Conceptual and Computational DFT in the Study of Aromaticity

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1. Introduction

Aromaticity is a key concept in physical organic chemistry.[1–4] It has been shown to be a useful quantity in the rationalization of structure, stability, and reactivity of many molecules.

The property is associated with the cyclic delocalization of electrons, resulting in extra stabilization in the case of aromatic compounds and destabilization in the case of antiaromatic compounds. In 1996, Jiao and Schleyer proposed the following definition of aromaticity: *Compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic electron delocalization also may result in bond length equalization, abnormal chemical shifts, and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilization. Those compounds with exalted paramagnetic susceptibility may be called antiaromatic.*[3]

Several criteria have been put forward in attempts to rationalize and quantify this property.[1–4] These can be roughly divided into four categories: energetic, structural or geometrical, magnetic, and reactivity-based measures. Many of these properties are available through quantum chemical calculations. Which quantity one chooses the best and the relationship between these different quantities (i.e., their orthogonality or nonorthogonality) is still a matter of debate.[5–9]

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When using the energetic criterion for establishing the aromaticity of a compound, one compares the excess of stability of the structure due to cyclic electron delocalization relative to a well chosen reference system, in most cases olefines or conjugated

polyenes.[1−4,10] Energetic data can be gathered from experiment and from quantum chemical calculations. However, since the contribution of aromaticity is only a part of the total energy content, it is very important to accurately describe the energies of all the molecules that are compared. This can be achieved by using isodesmic, homodesmotic, or hyperhomodesmotic reactions, where one benefits optimally from error cancellation.[11−17] Moreover, other contributions, such as strain, may be present, overwhelming the influence of the aromaticity. Nevertheless, it remains important to use accurate energetic data and to use a well chosen reference structure. The choice of an appropriate reference system in the calculation of the resonance energy can be avoided when applying the so-called spin-coupled theory, developed by Cooper, Gerratt, and Raimondi.[18−25]

On the basis of geometrical considerations, molecules should show a decrease in aromatic character when they possess a high degree of bond alternation and deviate significantly from planarity. Several quantitative measures of this bond alternation have been proposed. Among the most important ones, we mention the Julg aromaticity index[26] and the harmonic oscillator model of aromaticity (HOMA).[27−29]

Several magnetic criteria have been put forward as measurements of the aromaticity of molecules. Aromaticity can be defined as the ability of a compound to sustain an induced ring current; these compounds are then called diatropic. Antiaromatic compound are called paratropic. Several methods can be used to measure if a compound can sustain a ring current. The most important ones are based on NMR chemical shifts and diamagnetic susceptibilities. Protons attached to aromatic rings typically undergo a downfield shift from the olefinic region. When the protons are above or in the aromatic ring, however, as, e.g., in the case of the inner protons of [n] annulenes,[2] an upfield shift is noticed in the ^{1}H NMR spectrum. For antiaromatic compounds, these directions are opposite. On the basis of this fact, one has used the Li chemical shift of the Li$^+$ complexed aromatic ring as an absolute measure of aromaticity.[30−36] Recently, Schleyer et al. introduced the so-called nucleus-independent chemical shift (NICS), which is the absolute magnetic shielding computed at the centers of the ring one is probing.[37] The size dependence of these values can be overcome by dissecting the NICS values, i.e., calculating independently the σ and π contributions to the chemical shift.[38]

Concerning the diamagnetic susceptibilities, two factors are important when measuring a compound's aromaticity: the anisotropy[39,40] and the exaltation.[41] Aromatic molecules were found to possess high diamagnetic susceptibility anisotropies $\Delta\chi$, i.e., large differences between the perpendicular and average in plane component of the diamagnetic susceptibility

$$\Delta\chi = \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}) \qquad (1)$$

where χ_{xx}, χ_{yy}, and χ_{zz} are the three principal components of the diamagnetic susceptibility.[3,39,40]

Moreover, their exaltation Λ, the difference between the true diamagnetic susceptibility χ_M and the one calculated by an additive scheme using atom and bond increments $\chi_{M'}$

$$\Lambda = \chi_M - \chi_{M'} \qquad (2)$$

is also high.[3,41] The exaltations are negative (diamagnetic) for aromatic compounds and positive (paramagnetic) for antiaromatic compounds. Both of these quantities are however size dependent.[42]

A final and less often used criterion is based on the chemical behavior, i.e., the reactivity of the system. Aromatic species will in most cases try to leave their π electron system unchanged and will thus prefer to undergo electrophilic substitution instead of addition. Not many indices have tried to quantify this effect in order to probe the aromaticity,[2] and famous exceptions to this reactivity behavior are known.[3]

It can thus be seen from this selection of the most important and most often used aromaticity criteria that the classification of a molecule as aromatic, nonaromatic, or antiaromatic as well as the quantification of the degree of aromaticity can only be made if accurate values of a series of energetic, geometric, or magnetic properties are available, both from theory and experiment. This is especially true for the indicators which are calculated from the differences of the properties of the parent system and a reference system.

In this review, we will deal with molecular properties obtained via quantum mechanical methods where comparison with experiment when available will be made. Note, however, that not all properties considered are amenable to experiment. We will in particular show how the study of aromaticity can benefit a lot from "density functional theory" (DFT).[43−52] During the past decade, this theory has received enormous attention and gained a lot of popularity in the quantum chemistry community. Although some theories were developed in the past using the electron density (for a review, see, e.g., ref 44), it obtained its definitive status after the formulation of two theorems proven by Hohenberg en Kohn in 1964, putting forward the electron density $\rho(\mathbf{r})$ as the basic variable of an atomic or molecular system instead of the wave function Ψ.[53] Moreover, these theorems state that the ground-state energy and electron density can be obtained from a variational principle, minimizing the energy with respect to changes in electron density. In 1965, Kohn and Sham offered a practical implementation scheme using orbitals to construct the electron density, leading to a set of exact one-electron Hartree−Fock-like equations, the Kohn−Sham equations, containing however the unknown exchange-correlation potential.[54] As such, DFT enables the approximate incorporation of electron correlation at a reduced computational cost in comparison with traditional correlated ab initio methods such as Møller−Plesset perturbation theory,[55] configuration interaction,[56,57] and coupled cluster theory.[58] It has been shown in the literature that many properties can be calculated with comparable accuracy as the above-mentioned much more expensive beyond SCF

wave function based methods. However, as will be shown in section 2, there also exists an interesting noncomputational side of this theory, where a lot of traditional or new chemical concepts found a rigorous definition or were introduced, some of which can also be used as aromaticity measures.

