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Separation of σ and π Energies

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This work presents an all-electron density functional theory implementation of the separation of σ and π energies. On the basis of the separation of the electronic density, ρ, into σ and π parts, an ansatz for the separation of the exchange-correlation energy is proposed. The behavior of the σ and π energy parts in benzene is investigated under different distortions. The effect of local and nonlocal functionals on the separation of the exchange-correlation energy is studied, too.

1. Introduction

The separation of σ and π energies represents a fundamental concept in chemistry (see, for example, refs 1 and 2 and references therein). It can be traced back to the very early years of quantum chemistry.[3] Even so, the arbitrary nature of such a separation is well recognized and it has proven extremely useful for the rationalization of many experimental observations, like concerted reactions[4,5] or π back-donations.[6] In a recent review,[1] several methods for all-electron $\sigma-\pi$ energy separations were discussed. A fundamental problem for the direct separation of σ and π energies represents the nuclear repulsion term. Usually, this term is incorporated into the σ energy term. However, such a partitioning divides the systems into charged fragments. In this case, the σ energy term includes all nuclear charges but only a reduced number of electrons, namely, the σ electrons. On the other hand, the π energy term is free of the nuclear repulsion and, therefore, possesses a negative charge corresponding to the number of π electrons. It is obvious that this separation is unbalanced and cannot be supported by reasonable physical arguments.[1] To circumvent this problem, Shaik, Hiberty, and collaborators[7] performed $\sigma-\pi$ energy separations with constant nuclear repulsion energy, V_{nn}, along the distortion coordinate. This technique was successfully applied to gain insight into the σ and π energy behavior of various conjugated systems. A key result of these studies was the observation of the distortive property of the π energy in benzene.[2] The constant nuclear repulsion energy constraint, however, limits the application range of this approach. It dictates the bond distances in the alternating reference structures, too. To circumvent this limitation, Hiberty et al.[8] have devised a method which is independent of the V_{nn} problem and is based on quasiclassical reference states formed with spin-alternating determinants. Also, with this approach, a π driving force toward distortion was found in benzene. As an alternative, a direct partitioning of the nuclear repulsion energy as a $\sigma-\pi$ energy separation scheme was proposed,[9] too. This scheme was motivated by the idea of neutral subsystems, and it was implemented at a semiempirical level of theory. Again, π distortive properties were found for many conjugated systems, including benzene. In this paper, we present the implementation of this method in the Kohn−Sham density functional theory (DFT) code deMon.[10] On the basis of the separation of the electronic density, ρ, into σ and π parts, ρ^{σ} and ρ^{π}, we propose a new ansatz for the separation of the exchange-correlation energy. The behavior of these parts is investigated in detail for the benzene molecule. Distortions toward resonance structures as well as distortions along normal mode coordinates are considered. The effect of local and nonlocal functionals is investigated, too.

2. Theory

The nuclear repulsion energy partitioning is based on the separation of the nuclear charge of an atom, A, as

$$Z_{\mathrm{A}} = n_{\mathrm{A}}^{\sigma} + n_{\mathrm{A}}^{\pi}$$

Such an assignment can be unequivocally made for most neutral hydrocarbons if the total number of π electrons is known. The $\sigma-\pi$ energy separation for the nuclear repulsion energy is then defined as

$$\begin{aligned} E_{\mathrm{NN}} &= \sum_{\mathrm{A}}\sum_{\mathrm{B}>\mathrm{A}} \frac{Z_{\mathrm{A}}Z_{\mathrm{B}}}{R_{\mathrm{AB}}} \\ &= \sum_{\mathrm{A}}\sum_{\mathrm{B}>\mathrm{A}} \frac{(n_{\mathrm{A}}^{\sigma}+n_{\mathrm{A}}^{\pi})(n_{\mathrm{B}}^{\sigma}+n_{\mathrm{B}}^{\pi})}{R_{\mathrm{AB}}} \\ &= \sum_{\mathrm{A}}\sum_{\mathrm{B}>\mathrm{A}} \frac{n_{\mathrm{A}}^{\sigma}n_{\mathrm{B}}^{\sigma}}{R_{\mathrm{AB}}} + \frac{n_{\mathrm{A}}^{\sigma}n_{\mathrm{B}}^{\pi}+n_{\mathrm{A}}^{\pi}n_{\mathrm{B}}^{\sigma}}{R_{\mathrm{AB}}} + \frac{n_{\mathrm{A}}^{\pi}n_{\mathrm{B}}^{\pi}}{R_{\mathrm{AB}}} \end{aligned}$$

