

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/8674268>

On the application of the HSAB principle through the use of improved computational schemes for chemical hardness evaluation

ARTICLE in JOURNAL OF COMPUTATIONAL CHEMISTRY · MAY 2004

Impact Factor: 3.59 · DOI: 10.1002/jcc.20027 · Source: PubMed

CITATIONS

36

READS

362

3 AUTHORS:



Mihai V. Putz

West University of Timisoara

96 PUBLICATIONS **713** CITATIONS

SEE PROFILE



Nino Russo

Università della Calabria

512 PUBLICATIONS **7,920** CITATIONS

SEE PROFILE



Emilia Sicilia

Università della Calabria

151 PUBLICATIONS **1,937** CITATIONS

SEE PROFILE

On the Applicability of the HSAB Principle through the Use of Improved Computational Schemes for Chemical Hardness Evaluation

MIHAI V. PUTZ,* NINO RUSSO, EMILIA SICILIA

*Dipartimento di Chimica and Centro di Calcolo ad Alte Prestazioni per Elaborazioni Parallele e Distribuite-Centro d'Eccellenza MURST, Università della Calabria,
I-87030 Arcavacata di Rende, Italy*

Received 29 October 2003; Accepted 28 December 2003

Abstract: Finite difference schemes, named Compact Finite Difference Schemes with Spectral-like Resolution, have been used for a less crude approximation of the analytical hardness definition as the second-order derivative of the energy with respect to the electron number. The improved computational schemes, at different levels of theory, have been used to calculate global hardness values of some probe bases, traditionally classified as hard and soft on the basis of their chemical behavior, and to investigate the quantitative applicability of the HSAB principle. Exchange acid-base reactions have been used to test the HSAB principle assuming the reaction energies as a measure of the stabilization of product adducts.

© 2004 Wiley Periodicals, Inc. J Comput Chem 25: 994–1003, 2004

Key words: HSAB principle; hardness; Compact Finite Differences

Introduction

Pearson's hard-soft acid-base principle^{1–6} (HSAB) states that “hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases.” In spite of the numerous objections, the HSAB principle proved to be very useful in many applications to chemistry and related fields, and, about 10 years ago, two of the articles^{1,3} concerning this subject were identified as among the most widely quoted articles in the chemical literature.

The really serious objection to the HSAB principle was that no exact definition of hardness was given, no way to assign numerical value to this concept existed, and, as a consequence, the classification of acids and bases as hard and soft was based only on the known chemical behavior of these species.

The problem of the hardness definition was solved in 1983 during the already mythical meeting between Pearson and Parr in Santa Barbara. To the question of Parr whether the quantity $(\partial\mu/\partial N)_v$ might be related to the idea of hardness, the answer of Pearson, after some hours of reflection, was affirmative. In the original article⁷ a series of convincing motivations is listed in support of the identification:

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

A factor 1/2 was introduced⁸ into the hardness formulation for symmetry reasons with respect to the chemical potential, μ , definition, but nowadays the tendency is to leave out it.⁹ Accordingly, this factor will be omitted in the present study.

From the time hardness was first defined^{7,8,10,11} within the density function theory (DFT), a huge amount^{12–22} of work has been devoted to the derivation of operational definitions and scales for different atomic systems, useful for the practical attachment of numbers to the rather intuitive concept. At the same time the two major principles, the HSAB and the maximum hardness (MH) principles,^{6,23} associated with hardness have been widely tested using several working formula and computational approaches at different levels of approximation.^{24–53} Several publications^{40,54} recommend the application of a local version of the HSAB principle in analyzing the site selectivity in molecules, because global properties may explain the reactivity, but to understand selectivity local quantities have to be used. Because, according to Klopman⁵⁵ terminology, soft-soft reactions are frontier controlled and predominantly covalent in nature, while hard-hard interactions are

Correspondence to: E. Sicilia; e-mail: siciliae@unical.it

*Permanent address: Chemistry Department, West University of Timisoara, Str. Pestalozzi; no. 16, Timisoara, RO-300115, Romania

Contract/grant sponsor: Università della Calabria

Contract/grant sponsor: MIUR

charge controlled and predominantly ionic in nature, the local softness is not an adequate descriptor in the latter case and an analogous local index should be defined.⁵⁶

This effort is motivated by the very fascinating perspective to better understand and explain chemical binding and reactivity of molecular systems through the use of concepts and principles that have long been part of the vocabulary of the chemist to describe chemical phenomena. Two recent reviews^{57,58} summarize very well the evolution of “chemical reactivity descriptors” theory and applications deriving from the development of DFT, and they contain a complete bibliography of this subject.

As it is well known, a finite difference approximation to eq. (1) gives:

$$\eta = I - A \quad (2)$$

where I and A are the vertical ionization potential and the electron affinity, respectively, according to the constancy of the external potential requirement of eq. (1). If experimental values of I and A are unknown, they can be calculated, at whatever level of theory, from the total energy values of any atom or molecule and its positive and negative stable ions.