2. Computational (Calculational) vs Conceptual DFT

In the second theorem of Hohenberg and Kohn,[53] a variational principle is formulated, stating that the ground-state density is that density that minimizes the energy of the system for a fixed number of electrons

$$\delta(E - \mu \int \rho(\boldsymbol{r}) \mathrm{d}\boldsymbol{r}) = 0 \qquad (3)$$

where μ is a Lagrange multiplier associated with the constraint of a constant number of electrons. This equation leads to the DFT analogue of the Schrödinger equation

$$\mu = v(\boldsymbol{r}) + \frac{\delta F}{\delta \rho(\boldsymbol{r})} \qquad (4)$$

where $v(\boldsymbol{r})$ is the external (i.e., due to the nuclei) potential and F the so-called Hohenberg–Kohn functional, containing the kinetic energy and the electron–electron repulsion energy. Kohn and Sham rewrote this as an orbital equation having the form[54]

$$\left[-\frac{1}{2}\nabla^2 + v(\boldsymbol{r}) + v_{xc}(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' \right] \psi_i = \epsilon_i \psi_i \quad (5)$$

where the only unknown quantity is the exchange-correlation potential $v_{xc}(\boldsymbol{r})$, the functional derivative of the exchange-correlation density functional E_{xc}

$$v_{xc}(\boldsymbol{r}) = \frac{\delta E_{xc}}{\delta \rho(\boldsymbol{r})} \qquad (6)$$

In eq 5, ψ_i are the Kohn–Sham orbitals, of which the squares must sum up to the total electron density of the system

$$\rho(\boldsymbol{r}) = \sum_i |\psi_i|^2 \qquad (7)$$

In recent years, many accurate forms of the exchange-correlation functional were derived, permitting the calculation of many atomic and molecular properties with accuracies comparable to computationally much more involved traditional ab initio wave function correlated methods. In section 4, we will indeed argue that computational DFT, to use the terminology put forward by Parr to describe the former aspect of contemporary DFT research,[49] can indeed be used to probe the aromaticity of large molecular systems in a cost-effective way using the different energetic, geometrical, and magnetic criteria listed in the Introduction.

However, it has become clear in recent years that there is also a very important "noncomputational" or conceptual side to DFT.[49] In this aspect of the theory, the central quantities are the so-called response functions, i.e., the response of the chemical system's properties (such as, e.g., the energy or the electron density) to perturbations in its number of electrons N and/or external potential $v(\boldsymbol{r})$. As can be realized, perturbing the number of electrons or the external potential of a molecule ultimately describes the whole of its chemistry. During the last two decades, the above-mentioned response functions have been identified with quantities, readily known by chemists but in most cases only empirically defined. Parr, Donnelly, Levy, and Palke identified the chemical potential, the Lagrange multiplier μ of eqs 3 and 4 with the electronegativity[59] defined by Pauling as "the power of an atom in a molecule to attract electrons to itself"[60] and for which many scales have been made available since (for a review, see, e.g., ref 61). Moreover, they showed that the chemical potential could be expressed as the derivative of the energy with respect to the number of electrons at constant external potential[59]

$$\mu = -\chi = \left(\frac{\partial E}{\partial N} \right)_{v(\boldsymbol{r})} \qquad (8)$$

in accordance with earlier work of Iczkowski and Margrave.[62] It should be remarked that when assuming a quadratic relationship between E and N and in a finite difference approximation, eq 8 can be rewritten as

$$\chi = \frac{\text{IE} + \text{EA}}{2} \qquad (9)$$

where IE and EA are the vertical ionization energy and electron affinity respectively, thereby recovering the electronegativity definition of Mulliken.[63] Moreover, theoretical justification was provided for Sanderson's principle of electronegativity equalization which states that when two or more atoms come together to form a molecule, their electronegativities become adjusted to the same intermediate value.[64–66]

Parr and Pearson identified the second derivative of E with respect to N with the chemical hardness η[67]

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\boldsymbol{r})} \qquad (10)$$

a quantity introduced in the late 1950s and early 1960s by Pearson in the framework of his classification of Lewis acids and bases, leading to the introduction of the hard and soft acids and bases principle.[68–71] This principle states that hard acids prefer to bond to hard bases and soft acids to soft bases.

Again, using a finite difference approximation and a quadratic $E = E(N)$ curve, this equation reduces to

$$\eta = \text{IE} - \text{EA} \qquad (11)$$

which, by using Koopmans theorem, becomes

$$\eta = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}} \qquad (12)$$

i.e., the difference between the orbital energy of the LUMO and the HOMO, the band gap. In the past,

large band gaps have been associated with stable structures. This finding is nicely captured in the maximum hardness principle, also formulated by Pearson, which states that "molecules will arrange themselves to be as hard as possible". Parr and Chattaraj provided a rigorous and widely general proof for this principle based on a combination of statistical mechanics and the fluctuation–dissipation theorem.[72]

The inverse of the global hardness is called the global softness[71,73]

$$S = \frac{1}{\eta} \tag{13}$$

which was empirically shown to be proportional to the polarizability of the system[74–76] and of which also exists a local version, the local softness, defined as[73]

$$s(\mathbf{r}) = \left[\frac{\partial \rho(\mathbf{r})}{\delta \mu}\right]_{v(\mathbf{r})} \tag{14}$$

This equation can be rewritten as

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})}\left(\frac{\partial N}{\partial \mu}\right)_{v(\mathbf{r})} \tag{15}$$

where the quantity $(\partial \rho(\mathbf{r})/\partial N)$ was introduced by Parr and Yang as the Fukui function $f(\mathbf{r})$,[77,78] a generalization of Fukui's frontier molecular orbital reactivity index.[79]

It is also possible, although not trivial, to define a local hardness.[80–87] It has been shown that this local hardness $\eta(\mathbf{r})$ can be approximated reasonably in the valence region of the atom or the molecule as[80,85]

$$\eta(\mathbf{r}) \approx -\frac{V^{\text{el}}}{2N} \tag{16}$$

where V^{el} is the electronic part of the molecular electrostatic potential $V(\mathbf{r})$

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}\mathrm{d}\mathbf{r}' \tag{17}$$

This electrostatic potential gives the interaction energy of the system with a unit positive charge[88–91] and as such can be used as a reactivity index toward electrophilic attacks.

In a more general way, the local softness and hardness can also be obtained from a kernel description. The softness kernel $s(\mathbf{r},\mathbf{r}')$ was introduced as[82]

$$s(\mathbf{r},\mathbf{r}') = \frac{\delta \rho(\mathbf{r})}{\delta u(\mathbf{r}')} \tag{18}$$

where $u(\mathbf{r}')$ is a modified potential, defined as $u(\mathbf{r}') = v(\mathbf{r}') - \mu$. In addition, one introduces the hardness kernel $\eta(\mathbf{r},\mathbf{r}')$ as

$$\eta(\mathbf{r},\mathbf{r}') = -\frac{\delta u(\mathbf{r})}{\delta \rho(\mathbf{r}')} \tag{19}$$

These kernels are true inverses, i.e.

$$\int s(\mathbf{r},\mathbf{r}')\eta(\mathbf{r}',\mathbf{r}'')\mathrm{d}\mathbf{r}' = \delta(\mathbf{r} - \mathbf{r}'') \tag{20}$$