The mixed second term in this sum is partitioned equally among the σ and π energies. Thus, we obtain

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

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

In its original formulation, the above separation of the nuclear repulsion energy was combined with an (Hartree−Fock) electronic energy partition of the following form:

$$E_{\mathrm{el}}^{\sigma} = E_{\mathrm{core}}^{\sigma} + E_{\mathrm{2e}}^{\sigma\sigma} + \frac{1}{2}E_{\mathrm{2e}}^{\sigma\pi}$$

$$E_{\mathrm{el}}^{\pi} = E_{\mathrm{core}}^{\pi} + E_{\mathrm{2e}}^{\pi\pi} + \frac{1}{2}E_{\mathrm{2e}}^{\sigma\pi}$$

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Here, E^{σ}_{core} and E^{π}_{core} denote the σ and π core energies based on the separation of the density matrix into σ and π parts. The terms $E^{\sigma\sigma}_{2e}$ and $E^{\pi\pi}_{2e}$ refer to the two-electron Coulomb and exchange terms that include only σ or π density matrix elements. The corresponding mixed terms are collected in $E^{\sigma\pi}_{2e}$ and are equally partitioned among the σ and π energies. Unfortunately, the direct $\sigma-\pi$ energy partitioning has been limited to semiempirical energy expressions so far. The main obstacle to generalizing this partitioning scheme represents the multideterminant nature of correlated wave functions.

As an alternative, the Kohn−Sham density functional theory (DFT) method[11] represents a first-principle one-determinant technique that includes correlation explicitly by the exchange-correlation energy functional. By construction, the electronic density of the fictitious noninteracting Kohn−Sham reference system is identical to the electronic density of the real system. Because this density can be separated into σ and π parts, a $\sigma-\pi$ energy partitioning can be performed in the Kohn−Sham system. The electronic energy of the Kohn−Sham system is given by[12]

$$E_{\text{el}}[\rho] = E_{\text{core}} + E_{\text{J}} + E_{\text{xc}}[\rho]$$

Here, E_{core} and E_{J} denote the core and two-electron Coulomb energies. These energies can be separated into σ and π parts as in the Hartree−Fock approach. Again, the separation of the two-electron Coulomb energy produces pure σ and π terms, denoted as $E^{\sigma\sigma}_{\text{J}}$ and $E^{\pi\pi}_{\text{J}}$, as well as a mixed term, $E^{\sigma\pi}_{\text{J}}$. Following the original work,[9] the mixed two-electron Coulomb term is partitioned equally among the σ and π energies. For the partitioning of the exchange-correlation energy function, $E_{\text{xc}}[\rho]$, that depends on the electronic density, ρ, a new approach is needed. On the basis of the separation of the electronic density, ρ, into σ and π parts, ρ^{σ} and ρ^{π}, we propose the following ansatz

$$\begin{aligned} E_{\text{xc}}[\rho] &= E_{\text{xc}}[\rho^{\sigma}] + E_{\text{xc}}[\rho^{\pi}] + \Delta E_{\text{xc}} \\ &= E^{\sigma\sigma}_{\text{xc}} + E^{\pi\pi}_{\text{xc}} + E^{\sigma\pi}_{\text{xc}} \end{aligned}$$

Again, the mixed term $E^{\sigma\pi}_{\text{xc}}$ is partitioned into equal parts that are assigned to the σ and π energies. Therefore, we find for the Kohn−Sham σ and π energy expressions

$$E^{\sigma} = E^{\sigma}_{\text{core}} + E^{\sigma\sigma}_{\text{J}} + \frac{1}{2}E^{\sigma\pi}_{\text{J}} + E^{\sigma\sigma}_{\text{xc}} + \frac{1}{2}E^{\sigma\pi}_{\text{xc}} + E^{\sigma}_{\text{NN}}$$

$$E^{\pi} = E^{\pi}_{\text{core}} + E^{\pi\pi}_{\text{J}} + \frac{1}{2}E^{\sigma\pi}_{\text{J}} + E^{\pi\pi}_{\text{xc}} + \frac{1}{2}E^{\sigma\pi}_{\text{xc}} + E^{\pi}_{\text{NN}}$$

3. Results and Discussion

The $\sigma-\pi$ energy separation discussed in the previous section has been implemented in the Kohn−Sham DFT program deMon.[10] The calculations were performed using the exchange-correlation contributions proposed by Vosko, Wilk, and Nusair (VWN)[13] and by Becke and Lee, Yang, and Parr (BLYP).[14,15] The DZVP basis set[16] was employed.

