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Efficient Computation of Density-Functional Orbitally Resolved Reactivity Indices

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An algorithm for computation of density-functional-based orbital reactivity indices, such as orbitally resolved hardness and softness tensors, total hardness and softness, and the Fukui indices, has been extended for systems with degenerate electronic states and implemented in the deMon computer code. The method treats explicitly degenerate orbitals, thus avoiding spurious numerical errors in hardness tensor computations. Benchmark calculations for a series of small molecules and some larger, highly degenerate systems reveal good computational performance and numerical stability. The influence of the choice of auxiliary basis functions on the results is also examined and discussed. The predicted orbital and total reactivity index values are found to be insensitive to the applied exchange-correlation functionals. Applications of the orbital Fukui indices to a series of $(4n + 2)$ π-electron $[n]$-annulenes show the possibility of rationalizing the reactivity of individual molecular orbital contributions.

Introduction

The concepts of reactivity theory, the so-called "reactivity indices", have been proven to be important predictive tools in analyzing chemical interactions and reactions. In the early stage of this theory, Pearson[1] introduced the quantities electronic hardness (η) and softness (S) in his hard−soft acid−base (HSAB) principle, which states "hard likes hard and soft likes soft". The species are classified as soft (hard) if their valence electrons are easy (hard) to polarize or to remove, and the relationship between hardness or softness and the chemical reactivity was given through the HSAB principle. In the development of the reactivity theory, Fukui has proposed the use of the density of the frontier orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) in order to evaluate the reactivity of a system toward electron donation and acceptance. A rigorous theoretical basis to those qualitative concepts was given by Parr and co-workers,[2] and they were identified within the framework of density-functional theory (DFT) as various energy derivatives with respect to the total number of electrons (N). Thus, the hardness is defined as the second derivative of the Kohn−Sham (KS) energy to the density at fixed external potential and the softness is the inverse of the hardness. Further, the hardness and softness are derived in their local version,[3] since they are functions of the positions. They measure the local response at a given point inside the molecular region to a global external perturbation. Thus, it became possible to assign numbers to the reactivity indices computed from first principles and to exploit these values to rationalize a wide range of chemical interactions, ranging from the atomic and molecular reactions,[4] surface adsorption processes,[5] and nanoscale objects.[6] An exhaustive description of the applications of the reactivity indices in physics and chemistry can be found in a monograph of Pearson.[7]

In the present study, we focus our attention on a numerical implementation of the algorithm[8] that uses fractional occupation numbers of KS orbitals to compute hardness tensor elements, from which softness tensor elements, total hardness, total softness, and orbital Fukui indices can be obtained. We communicate also an efficient extension of the algorithm to systems with degenerate states that allows spurious entries in hardness tensors to be avoided. The algorithm has been implemented in the deMon-2003[9] code. Although the scheme for computing the reactivity indices based on the orbitally resolved hardness tensor (ORHT), first proposed within X_α[10] and then within DFT,[8] has been already successfully applied to various chemical reactivity tasks,[11−18] it was not yet fully numerically optimized and implemented in a way to allow routine computations.

The paper is organized in the following way. A brief outline of the computational approach is presented in the first section. Then, the numerical implementation is described, giving attention to the extension of the method to degenerate orbitals. Further, we have addressed the question about the numerical stability of the hardness and Fukui index values against the magnitude of the occupation number perturbation (Δn), employing several combinations of exchange-correlation functionals and auxiliary basis sets. Benchmark results are presented and discussed. In the last section, the possibility of treating aromatic systems is illustrated by exploring Fukui indices and total hardness on a series of $(4n + 2)$ π-electron D_{nh} $[n]$-annulenes.

Theory

In this section, we briefly recall the most important formulas in the reactivity theory and the orbitally resolved hardness tensor (ORHT) computational scheme. A detailed description of the ORHT method within DFT can be found elsewhere.[11,19]

The chemical potential (μ) and the total hardness (η) are defined within DFT as the first and second derivative, respec-

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tively, of the KS energy to the number of particles, at constant external potential (v):

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v, \quad \eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_v = \left(\frac{\partial \mu}{\partial N}\right)_v \tag{1}$$