The local softness can be obtained from the softness kernel by integration

$$\int s(\mathbf{r},\mathbf{r}')\mathrm{d}\mathbf{r}' = s(\mathbf{r}) \tag{21}$$

In addition, one can obtain the local hardness from the hardness kernel by weighting it with an appropriate weighting function $\lambda(\mathbf{r}')$ and integrating

$$\int \lambda(\mathbf{r}')\eta(\mathbf{r},\mathbf{r}')\mathrm{d}\mathbf{r}' = \eta(\mathbf{r}) \tag{22}$$

where

$$\int \lambda(\mathbf{r}')\mathrm{d}\mathbf{r}' = 1 \tag{23}$$

Chattaraj, Cedillo, and Parr[92] formulated the variational principle for the hardness. The function $g(\mathbf{r})$ that minimizes the functional $\eta[g] = \int\int g(\mathbf{r})\eta(\mathbf{r},\mathbf{r}')g(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$ subject to the condition that $\int g(\mathbf{r})\mathrm{d}\mathbf{r} = 1$ is the Fukui function $f(\mathbf{r})$, and the value of the functional at the minimum, i.e., $\eta[f]$, is the chemical hardness of the system. Recently, Ayers and Parr used the basic DFT variational principles in the development of variational principles for important DFT-based descriptors of chemical reactivity, the Fukui function and the local softness.[93]

In the next section, we will show the importance of the computational side of density functional theory in the accurate calculation of some of the proposed indicators for aromaticity. In section 4 we will focus our attention on the contribution of conceptual DFT, with special emphasis on the hardness.

3. Computational DFT: Performance of DFT Methods in the Calculation of Aromaticity Measures

As stated in the Introduction, many aromaticity criteria can be calculated for molecules using quantum chemical calculation methods. For large molecules, it is now widely recognized that density functional theory provides a valuable and in some cases even the only alternative to get accurate values for these criteria.[52] The major drawback on using these DFT methods is that they cannot be systematically improved to the exact solution of the Schrödinger equation. As a result, the performance testing of the different density functionals is necessary and comparison of the results with experiment and high-level accurate ab initio wave function methods is always advisable. The performance of DFT methods in the description of structural, energetic, and magnetic molecular properties has been reviewed quite substantially in recent times, and we will thus not repeat these findings. DFT methods are, in general, capable of generating a variety of isolated molecule properties such as, e.g., dipole moments,[94,95] infrared frequencies[52] and intensities,[94,95] electrostatic potentials,[95,96] Fukui functions,[95,96] ionization energies,[97,98] electron affinities,[97,98] electronegativities,[97,98] hardnesses,[97,98] and geometries[52] quite accurately (NMR properties vide infra), especially via the hybrid func-

tionals, such as, e.g., B3LYP[99,100] and B3PW91[99,101] (for a review of the other different density functionals available, see, e.g., ref 52). As an example directly related to the study of aromaticity, in a study on bridged[14] annulenes, the B3LYP method was found to provide a good balance between delocalized and localized bond structures.[102] In a subsequent study of cyclic polyenes, it was found that the HF method tends to favor structures with localized bonds while DFT and MP2 methods tend to be in favor of overly delocalized aromatic structures.[103] Concerning reaction energies, the situation is somewhat more complicated. No really general conclusions can be drawn yet concerning the performance of DFT methods. It is, however, known that traditional ab initio wave function methods in most cases overestimate aromatic stabilization energies.[102,104] Consider, e.g., the case of benzene. The aromatic stabilization energy of this molecule

$$3\ CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \bigcirc + 3\ CH_2{=}CH_2$$

is experimentally found to be 19.7 ± 0.2 kcal/mol[105] based on the above depicted homodesmotic reaction. Both HF and MP2 overestimate this value, by 5.0 and 9.2 kcal/mol, respectively, when calculated with the 6-31G* basis set.[104] The B3LYP/6-31G* aromatic stabilization energy if found to be 19.5 kcal/mol at 298 K, which is in very good agreement with the experimental value.[106,107] Also, other studies are available stating the usefulness of DFT methods in the calculation of isodesmic and homodesmotic reaction energies.[52,108–115]

The performance of DFT methods in the calculation of NMR properties has also been the subject of many recent theoretical studies and reviews, and we will thus not go into details.[52,116–119] The techniques used in ab initio methods to deal with the gauge dependence of the shielding constants, such as GIAO, IGLO, and CSGT (for a review and references on these methods, see ref 119), have also been combined with DFT methods, but not any of these seems to be superior to the others.[119] It can, however, be concluded in general that for compounds containing elements of the first row, the gradient-corrected and hybrid functionals seem to provide shifts of roughly the same accuracy, which are usually better than the corresponding Hartree−Fock results.[52] The improvements are, however, not systematic, and better results are obtained at the MP2 level,[52] although there are some famous counterexamples such as the case of the ^{13}C chemical shifts in o-benzyne, where HF and MP2 fail and DFT performs well.[120] It can be concluded that the results are sufficiently accurate for most purposes, so that the DFT methods emerge as the best cost/quality methods for NMR calculations of large organic molecules.[52] For very large systems, also MNDO NMR calculations have been developed.[121] In a recent study, Patchkovskii and Thiel applied this methodology to the calculation of NICS values for a large number of organic molecules including transition states of a number of pericyclic reactions.[122] They found that the semiempirical NICS

values were smaller in absolute value than the ab initio ones but that they often showed the same trends. Moreover, the semiempirical NICS values correctly assign the aromatic or antiaromatic character of the molecule. It has also been shown that magnetic susceptibilities can be evaluated to a reasonable accuracy by among other DFT methods.[3,123−130] Ruud, Helgaker, and Jørgenson studied the effect of electron correlation on molecular magnetizabilities.[127] They concluded, as was also seen in earlier papers,[125,128] that the effect of electron correlation on the calculated magnetizabilities is in most cases small, except for systems showing large static correlation effects. Also, the calculated anisotropic magnetizabilities were found to lie within the experimental error bars. In a recent study, Wilson, Amos, and Handy investigated the performance of DFT methods in the prediction of magnetizabilities and nuclear shielding constants. They concluded that DFT magnetizabilities calculated using hybrid density functionals were of the same quality as MP2. Moreover, it was also stated that gradient-corrected functionals yield results inferior to Hartree−Fock.[130]

In this review, we will also put forward a series of other measures of the aromaticity such as polarizabilities, electrostatic potentials, properties of the electron density, and hardness. The performance of DFT methods in their calculation has also been reviewed quite recently among others by the present authors, so the reader is referred to these works for details.[52,95,98]

4. Conceptual DFT and Aromaticity

A. The HOMO–LUMO Gap, Absolute and Relative Hardness

In this section, it is shown that some properties and quantities arising from the noncomputational or conceptual side of density functional theory can be proposed as aromaticity measures.

