The convergence was based on the Cartesian gradient and displacement vectors with a threshold of  $10^{-4}$  and  $10^{-3}$  a.u., respectively.

In order to investigate the normal mode coordinate distortions, a vibrational analysis was performed. The second derivatives were calculated by numerical differentiation (two-point finite difference) of the analytic energy gradients, using a displacement of 0.001 a.u. from the optimized geometry for all  $3N$  coordinates. The harmonic frequencies were obtained by diagonalizing the mass-weighted Cartesian force constant matrix.

## 3 Energy separation

For the separation of the energy in DFT, we consider the formulation for the converged self-consistent field (SCF) energy  $E_{\text{SCF}}$ , which is derived from the variational approxima-

tion of the Coulomb potential [16–18]. This  $E_{\text{SCF}}$  expression was reformulated for the linear combination of Gaussian-type orbitals (LCGTO) DFT methods [19] as:

$$E_{\text{SCF}} = \sum_{\mu,\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu,\nu} \sum_k P_{\mu\nu} \langle \mu\nu || k \rangle x_k + E_{xc}[\rho],$$

where the symbol  $||$  represents the  $1/|\mathbf{r}_1 - \mathbf{r}_2|$  operator and the expansion coefficients  $x_k$  are defined as:

$$x_k = \sum_l \sum_{\mu,\nu} P_{\mu\nu} \langle k || l \rangle^{-1} \langle \mu\nu || l \rangle,$$

with  $\langle k || l \rangle^{-1}$  denoting the elements of the inverse charge density electron repulsion integral matrix. For clarity of presentation, the charge conservation constraint has been dropped in this formulation.

In order to introduce the  $\sigma$ - $\pi$  energy separability, we consider the separation of the density matrix in a  $\sigma$  and a  $\pi$  part:

$$P_{\mu\nu} = P_{\mu\nu}^{\sigma} + P_{\mu\nu}^{\pi},$$

$P_{\mu\nu}^{\sigma}$  is calculated only from the  $\sigma$  MOs and  $P_{\mu\nu}^{\pi}$  from the  $\pi$  MOs of the system. With the separability of the density matrix, the energy expressions  $E_{\text{SCF}}^{\sigma}$  and  $E_{\text{SCF}}^{\pi}$  can be formulated as:

$$E_{\text{SCF}}^{\sigma} = \sum_{\mu,\nu} P_{\mu\nu}^{\sigma} H_{\mu\nu} + \frac{1}{2} \sum_{\mu,\nu} \sum_k P_{\mu\nu}^{\sigma} \langle \mu\nu || k \rangle x_k^{\sigma} + E_{xc}^{\sigma}[\rho] + \frac{1}{2} E_{\text{SCF}}^{\sigma\pi},$$

and

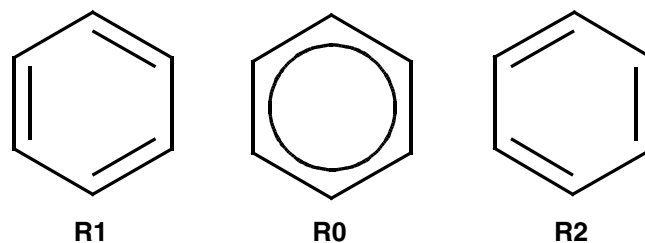
$$E_{\text{SCF}}^{\pi} = \sum_{\mu,\nu} P_{\mu\nu}^{\pi} H_{\mu\nu} + \frac{1}{2} \sum_{\mu,\nu} \sum_k P_{\mu\nu}^{\pi} \langle \mu\nu || k \rangle x_k^{\pi} + E_{xc}^{\pi}[\rho] + \frac{1}{2} E_{\text{SCF}}^{\sigma\pi},$$

respectively.