In Figure 1, the σ and π energies of benzene, calculated with the VWN and BLYP functionals are plotted along the resonance coordinate that is defined as

$$r = \sum_{i}^{\text{atoms}} |\Delta\vec{r}| = \sum_{i}^{\text{atoms}} (\Delta x_i^{\,2} + \Delta y_i^{\,2} + \Delta z_i^{\,2})^{1/2}$$

Here, Δx_i, Δy_i, and Δz_i denote the changes of the positions of the ring atoms relative to the center of mass, as described in ref 9. The relative σ and π energies are reported in kilocalories per mole. These energies are the results of the partial optimization of the hydrogen atoms keeping the carbon atoms fixed. The top of Figure 1 shows the result of the calculation with the VWN functional. The σ and π energies in the middle of Figure 1 are calculated with the BLYP functional using the partial optimized geometries obtained with the local approxima-

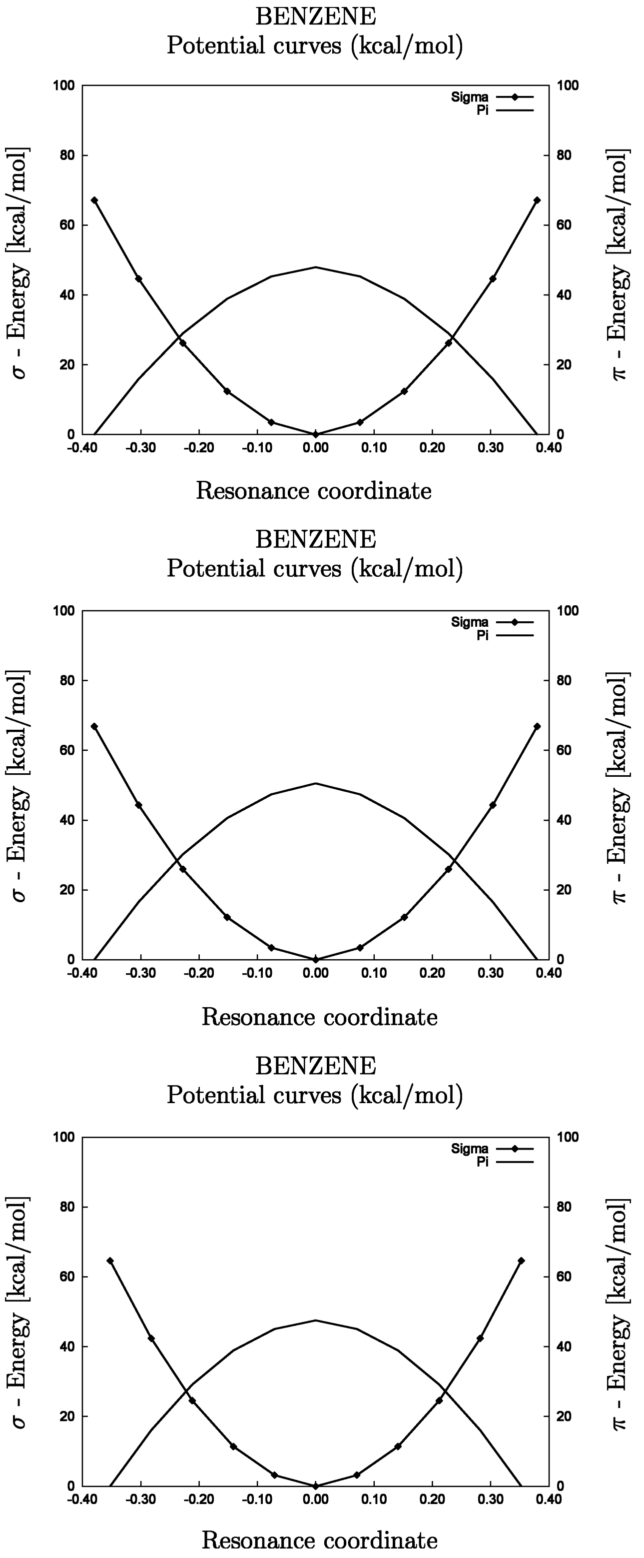

Figure 1. Dependency of σ and π parts of the total energy of benzene along the resonance coordinate. The calculations have been performed with the VWN functional (top) and with the BLYP functional considering the geometry obtained with the VWN functional (middle) and with the BLYP functional (bottom).

tion. The bottom of Figure 1 shows the result obtained with the partial optimized geometries and energies performed with the BLYP functional.