Haddon and Fukunaga showed that a direct relationship exists between the resonance energies and the HOMO−LUMO gaps in [4n + 2] annulenes and thereby, as one of the first, demonstrated the connection between the thermodynamic and kinetic criterion of the aromatic character.[131] Indeed, they showed that

$$RE = -\frac{(\pi p_{rs})^2(\epsilon_{LUMO} - \epsilon_{HOMO})}{24} \qquad (24)$$

where RE is the resonance energy and p_{rs} the bond order of the r−s bond. Moreover, it was demonstrated by the same authors that a similar relationship exists between the resonance energies and the reduced ring currents for these systems.[132]

As stated in section 2, the HOMO−LUMO gap is an approximation to the global hardness of the system, measuring stability. It is, however, no surprise that hardness and aromaticity show some relationship. In a number of studies, some of them already dating from the late 1960s and early 1970s, a small HOMO−LUMO gap has been associated with antiaromaticity.[133−141]

Minsky, Meyer, and Rabinovitz[138] studied doubly charged systems derived from fused benzenoid polycyclic compounds and found a linear relationship between the paratropic ^{1}H NMR shifts $\Delta\delta$ and the HOMO−LUMO energy gap. Indeed, they found for dications and dianions

$$\Delta\delta(\text{ppm}) = -1.23\Delta_{\text{HL}} + 4.31 \qquad (25)$$

and

$$\Delta\delta(\text{ppm}) = -2.50\Delta_{\text{HL}} + 6.40 \qquad (26)$$

respectively, where Δ_{HL} is the HOMO−LUMO gap in eV.

Sinanoğlu et al. used the HOMO and LUMO bonding types as indicators of aromaticity.[142,143] Cioslowski and Polansky derived relationships between the Huckel π electron energy, the number of Kekulé structures, and the HOMO−LUMO separation.[144] For benzenoid hydrocarbons, Cioslowski derived the following relationship between for the HOMO−LUMO gap Δ_{HL}

$$\Delta_{\text{HL}} = 2[-2.90611(2n_{CC}/n_C)^{1/2} + 3.91744K^{2/N}] \quad (27)$$

where n_{CC} and n_C are the numbers of carbon−carbon bonds and carbon atoms, respectively, and K the number of Kekulé structures.[145]

Choi and Kertesz[103] studied the properties of [4n] and [4n + 2] annulenes as a function of n, up to n = 66 at the Hartree−Fock and DFT levels of theory. They calculated various indices of aromaticity and studied the bond length alternation. They found that the bond length alternation increased with increasing N and that, at the B3LYP/6-31G* level, the structural transition from the delocalized to the localized structures occurs when the HOMO−LUMO gap approaches 2.0 eV.

Fowler pointed out that the HOMO−LUMO separation cannot be seen as a general criterion for the aromaticity or kinetic stability of polycyclic aromatic hydrocarbons, since this energy separation is generally smaller for the larger hydrocarbons whether they are kinetically stable.[146] As a result, Aihira et al. proposed using the HOMO−LUMO separation multiplied by the number of conjugated atoms[147−150] and successfully applied this index to measure the kinetic stability of polycyclic aromatic hydrocarbons[147] and fullerenes.[148−150] Moreover, this so-called T index was found to correlate with the chemical reactivity at the most reactive site for a number of fullerene isomers containing isolated pentagons.[150]

Zhou, Parr, and Gharst[151] put forward the absolute hardness as a measure of aromaticity. Their argumentation is based on the fact that both aromaticity and hardness are measures of high stability and low reactivity. In their contribution, a simple proof for this fact was given. Consider a species S. The energy change for the process

$$S^+ + S^- \rightarrow 2S$$

can be shown to be equal to

$$\text{EA}_S - \text{IE}_S = -\eta_S \qquad (28)$$

i.e., the difference between the electron affinity and the ionization energy of the species S, which is equal to the negative of the hardness.

In a first contribution, the relationship was studied between the absolute hardness, obtained from Huckel theory, and the resonance energy per π-electron (REPE), defined as

$$\text{REPE} = \frac{E_\pi - E_{\text{ref}}}{N} \qquad (29)$$

where E_π is the total π energy, E_{ref} the energy of a well-chosen reference system, and N the number of π electrons. Several scales have been proposed for this REPE, which differ only in the definition of their reference structure.[152−154] For benzenoid hydrocarbons, it was shown that an excellent linear correlation exists between both the Hückel and experimental hardnesses and the Hess and Schaad (REPE(HS)) and Aihara−Gutman−Milun−Trinajstic (TREPE) REPE scales. For alternant conjugated hydrocarbons, however, it was noted that only the HOMO orbital energy, an approximation to the hardness when the electron affinity of LUMO energy is set to zero, is necessary to measure the aromaticity; for heterocycles, however, the correlation between the aromaticity measures and the HOMO orbital energies failed, whereas there is a good correlation with the hardness. In the next contribution, the concept of relative hardness was introduced, which is the hardness difference between the molecule and some hypothetical acyclic reference structure.[155] It was found that also this relative hardness or "hardness exaltation" correlated very well with the REPE indices and that it thus can also serve as a measure of aromaticity, as can be seen from Figures 1 and 2, where the relative hardness was plotted against the Hess and Schaad resonance energies for conjugated and heteroconjugated hydrocarbons.
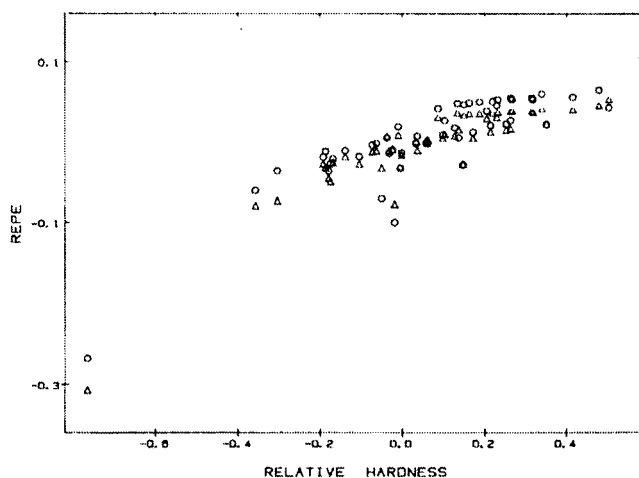

Figure 1. Correlation of the resonance energies per π-electron (in units of β) with the relative hardness (in units of $-\beta$) for a series of conjugated hydrocarbons. Points $\triangle$ indicate TREPE, points $\bigcirc$ indicate REPE (Hess and Schaad). (Reprinted with permission from ref 155. Copyright 1989 American Chemical Society.)
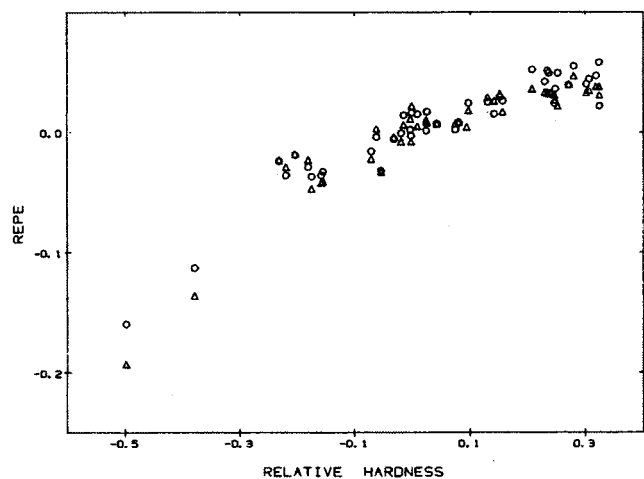
Figure 2. Correlation of the resonance energies per π-electron (in units of β) with the relative hardness (in units of $-\beta$) for a series of heteroconjugated hydrocarbons. Points $\triangle$ indicate TREPE, points $\bigcirc$ indicate REPE (Hess and Schaad). (Reprinted with permission from ref 155. Copyright 1989 American Chemical Society.)