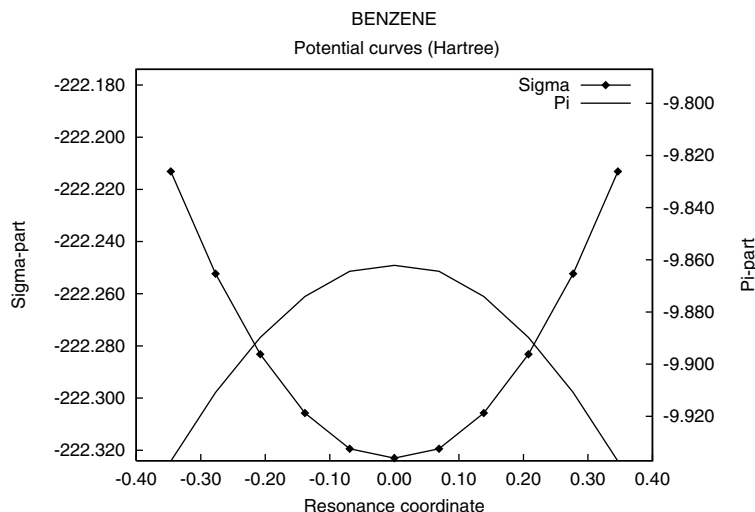
Following the original implementation of Jug and Köster [7], the energy expressions  $E_{\text{SCF}}^{\sigma}$  and  $E_{\text{SCF}}^{\pi}$  contain one half of the mixed  $\sigma$ - $\pi$  term  $E_{\text{SCF}}^{\sigma\pi}$

$$E_{\text{SCF}}^{\sigma\pi} = \frac{1}{2} \sum_{\mu,\nu} \sum_k (x_k^{\pi} P_{\mu\nu}^{\sigma} + x_k^{\sigma} P_{\mu\nu}^{\pi}) \langle \mu\nu || k \rangle + E_{xc}^{\sigma\pi}[\rho].$$

One term of the energy which does not exist in the Hartree–Fock theory is the exchange-correlation energy term  $E_{xc}[\rho]$ .



**Fig. 1** Minimum structure R0 and resonance structures R1 and R2 of benzene



**Fig. 2** Dependence of  $\sigma$  and  $\pi$  energy parts of benzene on the resonance coordinate

To derive the separation of  $E_{xc}[\rho]$ , we use the following formulation

$$E_{xc}[\rho] = c \int \rho(\mathbf{r}) \epsilon_{xc}[\rho] d\mathbf{r}.$$

Because  $\rho$  is derived from the density matrix, one can easily define a pure  $\sigma$  part  $E_{xc}^{\sigma}[\rho]$

$$E_{xc}^{\sigma}[\rho] = c \int \rho^{\sigma}(\mathbf{r}) \epsilon_{xc}[\rho^{\sigma}] d\mathbf{r}.$$

A similar expression can be defined for  $E_{xc}^{\pi}[\rho]$  by using the  $\pi$  instead of the  $\sigma$  density. The mixed term  $E_{SCF}^{\sigma\pi}[\rho]$  is then calculated as the difference between the total exchange-correlation energy and the pure  $\sigma$  and  $\pi$  terms

$$E_{xc}^{\sigma\pi}[\rho] = E_{xc}[\rho] - E_{xc}^{\sigma}[\rho] - E_{xc}^{\pi}[\rho].$$

For the separation of the energy in  $E^{\sigma}$  and  $E^{\pi}$ , one also has to include the nuclear repulsion term  $E_{NN}$  because of

$$E = E_{SCF} + E_{NN}.$$

For the separation of  $E_{NN}$ , we used the same scheme as proposed by Jug and Köster [7]. In this scheme, the  $\sigma$  and the  $\pi$  parts of the core-core repulsion are defined in the following way

$$E_{NN}^{\sigma} = \sum_A \sum_{B>A} \left( \frac{n_A^{\sigma} n_B^{\sigma}}{R_{AB}} + \frac{1}{2} \frac{n_A^{\sigma} n_B^{\pi} + n_A^{\pi} n_B^{\sigma}}{R_{AB}} \right)$$

$$E_{NN}^{\pi} = \sum_A \sum_{B>A} \left( \frac{n_A^{\pi} n_B^{\pi}}{R_{AB}} + \frac{1}{2} \frac{n_A^{\sigma} n_B^{\pi} + n_A^{\pi} n_B^{\sigma}}{R_{AB}} \right).$$

The numbers  $n_A^{\sigma}$  and  $n_A^{\pi}$  are representing the number of  $\sigma$  and  $\pi$  electrons of the atom  $A$  in a molecule. It is important that their sum has to equal the nuclear charge of the atom

$$Z_A = n_A^{\sigma} + n_A^{\pi}.$$

Finally, one obtains for the terms of the separated  $\sigma$  and  $\pi$  energies the following results