Several approximations of varying accuracy have been proposed[7,20−22] for the hardness and softness in their global and local definitions. One of the most widely applied formulas for computing these quantities uses the three-point finite difference and expresses μ and η through the electron affinity (A) and ionization potential (I):

$$\begin{aligned} \mu &= -\frac{1}{2}(I + A) \\ \eta &= \frac{1}{2}(I - A) \end{aligned} \tag{2}$$

The latter formulas are usually further simplified using the HOMO−LUMO energies: $\mu = -(\epsilon_{\mathrm{HOMO}} + \epsilon_{\mathrm{LUMO}})$ and $\eta = \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}$. These equations directly employ one-electron change, although the exact definition demands an infinitesimal change of the number of electrons. In the case of HOMO−LUMO approximations, only the frontier orbital densities are involved in the hardness computation. Moreover, KS orbitals are different from the canonical molecular orbitals and the hardness calculation as the HOMO−LUMO gap is not straightforward.

The reactivity will be, however, largely determined by the response of all valence electrons and is governed by the whole spectrum and not just the frontier orbitals.[5] To this aim, an algorithm to compute reactivity indices (total hardness and softness, orbital Fukui indices, and orbital softnesses) from the orbitally resolved hardness tensor has been proposed initially within X_α formalism[10] and generalized later in the framework of DFT.[8] Computation of ORHT elements uses a fraction of an electron in the finite difference derivatives that are taken over all valence orbitals. A very similar protocol only for computing orbital hardness tensor elements was implemented in an older version of deMon code by Grigorov et al.[23] It is, however, of practical interest to use these hardness tensor elements to obtain the other local and global reactivity indices.

The idea to study the orbital response to small charge perturbation by means of the orbital energy derivative to the occupation number variation is given in the works of Neshev and Proynov.[24,25] The computational scheme within DFT has been derived by using Janak's theorem,[26] which defines the KS one-electron orbital energy (ϵ_i) as the first derivative of the total KS energy to the occupation number (n_i), analogously with Slater's proposal to use fractional occupations.[27] Each element in the hardness tensor (η_{ij}) is then obtained as the first derivative of ϵ_i to the occupation number (n_j).

$$\eta_{ij} = \frac{\partial^2 E}{\partial n_i \partial n_j} = \frac{\partial \epsilon_i}{\partial n_j} = \lim_{\Delta n_j \to 0} \frac{\epsilon_i(n_j - \Delta n_j) - \epsilon_i(n_j)}{\Delta n_j} \tag{3}$$

The difference quotient of eq 1 with finite Δn_j can be easily implemented to compute the hardness tensor (η_{ij}) numerically. The computational procedure thus requires self-consistent calculations first for the ground-state energy and then for each perturbed orbital with occupation $n_j = 1 - \Delta n_j$ and $n_j = 0 + \Delta n_j$, for the occupied and virtual orbitals, respectively.

The hardness (η), softness (S), softness tensor (s_{ij}), and orbital Fukui indices (f_i) are now easily accessible from the hardness tensor elements, and they are related in the following way

$$\eta = \frac{1}{S} = \frac{1}{\sum_{ij} s_{ij}} = \frac{1}{\sum_{ij} [\eta_{ij}]^{-1}} \tag{4}$$

$$\begin{gathered} f_i = \eta \sum_j s_{ij} \\ \sum_i f_i = 1 \end{gathered} \tag{5}$$

where the summations go over all orbitals or, with a valence-electron approximation, over the number of valence orbitals (N_{val}). Hence, the dimension of the hardness tensor is the number of treated orbitals. This general way of computing the hardness could be further exploited in the future, for example, by computing the hardness tensor for localized orbitals in the active region of some large molecular or surface structures and hence reducing the computational cost significantly. The hardness tensor can be generalized to open-shell systems, using the spin indexes α and β:

$$\eta_{ij}^{\alpha\beta} = \frac{\partial \epsilon_i^{\alpha}}{\partial n_j^{\beta}}$$

In the open-shell case, the summation in eq 1 runs over α and β valence orbitals, and the dimension of the hardness tensor is the number of treated α plus β orbitals.

The above outlined approach has been successfully applied in the studies of maximum hardness principle[11−13,15] and the active sites in a series of electrophilic and nucleophilic reactions.[14−18]

Implementation

In this section, we describe the implementation of orbital hardness and softness in the deMon code.[9] Some features of deMon, such as the use of an auxiliary density, make this implementation very efficient. However, as this implementation is general, it is straightforward to apply it to any other density-functional code.