In this contribution, it was also recognized that a clear dividing line exists between aromatic and antiaromatic species, set to about a Hückel hardness of -0.2β, where β is the carbon parameter of Hückel theory. The Hückel and relative Hückel hardness of benzene are, e.g., equal to -1.0β and -0.428β, respectively, those of cyclobutadiene are 0β and 0.765β, respectively. For comparison, the values for C_{60} are -0.378β and -0.316β, predicting this molecule to be aromatic.[156]

Zhou and Navangul calculated MNDO hardnesses for 14 benzenoid hydrocarbons and showed it to be a good indicator for their aromaticity.[157] Using the hardness criterion, kekulene, coronene, and the corannulene tetraanion were all predicted to be superaromatic,[158] also confirmed by calculations of Babic and Trinajstic[159] and Cioslowski, O'Connor, and Fleischmann in the case of kekulene.[160] Jiao and Schleyer, however, concluded, based on geometrical, energetic, and magnetic criteria of aromaticity, that kekulene is not superaromatic.[161]

After these two papers, the relationship between the hardness, on one hand, and the aromaticity, on the other hand, remained relatively unexplored.

Chamizo, Morgado, and Sosa put forward the absolute hardness, as calculated by the HOMO−LUMO gap, as a measure of the aromaticity of organometallic compounds.[162] They calculated the hardnesses for a series of metallacycles containing W, Co, Ti, Fe, and Ir and a series of 15 heterobenzenes and heterocyclopentadienes. For the latter, they found that the dividing line between aromatic and nonaromatic species approximately corresponds to 1.28 eV. They, moreover, found the aromaticity sequence

cyclopentadienyl anion >
     cyclosilapentadienyl anion, thiophene >
selenophene, phosphabenzene > arsabenzene >
                                    stibabenzene

as can be witnessed from their results in Table 1.

Table 1. Extended Hückel HOMO and LUMO Energies and Absolute Hardnesses from a Series of Aromatic Molecules (Taken ref 162; all values in eV)

compound	ϵ_{HOMO}	ϵ_{LUMO}	η
cyclopentadienyl anion	−6.82	−11.96	2.56
benzene	−8.27	−12.81	2.27
cyclosilapentadienyl anion	−6.42	−10.76	2.18
thiophene	−7.86	−12.20	2.17
selenophene	−8.15	−12.28	2.06
phosphabenzene	−9.43	−12.75	1.66
arsabenzene	−9.28	−12.41	1.56
stibabenzene	−9.62	−11.95	1.16
cyclobutadiene	−10.70	−10.70	0.00

In 1997, Bird studied the absolute hardness as a criterion for heteroaromaticity.[163] In this study, it was found that good correlations existed between the Zhou and Parr hardness values and the REPE values for polycyclic benzenoid hydrocarbons but that the correlation was not good when heterocyclic compounds were included. This was also confirmed in a 1998 study by Bean, where only a very low correlation between the HOMO−LUMO gap, on one hand, and geometric, energetic, and other delocalization measures was found for a series of five-membered heteroaromatic compounds.[164] However, Bird suggested using the reformulation of the hardness in terms of molar refractivity as suggested in the work of Komorowski[165,166]

$$\eta = \frac{19.6}{R_D{}^3} \qquad (30)$$

where R_D is indeed this molar refractivity, making the concept of hardness somewhat more accessible to the experimental chemist. Using this relationship, the hardnesses were calculated for a series of aromatic and heteroaromatic rings, showing good correlations with resonance energies and Bird's I_A index, based on the deviation of uniformity of bond orders in aromatic rings.[167−170] Table 2 lists some values of hardnesses obtained in this way for some selected molecules, together with their Bird index.

Roy, Choho, De Proft, and Geerlings studied the reactivity of acetaldehyde and some aromatic aldehydes toward acid-catalyzed oxygen-18 exchange reactions with DFT-based reactivity descriptors, the local softness, and local hardness.[171] It was found that while the local softness values reproduce intramolecular reactivity (i.e., site selectivity) trends, the intermolecular O-18 exchange sequence can only be explained via local hardness. The reactivity trends were also discussed using the concept of aromaticity. Byrn and Calvin argued that the reactivity (i.e., electrophilicity) of the carbonyl carbon in aromatic aldehydes would be decreased by delocalization of its positive charge through extended resonance.[172] This observation points to the fact that local hardness can be correlated with aromaticity. In this context, Roy, Choho, De Proft, and Geerlings calculated the global softnesses for the set of aromatic aldehydes; this softness was found to increase going from acetaldehyde to 9-phenanthraldehyde, an apparent conflicting situation with the fact that global hardness should be positively correlated with aromaticity.

Table 2. Absolute Hardnesses (taken from ref 155) (η(ZP), in units of β, and[163] η(B)) together with the Resonance Energy per π Electron (REPE, $\times 10^3$ β),[155] the Resonance Energy (RE, kcal/mol),[169,170] and the Bird Index I_A[169,170] for Some Selected Aromatic Molecules

compound	η(ZP)	REPE	RE	I_A	η(B)
furan	0.650	7	27.2	53	7.42
thiophene	0.796	32	43.0	81.5	6.74
pyrrole	0.859	39	34.8	85	7.12
pyrazole	0.783	55	40.4	90	7.35
imidazole	0.762	42	40.0	79	7.38
benzene	1.000		45.8	100	6.60
pyridine	0.773	58	43.3	86	6.78
pyrimidine	0.725	49	40.6	84	6.86
pyrazine	0.622	49	40.9	89	6.85
benzofuran	0.676	36	55.4	94	5.94
benzothiophene	0.695	44	69.8	119	5.66
indole	0.716	47	73.8	146	5.92
naphthalene	0.618	55	80.3	142	5.55
quinoline	0.525	52	81.0	134	5.65
isoquinoline	0.556	51	81.0	133	5.66
biphenyl	0.704	60	94.7	-	5.25
anthracene	0.414	47	111.5	206	4.82
phenanthrene	0.605	55	117.1	210	4.94
pyrene	0.445	51	141.4	-	4.65
tetracene	0.295	42	147.6	-	4.42
1,2-benzanthracene	0.452	50	147.2	-	4.44
chrysene	0.520	53	152.8	-	4.43
triphenylene	0.684	56	151.7	-	4.50
dibenz[a,b]anthracene	0.473	51	187.6	-	4.21
coronene	0.539	53	226.0	-	3.99