As resonance structures, D_{3h} Kekulé structures with single and double bonds of 1.52 and 1.32 Å are used. They are located around ±0.4 on the resonance coordinate. The D_{6h} equilibrium structure of benzene is located at the origin of the resonance coordinate.

Figure 1 shows that the σ energy possesses a positive curvature and the π energy a negative curvature at the equilibrium structure of benzene. This means that the π energy in benzene represents a driving force toward bond alternation, whereas the σ energy favors bond equalization. Due to the larger curvature of the σ energy, no bond alternation is seen in benzene. It should be noted that bond alternation is not equivalent to bond localization. The delocalization of the π electrons represents a stabilization of the system. However, it does not necessarily imply bond equalization. As an example, take butadiene. The delocalization of the π system lowers the energy and at the same time results in bond alternation. The same situation appears in benzene; however, the σ framework in benzene is more resistant toward alternation. This can be rationalized simply by the ratio of formal single and double C−C bonds in the system. In butadiene, two double bonds, representing the electrons in the π system, act against one single bond. As a result, the driving force of the π system toward alternation dominates. On the contrary, in benzene, the number of formal single and double bonds is equal. In this situation, the driving force of the σ system toward bond equalization dominates, as our calculations show.

These results are in qualitative agreement with the semiempirical calculations from ref 9. However, our DFT results show a much more delicate balance between the σ and π energy curvature. In particular, the negative curvature of the π energy is considerably larger in our study.

Comparing the results of the top, middle, and bottom of Figure 1, we notice that there are no significant changes between local and nonlocal functionals. We also studied the behavior of the σ and π energies in benzene along the b_{2u} mode distortion. The direction of this coordinate is different from the direction of the resonance coordinate used in Figure 1. Nevertheless, both distortions lead to structures with alternating bonds. Again, the above-defined metric for the distance measurement is used. Figure 2 shows the result of the calculation performed with the BLYP functional considering the partial optimized geometries obtained from the local approximation. As can be seen from Figure 2, the σ energy possesses a positive curvature and the π energy a negative curvature at the equilibrium structure of benzene along this mode.

4. Conclusions

In this work, an all-electron density functional theory implementation of the separation of σ and π energies was presented. An ansatz for the separation of the exchange-correlation energy was proposed. It represents the first formulation that allows dissecting the energies from a fully correlated system where both the σ and π energies involve electronic correlation. The behavior of the σ and π energies was investigated under different distortions for the benzene molecule. The effect of local and nonlocal functionals for the separation of the exchange-correlation energy was investigated, too. It was shown that there are no significant changes in the σ and π energy curves for local or nonlocal approximations.

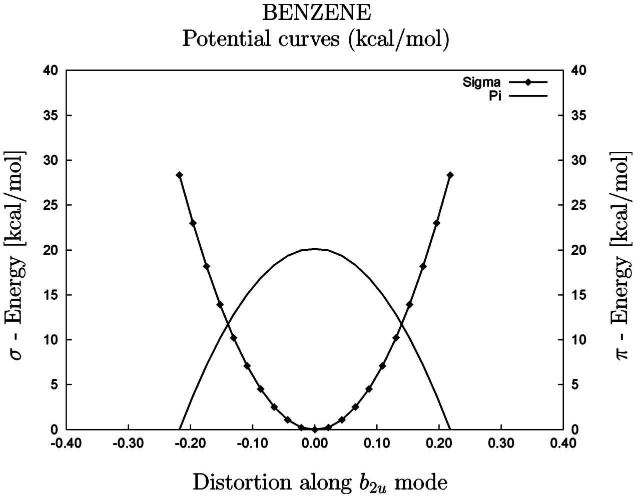

Figure 2. Dependency of σ and π parts of the total energy of benzene along the b_{2u} mode distortion.

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