In an initial single-point run, the "unperturbed" one-particle energies (ϵ_i), the molecular orbital (MO) coefficients, and the electron density of the system are computed. Then, the hardness tensor (η_{ij}) is calculated using the difference quotient of eq 1. For this purpose, the finite perturbation (Δn_i) is subtracted from the occupation number (n_i) of the ith orbital and self-consistent field (SCF) computations are carried out as many times as the number of perturbed orbitals. As the initial density of this SCF is very close to the perturbed one for small Δn_i, only a few SCF cycles are necessary. The influence of the perturbation on the result is discussed in the next section. The contribution of the core orbitals to the hardness is generally small and not important for chemical reactivity. In our implementation, the user can choose if the core orbitals are included in the calculation.

Special attention is required for degenerate orbitals. If one of the degenerate orbitals is perturbed, orbital symmetry is destroyed and usually convergence of the SCF is poor or even fails. In addition, for two degenerate orbitals, j and j', the hardness tensor elements η_{ij} and $\eta_{ij'}$ are equal; that is, equal rows/columns in the hardness tensor are produced and it cannot be inverted. We fix this problem by perturbing degenerate orbitals simultaneously. After determination of the degree of degeneracy (D) using a threshold (10^{-5} Hartree as the default), all degenerate orbitals are perturbed by $\Delta n_i/D$. The factor $1/D$ is due to the simultaneous perturbation of the degenerate orbitals, so that the resulting change of the occupation numbers for that system remains as Δn. In this way, each set of degenerate orbitals is accounted for only once in the hardness tensor and the corresponding η_{ij} values are directly multiplied by the degree of degeneracy (D). The latter can be easily seen, for instance, in the case of two degenerate orbitals (j and j'), from the following equation:

$$\eta_{ij} = \eta_{ij'} = \lim_{\Delta n \to 0} \frac{\epsilon_i\left(n_j - \frac{\Delta n_j}{2}\right) - \epsilon_i(n_j)}{\frac{\Delta n_j}{2}} \quad \text{for} \quad \epsilon_i = \epsilon_{i'}$$

Using this technique, spurious entries are removed from η_{ij}, which finally has the dimension of the number of nondegenerate orbitals. After degenerate orbitals are removed from η_{ij}, the reactivity indices can be computed following eq 2. The implementation of open-shell hardness follows exactly the same recipe and is straightforward.

Dependence of the Reactivity Indices on the Perturbation (Δ*n*)

We have deliberately chosen the hardness values (η) as benchmark for our implementation, since η is obtained from s_{ij} computations (eq 2) and in this way reflects the entire numerical algorithm. To illustrate how the implementation performs for local property computations, the Fukui indices of the σ-orbitals of halide acids, H_2O, H_2S, and NH_3 are reported as well. As it follows from eq 1, the accuracy of the hardness tensor elements and the consecutive reactivity indices (s_{ij}, η, S, and f_i) will essentially depend on the accuracy of the KS one-electron energies. On the contrary, the amount of perturbation (Δn) will contribute to the numerical precision of the one-electron energy values. For this reason, we have examined the numerical stability of the hardness values versus Δn, first, employing the local spin-density exchange-correlation approximation of Vosko, Wilk, and Nusair[28] (VWN) and setting the energy convergence tolerance equal to 10^{-12} Hartree. The orbital basis functions used in these computations are of double (DZVP)- and triple (TZVP)-ζ quality,[29] while for fitting the density auxiliary basis sets of various qualities were considered. (Auxiliaries are generated automatically, using the strategy of Godbout et al.,[29] covering the space of the orbital basis functions used in the calculation. The auxiliaries with polarization functions (denoted with an asterisk) are an extension to the standard A2, A3, and A4 basis set. They split the space into three regions (compared to two in the standard), the first with only s orbitals, the second with spd orbitals, and the third with spdfg orbitals, with each set of orbitals sharing the same exponent.) Additional test computations were performed for two gradient-corrected approximations (GGAs): (1) Perdew's 1986 for correlation[30] and Becke's 1988 GGA for exchange,[31] referred to as BP88, and (2) Perdew−Burke−Ernzerhof's 1996 exchange-correlation functional,[32] referred to as PBE, employing DZVP bases.