However, it is generally known that softness is proportional to the volume of the molecule. To account for the "volume effect" on the global softness, an "intrinsic global softness" S^{int} was introduced as

$$S^{int} = S/V \qquad (31)$$

where V is the volume of the corresponding molecule. It should be noted that this intrinsic global softness is nothing other than the local softness of the corresponding homogeneous system with the same global softness, i.e., with $\rho(\boldsymbol{r}) = N/V$ for all $\boldsymbol{r}$, N again being the number of electrons. Demanding that the intrinsic global softness and intrinsic global hardness should give one upon multiplication, the corresponding "intrinsic global hardness" is given as

$$\eta^{int} = \eta V \qquad (32)$$

Again, it should be noticed that this intrinsic global hardness is nothing other than the exact local hardness of the corresponding homogeneous system with the same global hardness. The volumes of the molecules were obtained by integrating the volume enclosed by the 0.001 au contour of the electron density. A very good correlation existed between this intrinsic global hardness and the aromaticity of the molecules, much better than, e.g., the correlation of the global softness and the aromaticity, as can be seen in Figure 3. It was therefore concluded that by filtering the volume effect out of the global softness, quantities arise, the intrinsic global softness and hardness, directly reflecting aromaticity.

Balawender, De Proft, Komorowski, and Geerlings showed that of the two available measures of the global hardness, only the HOMO−LUMO gap showed
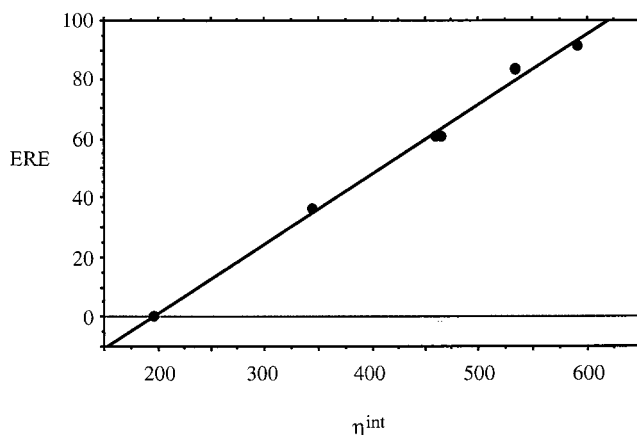

Figure 3. Correlation of the intrinsic global hardness and the empirical resonance energies for a series of aromatic aldehydes. (Reprinted with permission from ref 171. Copyright 1999 Wiley.)

Table 3. Magnetic Susceptibility Exaltations Λ, One-Half of the HOMO−LUMO Energy Gap $\Delta_{HL}/2$ (eV), and Right-Hand Side Derivative of the Molecular Valence $(\partial V_M/\partial N)^+$ for a Series of C_4H_4X Rings (Taken from ref 173)

X	Λ	$\Delta_{HL}/2$	$(\partial V_M/\partial N)^+$
CH^+	32.6	4.226	−0.134
SiH^+	13.2	4.478	−0.212
BH	12.8	4.814	−0.395
AlH	11.2	4.690	−0.274
CH_2	−2.4	5.929	−0.791
PH	−3.3	5.668	−0.852
SiH^-	−7.7	4.705	−0.947
O	−9.1	6.528	−0.998
S	−10.01	6.139	−1.074
NH	−12.11	6.640	−1.047
CH^-	−17.5	6.725	−1.148

a general correlation with the aromaticity as measured by the magnetic susceptibility exaltation, as shown in Table 3.[173]

They, however, showed that since this magnetic susceptibility exaltation is the difference of the magnetic susceptibilities of a conjugated system and that of a corresponding cyclic system with localized double bonds, it should be related to the change of molecular valence. In their work, they found that this difference is well approximated by the change of the molecular valence with the number of electrons at a constant external potential, which was calculated analytically at the HF/6-31G* level. In particular, the right-hand side derivative of the molecular valence (i.e., the change of the molecular valence when the number of electrons is increased) showed a very good correlation with the Λ values for a series of heterocyclic five-membered rings, as also shown in Table 3, and was thus proposed as a new measure of aromaticity. A clear advantage of this approach is that there is no need to choose a reference structure.

B. The Molecular Electrostatic Potential

As stated in the Introduction, a local version of the hardness exists, the local hardness, which was shown to be related to the electronic part of the electrostatic potential. The question thus arises if the electrostatic potential itself can be used to measure aromaticity.

In a study on cyclobutadiene, cyclooctatetraene, and 1,4-dihydropyrazine, Murray, Seminario, and Politzer used the electrostatic potential as a probe of electron delocalization by taking the minimum along the C= C double bonds and comparing it with the minimum found in ethylene.[174]

Suresh and Gadre revisited Clar's aromatic sextet theory[175,176] using the molecular electrostatic potential topography[177] (see also the references cited in this paper for details and applications of molecular electrostatic potential topography). This sextet theory describes the aromaticity of these compounds on the basis of a maximum number of sextets, which are six π electrons represented by a circle. They characterized the topography of the electrostatic potential of the π regions in 12 polycyclic benzenoid hydrocarbons. The positions of the (3, +3) critical points of the electrostatic potential or MEP minima were shown to lie close to the shorter bonds and should thus, as these authors state, provide insight on how the π electrons are shared between the different ring atoms. Benzene, which has six identical (3, +3) critical points, is thus be classified as the most perfect cyclic π-delocalized system, whereas the six-membered rings of the other hydrocarbons show less delocalization. The other polycyclic benzenoid hydrocarbons show three or less of these points (3, +3) critical points with different values. The average values of the electrostatic potential at the critical points for each ring and for the whole molecule were found to correlate with local aromaticity values estimated using the method of Li and Jiang[178] and the hardness values of Zhou and Parr, respectively, as can be seen from Figure 4 where the scaled up average values of the MEP at all the critical points of the molecule $\bar{V}_g^s$ are plotted against their Zhou–Parr hardnesses.
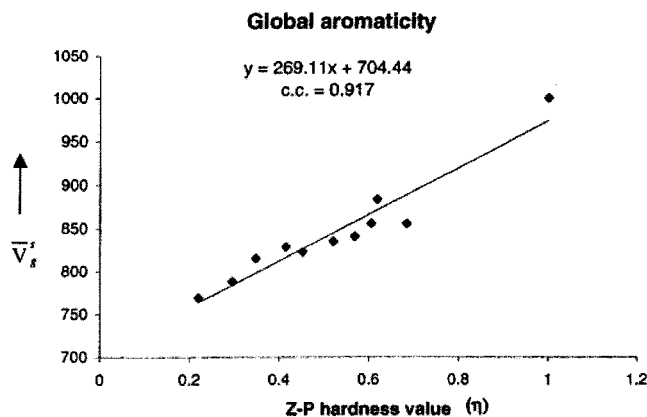

Figure 4. Plot of the scaled up average electrostatic potential at all the MEP critical points $\bar{V}_g^s$ against the Zhou–Parr hardnesses for a series polycyclic benzenoid hydrocarbons. (Reprinted with permission from ref 177. Copyright 1999 American Chemical Society.)