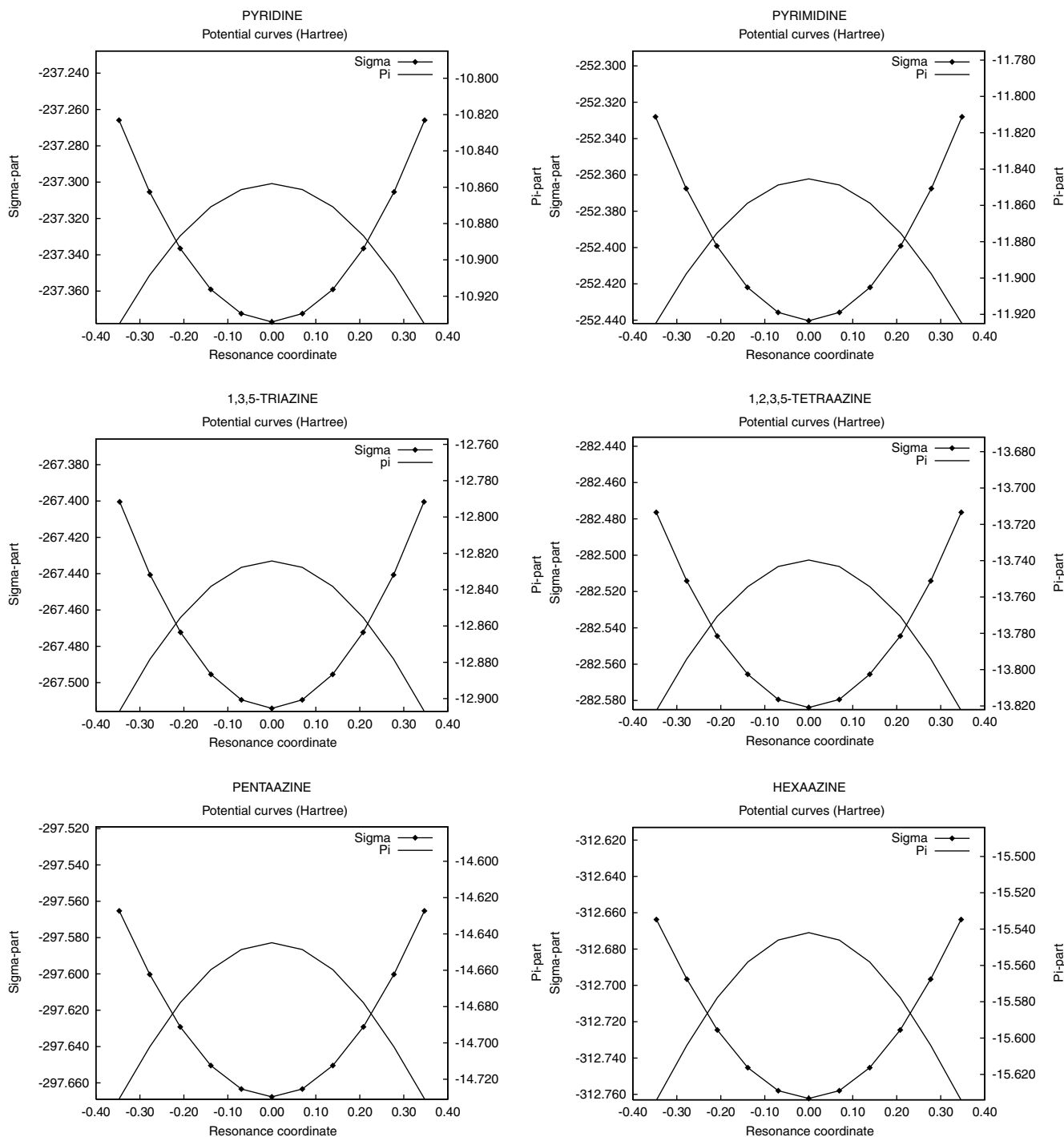
$$E^{\sigma} = E_{SCF}^{\sigma} + E_{NN}^{\sigma}$$

$$E^{\pi} = E_{SCF}^{\pi} + E_{NN}^{\pi}.$$

For the investigation of different ring systems, we implemented this scheme in the DFT program deMon [9].