In Figure 1, the dependence of η on the perturbation (Δn) is studied for H_2 and HF molecules. In this study, we include six sets of auxiliary functions to represent the auxiliary density. For clarity, we discuss only the results obtained with the VWN functional. The hardness is linearly dependent on the finite perturbation (Δn), as follows directly from eq 1, where the partial first-order derivative for each hardness tensor element is approximated with the finite difference. Indeed, all computations except the A2 computation of H_2 show such a linear region, going from large to small Δn values. For smaller Δn, numerical problems in the difference quotient start to be important, and numerical stability is lost. These numerical difficulties can be due to either an incomplete auxiliary basis, as in the case of A2 for H_2, or numerical difficulties due to an overdetermined auxiliary basis, as in the case of A3* and A4* for HF. However, if a (linear) extrapolation in the linear region of $\eta(\Delta n)$ is carried out, the resulting hardness is found to be nearly independent of the employed auxiliary basis. We have made similar observations for other numerical parameters, for instance, SCF tolerance and grid quality.

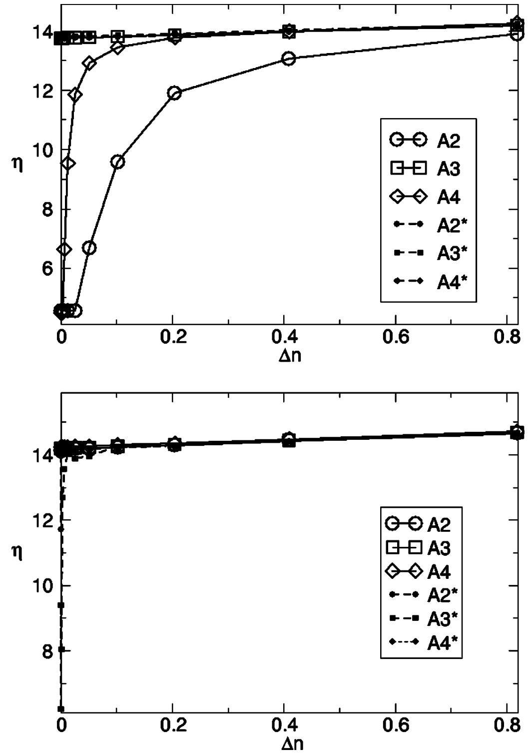

Figure 1. Dependency of the hardness (in electronvolts) on the perturbation (Δn) for various auxiliary basis sets for the VWN functional for H_2 (top) and HF (bottom). The function sets of the auxiliaries are (4, 0, 0)/(4, 3, 0) for A2; (5, 0, 0)/(5, 4, 0) for A3; (8, 0, 0)/(8, 7, 0) for A4; (2, 2, 0)/(3, 2, 2) for A2*; (3, 2, 0)/(3, 3, 3) for A3*, and (4, 4, 0)/(5, 5, 5) for A4*, for H/F atoms, respectively. The nomenclature gives the number of (s, spd, spdfg) sets.

The hardness values and Fukui indices (f_σ) for a series of benchmark molecules using the VWN, BP88, and PBE functionals are collected in Tables 1 and 2, respectively. The computations were carried out again for the same Δn range used in the cases of H_2 and HF. The main result is that η and f_σ are nearly independent of the functional used, which is in contradiction to other approximations of the reactivity indices that explicitly use virtual orbitals. Only for molecules with a small hardness, like naphthalene, small differences between the local density approximation (LDA) and the GGA are found. The use of TZVP bases at the LDA level of theory did not yield significantly different values for the hardness (Table 1) and Fukui indices (Table 2). Hence, it is also advantageous concerning computing time to write orbitally resolved reactivity indices within DFT.