C. Polarizability Related Measures of Aromaticity

As stated in section 2, the hardness correlates inversely with the polarizability. In view of section 4.A, it is quite normal that various aromaticity indices have been proposed based on the molecular polarizability. Bulgarevich suggested that the π

Table 4. Polarizability Exaltations Γ (au) and Hardnesses η (eV) for a Series of C_4H_4X Five-Membered Rings (X = O, S, Se, and Te) (All values taken from ref 183)

C_4H_4X X =	Γ	η
O	−26.45	5.33
S	−25.63	5.01
Se	−25.06	4.91
Te	−24.65	4.48

contribution to the in-plane polarizability divided by the number of endocyclic bonds was to be used as an aromaticity indicator.[179] The same author also suggested using the ratio of the longitudinal polarizability of the formal single bond and the formal double bond in the Lewis formula of the structure.[179] The mean polarizabilty of the molecule was suggested by Lazzeretti and Tossell as an indicator of aromaticity,[180] whereas Archibong and Thakkar suggested the excess of in-plane over out-of-plane polarizability.[181,182]

Millifiori and Alparone put forward the dipole exaltation polarizability parameter Γ as a measure of aromaticity[183]

$$\Gamma = \langle\alpha\rangle_M - \langle\alpha\rangle_M \qquad (33)$$

where $\langle\alpha\rangle_M$ is the mean dipole polarizability and

$$\langle\alpha\rangle_M = \sum_i \langle\alpha\rangle_i \qquad (34)$$

with $\langle\alpha\rangle_i$ as the mean atomic or group polarizability.

In Table 4, these polarizability exaltations are listed for a series of C_4H_4X systems (X = O, S, Se, and Te), together with the global hardnesses.

Katritzky et al. argued that the polarizability captures a mixture of "magnetic" and "classical" aromaticity.[5]

D. The Electron Density and Related Properties

The fundamental property of DFT is the electron density $\rho(\mathbf{r})$, and it was thus tempting to test its predictive power for aromaticity. In the past, the topological theory of the electron density distribution as developed by Bader et al. (for a general overview of this theory, see ref 184 and the references therein) has been used to study the features of aromatic and antiaromatic molecules. Some of the central points in the Atoms In Molecules theory are the so-called critical points, the points in space where the gradient vector of the electron density is zero, i.e., $\nabla\rho(\boldsymbol{r}) = 0$. These critical points are characterized as the rank and signature of the Hessian matrix of the electron density. The rank equals the number of nonzero eigenvalues of this Hessian matrix, and the signature is the algebraic sum of the signs of the eigenvalues $(\lambda_1, \lambda_2, \lambda_3)$. The positions of the nuclei are (3, −3) critical points (maxima), the (3, −1) critical points are bond critical points, the (3, +1) critical points are ring critical points, and the (3, +3) critical points are cage critical points. The amount of π character of a bond was proposed to be determined by the so-called ellipticity ϵ of the charge density at the bond critical

point and the bond order n,[185−188] where

$$\epsilon = \frac{\lambda_1}{\lambda_2} - 1 \tag{35}$$

$$n = \exp[A(\rho_c - B)] \tag{36}$$

In eq 35, λ_1 and λ_2 are two negative eigenvalues of the charge density Hessian at the bond critical point, ρ_c is the electron density at this point, and A and B are constants. The remaining eigenvalue λ_3 measures the curvature of the electron density perpendicular to the ring plane. For the C−C bond in ethane, $\lambda_1 = \lambda_2$ and thus the conjugation between single and double bonds will be characterized by the fact that $\epsilon > 0$. Moreover, in this case, $n > 1$. The relative π character of a bond can then be determined by the ratio of its ϵ value and the ϵ value of C=C bond in ethylene. Howard and Krygowski performed HF/6-31G** calculations on some polycyclic aromatic hydrocarbons.[189] They concluded that the electron density, the Laplacian of the density, and ϵ at the bond critical points were found linearly related to the bond lengths. The same descriptors at the ring critical points, however, are linearly related to the HOMA aromaticity index. Moreover, they concluded that the most suitable ring critical point aromaticity descriptor is the eigenvalue λ_3. It was also found that the π density topological descriptors correlate almost equally well with the HOMA and also the NICS indices for these compounds. In the same work, the hardnesses of these compounds are reported also; benzene is found to be the hardest molecule and thus the most aromatic molecule of the series, in agreement with other aromaticity measures.

Murray, Abu-Awwad, and Politzer computed the average local ionization energy and electrostatic potentials on the surfaces of nine aromatic hydrocarbons.[190] This average local ionization potential, originally defined in the framework of Hartree−Fock theory, is given as

$$\bar{I}(\boldsymbol{r}) = \sum_i \frac{\rho_i(\boldsymbol{r})|\epsilon_i|}{\rho(\boldsymbol{r})} \tag{37}$$

where $\rho_i(\boldsymbol{r})$ is the electron density of the ith atomic or molecular orbital, ϵ_i is its orbital energy, and $\rho(\boldsymbol{r})$ is the total electron density of the system. This function was interpreted as the average energy needed to remove an electron from position $\boldsymbol{r}$; low local values of the function in space thus point to places where the removal of electrons is relatively easy and can thus be interpreted as regions within the molecule where an electrophilic attack will preferably occur. Different studies using the usefulness of this index are available (see, e.g., the references cited in ref 190). Moreover, this index was also shown to be a measure of local polarizability and related to the DFT concept of local temperature.[191] On the molecular surfaces of the aromatic hydrocarbons, the average local ionization potential was shown to have minima in certain bond regions and near specific carbon atoms, characterizing bonds as olefin-like in the former case.

Table 5. Ring Bond Populations (in number of electrons) and Aromatic Stabilization Energies E(H) (kcal/mol) for a Series of Five-Membered Rings (All data taken from ref 192)

X	C−C	C=C	C−X	E(H)
CH$^+$	1.94	3.27	2.19	−59.05
BH	2.04	3.27	2.24	−22.45
CH$_2$	2.19	3.56	1.91	2.80
O	2.36	3.72	1.47	15.47
N	2.56	3.58	1.86	21.00
CH$^-$	3.00	3.00	3.00	23.35
AlH	2.11	3.13	2.40	−8.27
SiH$_2$	2.15	3.23	2.26	−2.22
PH	2.29	3.34	2.05	5.92
S	2.50	3.48	1.76	18.74
P	2.77	2.99	2.44	21.39
GeH$_2$	2.16	3.25	2.29	−0.06
AsH	2.25	3.31	2.03	4.21
Se	2.49	3.45	1.72	17.05

Chesnut and Bartolotti described the aromaticity of a series of substituted five-membered cyclopentadienyl systems using the electron localization function (ELF),[192] which is defined for a single determinant wave function built from Hartree−Fock or Kohn−Sham orbitals as

$$\text{ELF} = \frac{1}{1 + (D/D_h)^2} \tag{38}$$

where

$$D = \frac{1}{2}\sum_i |\nabla\psi_i|^2 - \frac{1}{8}\frac{|\nabla\rho|^2}{\rho} \tag{39}$$

and

$$D_h = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3} \tag{40}$$

This localization function can be interpreted as a local measure of the Pauli repulsion between the electrons as a result of the Pauli exclusion principle.[193] It allows the definition of regions in the molecule that are associated with different electron pairs. This concept was developed further and applied by Savin, Silvi, and co-workers, among others the topology of the ELF has been analyzed (see, e.g., the references cited in ref 192); one can define basins in which one or more electron pairs can be found. Chesnut and Bartolotti found that the basin properties of the formally single bond in the cyclopendienyl system correlated very well with the homonuclear homodesmotic stabilization energies of these systems, as can be seen from Table 5 where the ring bond populations of the different bonds are listed together with these stabilization energies.