#### 4 Distortions

To answer the question why for example benzene has a minimum structure with equal C–C bond lengths and not a Kekulé structure with alternating C–C bond lengths, one has to distort the benzene structure towards the Kekulé structure and follow the changes in energy. This leads to the problem how to perform these distortions. As shown in two recent review articles [4,5], there are several possibilities to do such a distortion towards a Kekulé structure. To have a unique way for these distortions, we tried to follow normal modes. For benzene, one can separate the normal modes in five groups: (1) out-of-plane vibrations, (2) vibrations of H–C bonds, (3) vibrations of C–C bonds, (4) vibrations of angles between H and C atoms and (5) vibrations of angles between C atoms. We looked at the vibrations of benzene of the third and fifth group. All the modes showed qualitatively the same behavior for the  $\sigma$  and the  $\pi$  energy. But problems occurred when we investigated the five-membered rings. For example in imidazole there was no normal mode which distorts the molecule in the direction of a structure with alternating bond lengths between the atoms in the ring. Only parts of the molecule were distorted by the normal modes. Therefore, we decided to choose distortions in the direction of fictitious Kekulé structures in which the double and single bond lengths between the atoms in the ring were set to experimental values like it was done in a previous study [7]. We use here the terms alternating and equal bond lengths instead of localized and delocalized bonds because in a system with alternating bond lengths the  $\pi$  electrons can still be delocalized to a certain amount. An example for this is butadiene. To measure the amount of distortion along these directions, we used the resonance



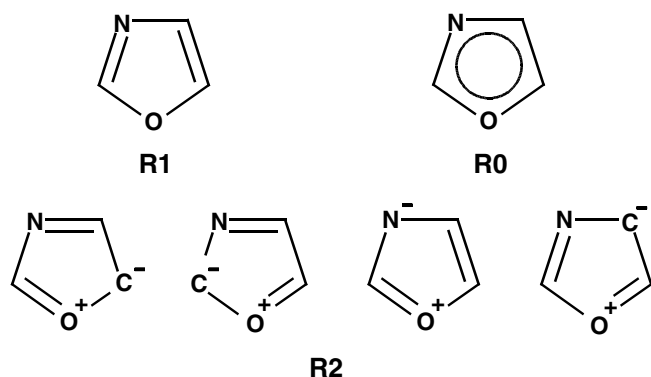
**Fig. 3** Dependence of  $\sigma$  and  $\pi$  energy parts of pyridine, pyrimidine, 1,3,5-triazine, 1,2,3,5-tetraazine, pentaazine and hexaazine on the resonance coordinate

coordinate  $r$ , which is defined in the following way:

$$r = \sum_i^{\text{atoms}} |\Delta \mathbf{r}_i| = \sum_i^{\text{atoms}} \sqrt{\Delta x_i^2 + \Delta y_i^2 + \Delta z_i^2}.$$

$|\Delta \mathbf{r}_i|$  is the length of the vector which connects the positions of an atom in two different structures.  $r = 0$  is always the

optimized, not distorted structure, here denoted as R0. The only exception from this rule is the neutral cyclobutadiene molecule, which will be discussed later. A negative value of  $r$  indicates the distortion towards the fictitious structure R1 and a positive value of  $r$  indicates the distortion towards the fictitious structure R2. The structures R0, R1 and R2 in the case of benzene are shown in Fig. 1. The structures between



**Fig. 4** Minimum structure R0 and resonance structures R1 and R2 of 1,3-oxazole

R0 and R1 or R0 and R2 were obtained by linear interpolation.

## 5 Six-membered rings

The result for benzene is shown in Fig. 2. The results are similar to the ones from Jug and Köster [7] but less pronounced in the difference between  $\sigma$  and  $\pi$  energy, which means that the balance between the  $\sigma$  and  $\pi$  energy curvature is more delicate. However, still one can conclude that the structure with equal bond lengths between the ring atoms is preferred over the ones with alternating bond lengths. This is due to the domination of the  $\sigma$  energy which destabilizes the molecule when it is distorted from its minimum structure.