The last aromatic molecules presented in Table 1 were chosen because they contain a high number of degenerate orbitals, thus being an appropriate test for the numerical stability of our technique to treat degeneracy. For these molecules, the con-

TABLE 1: Hardness (η, in eV) at Various Levels of DFT for Benchmark Molecules, Using the DZVP and TZVP Basis Sets (TZVP is Not Available for I and Br)[29] and A2 Auxiliaries (See Text)[a]

system	VWN	BP88	PBE	VWN	exptl[b]
HF	14.10 (10.28)	14.20 (10.15)	14.14 (10.65)	13.17	11.0
HCl	9.38 (8.17)	9.30 (7.84)	9.36 (7.87)	9.06	8.0
HBr	8.08 (7.26)	7.94 (6.27)	7.92 (6.74)		
HI	7.20 (6.44)	7.16 (6.17)	7.16 (6.23)		5.3
H_2O	11.58 (8.51)	11.54 (8.36)	11.56 (8.41)	11.04	9.5
H_2S	8.18 (7.68)	8.12 (7.64)	8.14 (7.682)	8.56	6.2
NH_3	10.20 (7.33)	10.20 (7.47)	10.06 (7.52)	9.54	8.2
benzene	1.96 (5.57)	2.30 (5.48)	2.30 (5.66)	2.28	
naphthalene	1.22 (4.18)	1.82 (4.14)	1.78 (4.15)	1.75	

[a] Geometries have been optimized at the same levels of theory. [b] The experimental hardness values are taken from ref 7. Note that the experimental hardness is obtained from the measured ionization potential and electron affinity ($\eta = 1/2(I - A)$). In parentheses are reported the hardness values (in electronvolts) coming from the calculated IP and AE values. For IP and AE, SCF computations at the same levels of theory have been performed.

TABLE 2: Fukui Indices for the σ-Orbitals of HF, HCl, HBr, HI, H_2O, H_2S, and NH_3, Using the VWN, BP88, and PBE Exchange-Correlation Functionals and the DZVP Basis Set and the VWN Exchange-Correlation Functional and the TZVP Basis Set[a]

system	HF	HCl	HBr	HI	H_2O	H_2S	NH_3
f_σ[b]	0.58	0.78	0.82	0.74	1.03	1.03	0.52
f_σ[c]	0.65	0.82	0.85	0.76	1.14	1.15	0.54
f_σ[d]	0.65	0.82	0.85	0.76	1.13	1.15	0.55
f_σ[e]	0.57	0.81			0.90	1.07	0.60

[a] All the computations were carried out employing A2 auxiliaries (see text). Geometries have been optimized at the same levels of theory. [b] The VWN exchange-correlation functional and the DZVP basis set. [c] The BP88 exchange-correlation functional and the DZVP basis set. [d] The PBE exchange-correlation functional and the DZVP basis set. [e] The VWN exchange-correlation functional and the TZVP basis set.

vergence criteria were difficult to satisfy when higher perturbation ($\Delta n > 0.03$) was considered. The latter is not surprising because the system stability is determined in general by the eigenvalues of the matrix whose elements are energy derivatives of second order (Hessian) with respect to the coordinates or to the occupation numbers,[16] that is, in our case, the eigenvalues of the hardness matrix. Naphthalene is less stable compared, for example, to halide acids, whose orbital reactivity index values were obtained to be almost not sensitive to the magnitude of Δn (vide supra). This also demonstrates the advantage of the proposed methodology, which can deal with rather small perturbations.

The experimental data for η are reported in Table 1 as well. Note that there is no direct way to measure hardness or softness. The experimental hardness is the difference between the measured ionization potential and the electron affinity.[7] This means the operational definition of η (eq 2) has been used to obtain the experimental hardness, while our η values are computed from another approximation that is closer to the exact hardness definition of eq 1. Therefore, only the relative trends can be compared. As is known, the hardness and other reactivity index numbers are expected from the chemical evidence:[7] (1) water is harder than hydrogen sulfide and ammoniac; (2) the hardness of the halide acids is in the order HF > HCl > HBr > HI, as follows from the classification of the hard−soft compounds;[7] and (3) the smallest f_σ value of HF correlates well with the anomalous behavior of hydrofluoric acid, which is a weak acid, whereas HCl, HI, and HBr are strong acids. To provide direct comparison with the experimental data, we have reported in Table 1 the hardness values obtained as half of the difference between the ionization potentials (IPs) and electron affinities (EAs) (eq 2), as well. For this purpose, IPs and AEs were calculated employing the SCF procedure for the corresponding neutral and charged molecules. The observed good agreement between the experimental and theoretical date reveals the known fact that DFT is able to reproduce well the experimental ionization potentials and electron affinities.