E. Activation Hardness and Hardness Change during a Chemical Reaction

Up to now, essentially aromaticity descriptors for starting and final products have been discussed. In

recent years, interest arose in the evolution of these quantities along the reaction path. Particular attention has been devoted to the case of the hardness, in the context of the maximum hardness principle.

When looking at the change of the hardness along the reaction path (the so-called "hardness profile"), it was found in many cases that the hardness goes through a minimum at the transition state.[194–219] Studies are also available where the aromaticity is measured along a reaction path.[25,27,28,220–222]

In a chemical reaction, a more stable transition state, measured by the magnitude of the activation energy, implies an easier chemical reaction. Aromatic transition states are also known to facilitate the chemical reaction. Zhou and Parr defined the activation hardness as the hardness difference of the products and the transition state and found, in the case of electrophilic aromatic substitution, that the smaller the activation hardness, the faster the reaction is.[223] For this specific reaction they also found a correlation of the activation hardness and Wheland's cation localization energy, also proposed as an indicator of aromaticity.[224] This finding can indeed be interpreted as a manifestation of the maximum hardness principle. A transition state with a high hardness is more stable than one with a smaller hardness and is therefore easier to reach energetically. The same can be said about two transition states with different aromaticity. Again, hardness and aromaticity parallel each other. The activation hardness has been used in numerous applications for the prediction of site selectivity in chemical reactions.[196,198,200,202,208,211,213,214,216,217,218,225]

5. Conclusion

The study of aromaticity remains a very important topic in the chemical literature. Many indicators of this concept are available, many of which are accessible through quantum chemical calculations. In recent years, density functional theory has been a shooting star in molecular quantum mechanics. The development of better and better exchange-correlation functionals made it possible to calculate many molecular properties with comparable accuracies to traditional correlated ab initio methods, with more favorable computational costs. Unfortunately, contrary to wave function ab initio methods, a systematic methodology to improve these functionals toward the exact solution of the nonrelativistic, Born–Oppenheimer time-independent Schrödinger equation is not available. The development and refinement of this theory has its impact on the study of aromaticity in two distinct ways. Many of the traditional aromaticity indicators, based on structural, energetic, and magnetic criteria, can be calculated quite accurately using DFT methods for large molecular systems, as shown among others in this work. It also has been emphasized that the noncomputational or conceptual side of DFT is a basis for a nonempirical theory of chemical reactivity in which response functions emerge, some of which have been proposed as measures of aromaticity themselves. The central function in DFT is the electron density, of which the topology has also been used to quantify the aromaticity of

molecules. Properties derived from the density such as the electron localization function and the local ionization potential have also been discussed. Another important concept is the HOMO–LUMO gap, later generalized to hardness, which, based on Pearson's principle of chemical hardness, can be used as an indicator of stability, since "molecules will arrange themselves to be as hard as possible". Other indicators included polarizability, inversely related to the hardness and the electrostatic potential, proven to be an approximation to the local hardness. To summarize, it has been shown that density functional theory is at the present time a priceless tool to study the aromaticity of molecules and that the chemical reactivity concepts originating from DFT can provide an alternative approach to the aromaticity concept. Providing a new DFT-based definition of aromaticity was not the aim of this contribution. The existing definitions highlighting different aspects of this classical concept are remarkably complementary, and DFT helps to quantify them and to study their interrelationships.

6. Acknowledgments

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(11) Since not all readers might be familiar with these three concepts, we will briefly explain what they stand for. An isodesmic reaction is defined by Hehre, Ditchfield, Radom, and Pople in their publication in 1970 (ref 12) as "a hypothetical (not existing in reality) chemical process in which the number of bonds of each formal type remains the same on each side of the reaction but with changes occurring in their mutual relationships". The heat of isodesmic reactions thus is a measure of deviations from the additivity of bond energies. The resonance energy of benzene can, e.g., be calculated by the following isodesmic reaction

$$3\ CH_2{=}CH_2 + 3\ CH_3{-}CH_3 \longrightarrow \text{[benzene ring]} + 6\ CH_4$$
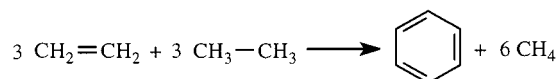
As can be seen, both on the left- and right-hand side of the equation, there are 3 C=C, 3 C–C and 30 C–H bonds. The resonance energy of benzene can then be defined as the negative of the energy of formation of benzene from nonconjugated molecules in an isodesmic reaction. However, as can be seen from the above-mentioned reaction, 3 $C(sp^3)$–$C(sp^3)$ single bonds are

transformed into 3 $C(sp^2)-C(sp^2)$ single bonds and this hybridization effect is not properly taken into account. This can be taken care of by changing the isodesmic equation by a so-called homodesmic equation, proposed by George and co-workers (refs 13 and 14), where there are equal numbers of atoms in their various states of hybridization in both the reactants and products and also where there is a matching of element−hydrogen bonds in terms of the number of hydrogen atoms joined to the individual elements in the reactants and products. For benzene, this then becomes

$$3 \; CH_2\!=\!CH\!-\!CH\!=\!CH_2 \longrightarrow \text{[benzene]} + 3 \; CH_2\!=\!CH_2$$
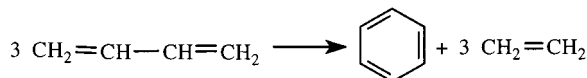
In this equation, there are 3 CH−CH bonds on both sides but the 6 CH_2=CH bonds are replaced by 3 CH_2=CH_2 and 3CH= CH bonds. It is then again possible to define an even more restricted reaction type, called a hyperhomodesmotic reaction (see ref 15), in which both bond types are conserved as

$$3 \; CH_2\!=\!CH\!-\!CH\!=\!CH\!-\!CH\!=\!CH_2$$

$$\longrightarrow \text{[benzene]} + 3 \; CH_2\!=\!CH\!-\!CH\!=\!CH_2$$
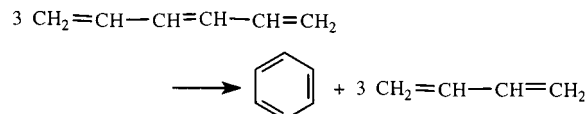
Indeed, there are 6 CH_2=CH, 6 CH−CH, and 3 CH=CH bonds in both reactants and products.

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