The results for other six-membered ring systems, which were obtained by substituting successively the CH groups in benzene by nitrogen atoms ending up at hexaazine, are shown in Fig. 3. Also, in these systems the structures with equal bond lengths in the ring are determined by the curvature of the  $\sigma$  energy. Like benzene, these systems show the tendency that the  $\pi$  electrons would prefer a structure with alternating bond lengths. In the series from one to six substituted CH groups, the largest changes in the curvature can be found for the  $\pi$  energy, whereas the curvature for the  $\sigma$  energy stays more or less the same. From the comparison with the results from Jug and Köster [7], one can conclude that in the SINDO1 method [20] the influence of the  $\pi$  electrons is underestimated.

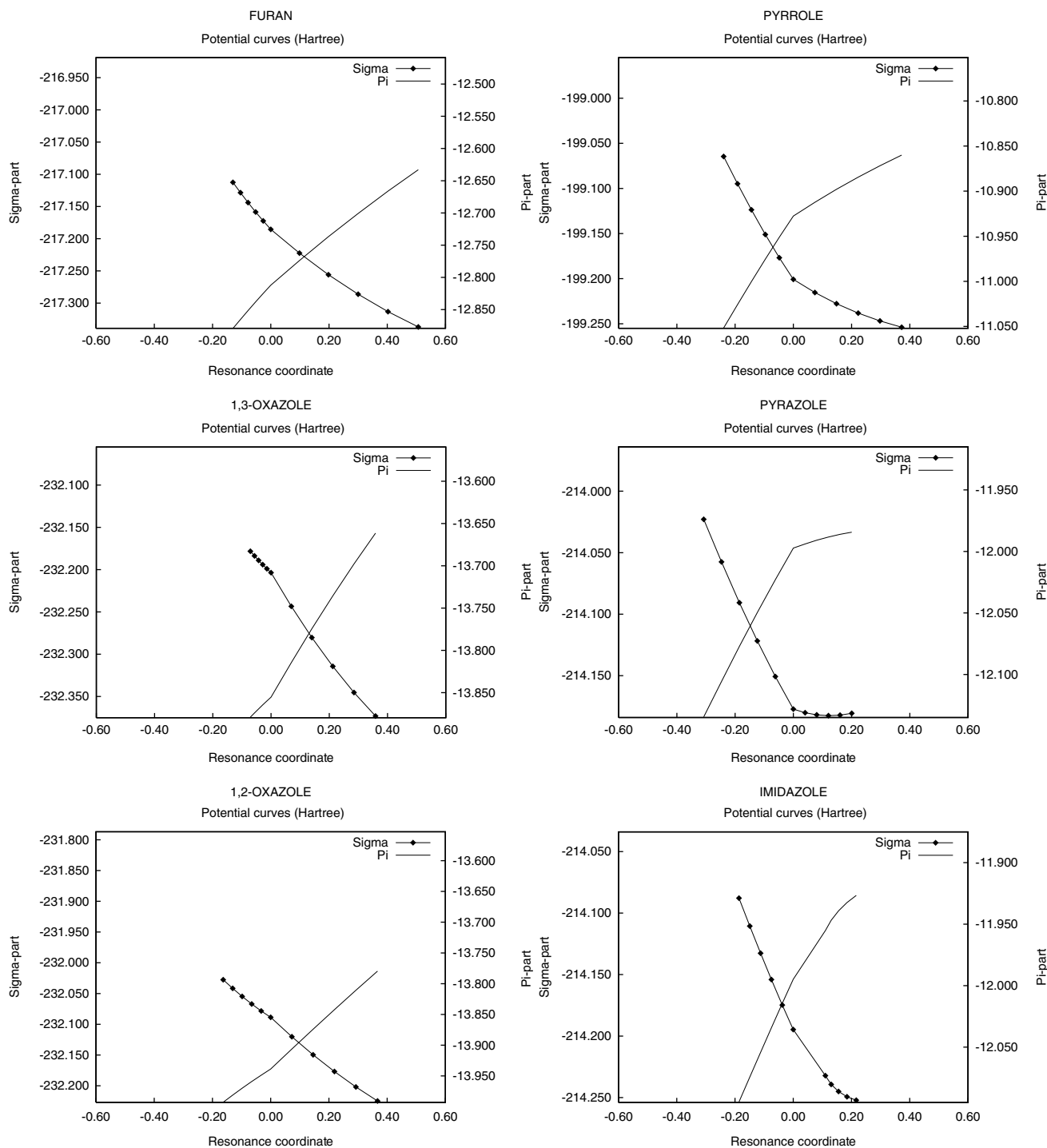
Comparing the curves obtained for benzene and hexaazine, one can observe that the  $\pi$  part of hexaazine is much larger than for the benzene, meaning that the  $\pi$  electrons in  $N_6$  have a much higher tendency to alternate the bond lengths than the  $\pi$  electrons in benzene. As a consequence, the total potential curve for hexaazine is very flat. This agrees with the fact that  $N_6$  is only metastable on the potential surface and will easily dissociate in  $3N_2$  with a small energy barrier for the transition structure. This was also observed in the semiempirical study performed by Jug and Köster [7].