TABLE 3: Hardness of D_{nh} [n]-Annulenes from the ORHT Method (η), Hardness from the HOMO−LUMO Difference (η_{H-L}), in eV, and Orbital Fukui Indices for Some Selected π- and σ-Orbitals of ($4n + 2$) [n]-Annulenes, Computed Using the PBE Exchange-Correlation Functional, the DZVP Basis Set, and A2 Auxiliaries (See Text)[a]

system	η_{H-L}	η	f_π	f_σ
$C_3H_3^+$	9.09	3.06	0.051 (8)	−0.421(4)
$C_4H_4^{2+}$	4.81	2.60	0.027 (11)	−0.383 (5)
$C_4H_4^{2-}$	3.59	2.52	−0.039 (13)	−0.334 (5)
			0.118 (14 + 15)	0.262 (6 + 7)
$C_5H_5^-$	5.55	2.46	−0.094 (16)	−0.555 (6)
			0.096 (17 + 18)	0.142 (7 + 8)
C_6H_6	5.12	2.30	−0.328 (17)	−0.36 (7)
			0.003 (20 + 21)	−0.04 (8 + 9)
$C_7H_7^+$	4.29	2.24	−0.134 (20)	−0.623 (8)
			−0.003 (23 + 24)	−0.232 (9 + 10)
$C_8H_8^{2+}$	3.39	2.10	−0.085 (21)	−0.280 (9)
			−0.044 (26 + 27)	−0.150 (10 + 11)
$C_8H_8^{2-}$	4.15	1.90	0.080 (23)	−0.151 (9)
			−0.053 (26 + 27)	−0.215 (10 + 11)
			−0.115 (28 + 29)	−0.185 (12 + 13)
$C_{10}H_{10}$	3.29	1.20	0.437 (27)	1.573 (11)
			−0.118 (30 + 31)	1.006 (12 + 13)
			−0.800 (34 + 35)	−1.370 (14 + 15)

[a] In parentheses, the numbers of orbitals—all π-orbitals and the isolobal σ-orbitals—are given (for further details, see ref 35). Geometries have been optimized at the same levels of theory.

To conclude this section, we emphasize that the absolute values of the reactivity indices do not provide any physical information. The reactivity index numbers can provide knowledge only if a particular chemical behavior for a set of compounds is studied. Therefore, we believe it is of great importance to ensure a stable numerical algorithm for computing global and local reactivity indices, taking into account the response of all orbitals in the system rather than comparing their values coming from different working definitions.

Reactivity Indices of Aromatic Molecules

Aromatic molecules have a special reactivity, and molecular reactivity is considered as one of the categories defining aromaticity.[22,33−35] Since aromaticity describes compounds that are energetically stabilized due to the presence of cyclic delocalized electrons,[35−37] it is expected that aromatic compounds can be characterized by their relatively large hardness values. The latter is in general associated with higher stability, or lower reactivity, as is aromatic stabilization. Although the attempts to correlate hardness with aromaticity date from the late 1960s, the relationship of hardness and aromaticity was neither fully exploited[22] nor extended to the involvement of the Fukui functions.

We discuss below the orbitally resolved total hardness and Fukui indices of σ- and π-orbitals belonging to ($4n + 2$) π-electron systems that are listed in Table 3. The HOMO−LUMO total hardness (η_{H-L}) is also given because this is one of the most applied approximations in the reactivity-based description of aromaticity.[38−42] The total hardness from the ORHT method is inversely dependent on the number of active orbitals that constitute the hardness tensor. Therefore, η values for the $(4n + 2)$ [n]-annulenes decrease with an increasing number of electrons. The same is true for HOMO−LUMO gaps, which decrease in Hückel theory with increasing ring size. This trend is generally true, as also other indices of aromaticity correlate reciprocally with the ring size.[22,43] Special cases in the series of [n]-annulenes are ions with the same ring topology but different numbers of electrons. The series of annulenes contain two species with the same number of vertices but a different number of π-electrons: $C_4H_4^{2+}/C_4H_4^{2-}$ and $C_8H_8^{2+}/C_8H_8^{2-}$. In both cases, Hückel theory gives a degenerate orbital which has zero energy and is hence neither bonding nor antibonding (the LUMO in the cationic species and the HOMO in the anionic species). Therefore, the aromatic stabilization of both systems should be rather similar. This is exactly what we find within the ORHT: the molecular hardness of these species differs by <5%. On the other hand, it is obvious that η_{H-L} fails to describe the reactivity of these molecules: the LUMO of the cation is the HOMO of the anion, and hence, the HOMO−LUMO gap is computed between different orbitals for $C_4H_4^{2+}/C_4H_4^{2-}$ and $C_8H_8^{2+}/C_8H_8^{2-}$, respectively.