## 6 Five-membered rings

As an example for this class of systems, we choose pyrrole, pyrazole, imidazole, furan, 1,3-oxazole and 1,2-oxazole. A problem in these systems is the definition of the Kekulé-like structures. There exist in general five different structures each with two double and three single bonds. But four of them show a charge separation. For comparison with the results of Jug and Köster [7], we denote the structure with no separated charges as R1. The others were superimposed and the resulting structure is denoted as R2. Figure 4 shows the structures R0, R1 and R2 for the 1,3-oxazole case. One has to mention that  $n_N^\pi$  which is used for the calculation of the  $\sigma$  and the  $\pi$  part of the core-core repulsion, is two for the N atom in the N-H group and one otherwise. Also, the  $n_O^\pi$  value is two. The corresponding  $n_N^\sigma$  values are calculated by subtracting the  $n_N^\pi$  value from the nuclear charge. The calculated  $\sigma$  and  $\pi$  energies for the studied five-membered rings are shown in Fig. 5. All systems show more or less the same behavior. For distortions in the direction towards the Kekulé-like structure R1, the  $\sigma$  energy shows a destabilization while the  $\pi$  energy tends to stabilize the system. However, the comparison of the absolute values of the changes reveals that the contribution of the  $\sigma$  part is dominant. In this sense, the five-membered ring systems behave similar to the six-membered ones. One can conclude that also in the five-membered ring systems the equality of the bond lengths between the atoms in the rings is determined by the  $\sigma$  electrons of the system and not by the  $\pi$  electrons. The latter ones would prefer a system with alternating bond lengths. The picture is different when the distortion is done towards the superimposed structure R2. There, the  $\pi$  energy shows a destabilization and the  $\sigma$  energy shows a stabilization of the system. As a result of the superimposition of the four different structures, we observed that only two bonds changed relative to the minimum structure R0. These bonds are double bonds in the structure R1. In this case, the bond lengths are not shorter than in the minimum structure but longer. This causes the reversed behavior.

## 7 Cyclobutadiene

We also investigated cyclobutadiene as a neutral, dicationic and dianionic molecule. The latter one was not investigated by Jug and Köster [7]. From the Hückel  $4n + 2$  rule, the neutral molecule is antiaromatic and the dicationic as well as the dianionic molecules are aromatic with equal C-C bond lengths. Again, the R0 structure related to  $r = 0$  is a structure with equal C-C bond lengths with a  $D_{4h}$  symmetry. R1 and R2 are rectangular structures with  $D_{2h}$  symmetry. As mentioned earlier the structure R0 is not the minimum structure for the neutral molecule. The minimum structure is related to R1 or R2 but with a smaller double bond and a larger single bond length. Therefore, the  $|r|$  value for the minimum structure of the neutral molecule is larger than the one for R1 or R2. In order to optimize the R0 structure for the neutral molecule in  $D_{4h}$  symmetry, fractional occupation was used to

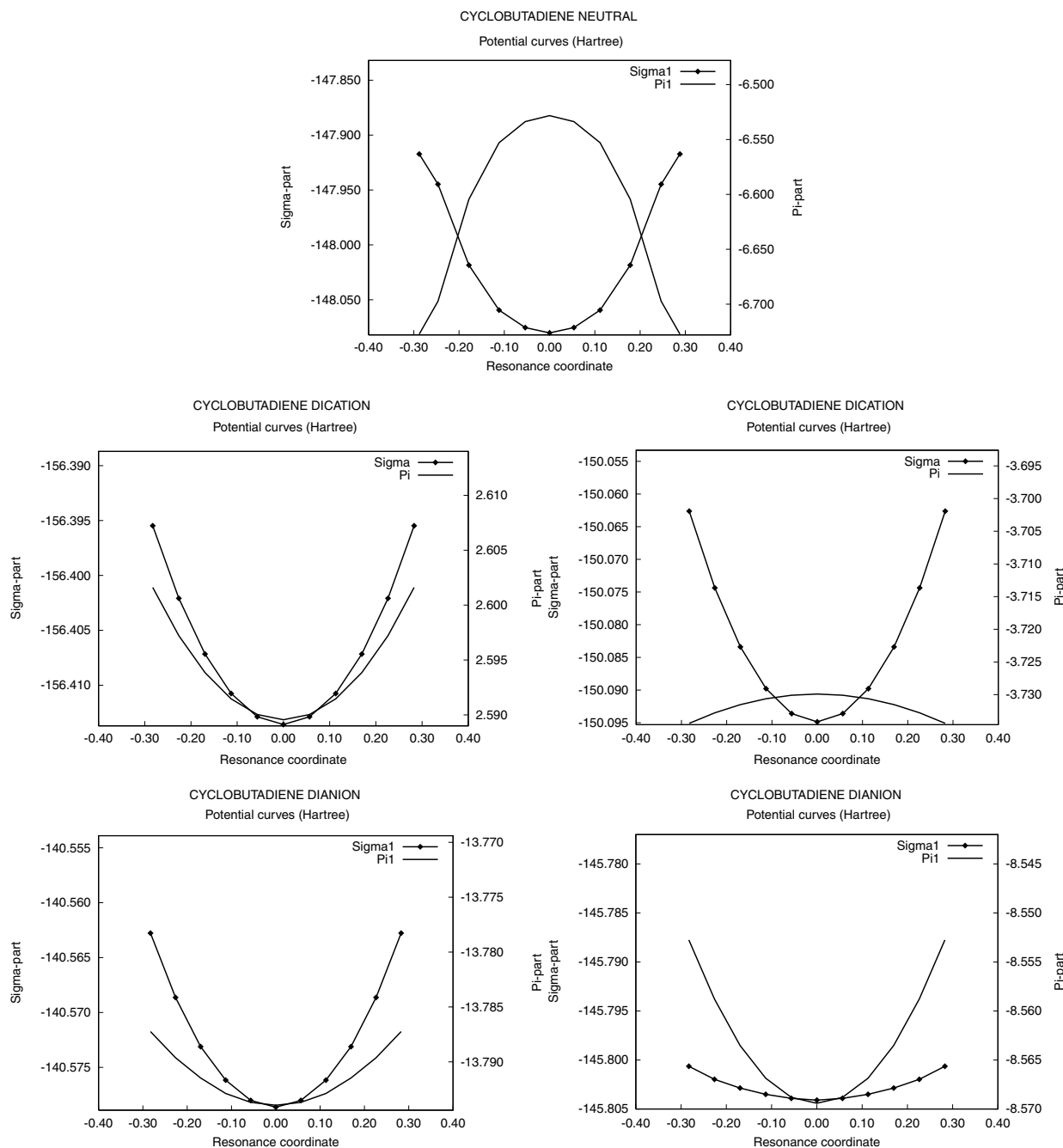


**Fig. 5** Dependence of  $\sigma$  and  $\pi$  energy parts of furane, pyrrole, 1,3-oxazole, pyrazole, 1,2-oxazole and imidazole on the resonance coordinate

keep the degeneracy of the HOMO. The  $\sigma$  and the  $\pi$  potential energy curves are shown in Fig. 6 on the left side. For the neutral molecule, the energy of the  $\pi$  electrons shows a stabilization for the structure with alternating C–C bond lengths compared with structure R0. However in contrast to benzene, here the curvature for the  $\pi$  energy is dominant. The conclusion is that the driving force for the minimum structure of

the neutral cyclobutadiene is the behavior of the  $\pi$  electrons. For the charged systems, the picture is different. There, both  $\sigma$  and  $\pi$  energies show a destabilization of the structure with alternating bond lengths compared with structure R0. This behavior is clearly different from the one of benzene.