The ORHT hardness decreases monotonically with increasing ring size and number of π-electrons, which is comparable with experimental observations and not reflected in the η_{H-L} approximation. The ORHT approach gives the possibility of overcoming the size dependency of the total hardness, including local reactivity properties, for example, the Fukui indices, in the description and interpretation of aromaticity.

As the Fukui indices are directly proportional to the orbital softness, a lower f value indicates a harder, more localized orbital and vice versa. Orbitals that are characterized by negative Fukui indices are considered as nonreactive, having an opposite behavior with respect to the other MOs of the molecule toward a particular reaction.[44] Usually, aromatic systems are known as species that “try to leave their π-electrons unchanged”.[22] The results in Table 3 reveal that most of the f_π and f_σ values are negative or near zero, thus indicating these orbitals are nonreactive or are harder compared to the other valence MOs in the molecule. For $C_3H_3^+$ and $C_4H_4^{2+}$ species, the tendency of σ- and π-MOs to keep their electrons is well evidenced by the f_σ and f_π values.

In the case of $C_4H_4^{2-}$, we note that the Fukui index values characterize the higher-energy σ-MO and frontier π-orbitals as relatively soft, delocalized orbitals, while the low-energy σ- and π-MOs are expected to be nonreactive. Thus, the relatively low reactivity, or the aromatic character, would be predominantly due to the contributions of the low-lying σ- and π-MOs. With increasing molecular size, the f_π values of the frontier degenerate set of π-electrons decrease, approaching zero for C_6H_6 and $C_7H_7^+$ and becoming negative for $C_8H_8^{2+}$. The same behavior, even more pronounced, is observed for the degenerate set of σ-electrons.

The Fukui indices of the last two species considered here ($C_8H_8^{2-}$ and $C_{10}H_{10}$) indicate the lowest-energy π-orbitals are relatively soft, delocalized orbitals. As the degree of localization decreases in going to the higher-energy π-orbitals, the negative f_π value for the second degenerate π-set correctly characterizes these orbitals as nonreactive, with greater ability to keep their electrons unchanged. Recently computed MO-NICS[35] revealed greater contributions of the π lowest-energy MO-NICS values that are attributed to the higher degree of delocalization of these π-MOs. The MO-NICS calculations show also that $C_8H_8^{2-}$ is more aromatic than $C_8H_8^{2+}$. In the case of the former molecule, two more π-orbitals are occupied. Our f_π values indicate these two frontier MOs are nonreactive.

Summary

An efficient algorithm for the computation of density-functional-based orbital reactivity indices, such as the orbitally resolved hardness and softness tensors, total hardness and softness, and Fukui indices, is proposed and implemented in the deMon-2003 code. The theory accounts for all valence orbitals in the computations of the hardness, thus allowing direct and relatively easy computations of the local reactivity indices as well. The algorithm automatically treats degenerate orbitals. The good computational performance of the algorithm is illustrated for a series of small molecules and some large, highly degenerate systems as well. The numerical stability is tested for a set of 10 different values of the occupation number perturbations, ranging from $\Delta n = 0.0001e$ to $\Delta n = 0.8e$. The influence of the basis set and the choice of auxiliary basis functions to fit the density in the deMon code on the numbers is also examined and discussed. The approach is found to be insensitive to the applied exchange-correlation functionals.

The relationship between the reactivity-based concepts and aromaticity is illustrated for a series of $(4n + 2)$ [n]-annulenes. The orbital Fukui indices correctly attribute low reactivity to the isonodal σ- and π-molecular orbitals in the aromatic compounds, ranging from $C_3H_3^+$ to $C_{10}H_{10}$. The high degree of delocalization of the lowest-energy π-orbitals in $C_8H_8^{2-}$ and $C_{10}H_{10}$ is indicated by the larger f_π values for these MOs. The low reactivity of those aromatic compounds is most probably due to the frontier sets of degenerate π-orbitals, for which negative f_π values have been obtained.

Further applications of this fully optimized numerical implementation toward reactivity study of various problems can be easily performed with relatively small computational costs and human resources.

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