One of the main ideas in the separation of the core–core repulsion in a  $\sigma$  and in a  $\pi$  part in the work of Jug and Köster



**Fig. 6** Dependence of  $\sigma$  and  $\pi$  energy parts of cyclobutadiene, cyclobutadiene dication with  $n_C^\pi = 1.0$ , cyclobutadiene dication with  $n_C^\pi = 0.55$ , cyclobutadiene dianion with  $n_C^\pi = 1.0$  and cyclobutadiene dianion with  $n_C^\pi = 1.38$

[7] was that one electron in the  $\sigma$  system of an atom compensates one ' $\sigma$ ' core charge of that atom and one electron in the  $\pi$  system compensates one ' $\pi$ ' core charge. In benzene, this leads to an  $n_C^\sigma$  value of five and an  $n_C^\pi$  value of one. The same numbers were used for the charged molecules of cyclobutadiene discussed above. But in the dication, the number of  $\pi$  electrons is  $\frac{1}{2}$  per carbon atom. And the 'half  $\pi$  electron' stands opposite to one ' $\pi$ ' nuclear charge. Whereas, for the  $\sigma$  part the relation is still one to one. To have an equal

compensation on the  $\pi$  and  $\sigma$  site, one has to consider that

$$\frac{n_C^\pi}{n_C^\sigma} = \frac{0.5}{5},$$

and that  $n_C^\sigma + n_C^\pi$  equals 6. From these relations, one obtains new values for  $n_C^\pi$  and  $n_C^\sigma$ , namely  $n_C^\pi \approx 0.55$  and  $n_C^\sigma \approx 5.45$ . For the dianionic molecule, this leads to  $n_C^\pi \approx 1.38$  and  $n_C^\sigma \approx 4.62$ . The results of the calculations with these values are shown in Fig. 6 on the right side. In the dicationic

system, the curvature of the  $\pi$  energy is reversed. Therefore, the trend is now qualitatively the same as for example in the case of benzene. However, in the cyclobutadiene dication the  $\pi$  energy is much less important relative to the  $\sigma$  energy. This is sensible because there are less  $\pi$  electrons in the systems relative to the  $\sigma$  electrons. For the dianionic system, only the relative strengths of the  $\sigma$  and  $\pi$  curvature change. Here, the  $\pi$  energy becomes dominant because the number of  $\pi$  electrons was increased compared with the neutral molecule. Opposite to the six- and five-membered ring systems in the dianionic molecule, the curvature for the  $\pi$  energy is positive. This can be explained because there are 6  $\pi$  electrons in the system but the distortion was done under the assumption that there are only two double bonds. It is not possible to create a symmetric Kekulé-like structure with three double bonds. The result with the changed  $n_C^\sigma$  and  $n_C^\pi$  values shows that this change is important. It leads to a unified behavior of the  $\sigma$  and  $\pi$  electrons in aromatic systems.

## 8 Concluding remarks

It was shown that it is possible to separate the total energy in a  $\sigma$  and in a  $\pi$  part at the DFT level of theory. The DFT results obtained for several six-, five- and four-membered ring systems are qualitatively the same as at the semiempirical level. Moreover, no qualitative difference is observed if local and non-local approximations are used. Normal mode coordinate distortions were investigated. This cannot be used as a general approach since it provides different results for six- and five-membered rings. For benzene, all investigated modes show qualitatively the same behavior for the  $\sigma$  and  $\pi$  energy curves, whereas for the five-membered rings, only parts of the molecule are distorted by the normal modes. In ring systems which fulfill the Hückel  $4n + 2$  rule, the minimum structure with equal bond lengths between the ring atoms is determined by the  $\sigma$  electrons. The  $\pi$  electrons would prefer

a structure with alternating bond lengths. However, they are overruled by the  $\sigma$  electrons. This is a general concept. It does not depend on the level of theory in the SCF calculations used for the analysis. It was also shown that the separation of the core–core repulsion is a crucial point in the separation. To avoid the assignment of different values for  $n_A^\sigma$  and  $n_A^\pi$  in different systems, a more generalized scheme is needed.

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