An alternative to the computational labor associated with the theoretical calculation of I and A is offered by the Koopmans’ theorem that can be applied to further approximate eq. (2) as

$$\eta = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \quad (3)$$

where $\varepsilon_{\text{LUMO}}$ and $\varepsilon_{\text{HOMO}}$ are the energy values associated with the lowest unoccupied (LUMO) and highest occupied (HOMO) molecular orbitals. Koopmans’ theorem and the same orbitals idea lose their utility if the improvement of HF theory, through Configuration Interaction, is taken into account. Concerning density functional (DF) methods, from the beginning of their utilization, the Kohn-Sham orbitals have been viewed just as an auxiliary construct and the problem of the attribution to them of a physical meaning has not yet been solved. Moreover, eq. (3) indicates that hardness is related to the energy gap between occupied and unoccupied orbitals, and, as correctly pointed out by Chermette,⁵⁷ possible discontinuities in the derivative of the energy with respect to the number of electrons for systems possessing a HOMO-LUMO energy gap, like molecules (with discrete energy levels), may be encountered. The situation outlined above seems to discourage the use of the last working formulas and other computational definitions^{12–22} have been proposed to improve it. The articles dealing with this subject published in the last two decades, however, clearly demonstrate that eq. (3) is the most routinely used, both in gas-phase and in solvent and at noncorrelated and correlated levels of theory, because of the simplicity and readiness by which it can be evaluated, even if the limits of its applicability are not yet fixed. Moreover, the interpretation of the tests of HSAB and MH principles, performed using this approximate operational definition, is controversial and raises the question of whether the approximation adopted to evaluate hardness in a popular usable form can limit the applicability of the same principles.

For a less crude approximation to the analytical hardness definition as the second-order derivative of the energy with respect

Table 1. Coefficients Defining Numerical Compact Finite Difference Schemes for Evaluating Second Order Derivatives.

Scheme	a_2	b_2	c_2	α_2	β_2
2C	1	0	0	0	0
4C	$\frac{4}{3}$	$-\frac{1}{3}$	0	0	0
6C	$\frac{12}{11}$	$\frac{3}{11}$	0	$\frac{2}{11}$	0
SP	$\frac{6}{5}$	0	0	$\frac{1}{10}$	0
6T	$\frac{3}{2}$	$-\frac{3}{5}$	$\frac{1}{5}$	0	0
8T	$\frac{147}{152}$	$\frac{51}{95}$	$-\frac{23}{760}$	$\frac{9}{38}$	0
8P	$\frac{320}{393}$	$\frac{310}{393}$	0	$\frac{344}{1179}$	$\frac{23}{2358}$
10P	$\frac{1065}{1798}$	$\frac{1038}{899}$	$\frac{79}{1798}$	$\frac{334}{899}$	$\frac{43}{1798}$
SLR	0.216	0.173	0.177	0.502	0.056

the electron number, in the present work we have used alternative finite difference schemes, named Compact Finite Difference Schemes with Spectral-like Resolution (SLR),⁵⁹ which provide improved results with respect to the traditional finite difference ones. The improved computational schemes, at different levels of theory, have been used to calculate global hardness values of some bases and to investigate the quantitative applicability of the HSAB principle.

Methods

Given the values of a function $f(n)$ on a set of nodes the finite difference approximations to the second, f''_n , derivative of the function at the node n , depend on the function values at nodes near n . In the spectral methods, instead, the value of f''_n depends on all the nodal values. The Padé or Compact Finite Difference Schemes⁶⁰ mimic this global dependence. The schemes used here are generalizations of the Padé scheme and are derived by writing an approximation of the form:

$$\beta_2 f''_{n-2} + \alpha_2 f''_{n-1} + f''_n + \alpha_2 f''_{n+1} + \beta_2 f''_{n+2} = c_2 \frac{f_{n+3} - 2f_n + f_{n-3}}{9} + b_2 \frac{f_{n+2} - 2f_n + f_{n-2}}{4} + a_2 (f_{n+1} - 2f_n + f_{n-1}) \quad (4)$$

where f''_n represents the finite difference approximation to the second order derivative at node n .

The involved sets of coefficients $\{a_2, b_2, c_2, \alpha_2, \beta_2\}$ are derived⁵⁹ by matching the Taylor series coefficients of various orders and the imposed constraints correspond to the formal truncation error of the eq. (4) approximation. The general relation of eq. (4) coupled with the appropriate constraint generates several families of n^{th} order schemes that are classified as: the second (2C)-, fourth (4C)-, and sixth (6C)-order central differences; standard Padé (SP) schemes; sixth (6T)- and eighth (8T)-order tridiagonal schemes; eighth (8P)- and tenth (10P)-order pentadiagonal

schemes up to SLR ones. In parentheses are reported the symbols by which we will indicate the different schemes in the next sections, while the numerical values of the coefficients defining each scheme are collected in Table 1.

Assuming that the function $f(n)$ is the total energy $E(N)$ in the actual node that corresponds to the number of electrons, the Compact Finite Difference hardness approximation becomes:

$$\begin{aligned} \eta = \frac{\partial^2 E}{\partial N^2} \Big|_N &= 2a_2 \frac{E_{N+1} - 2E_N + E_{N-1}}{2} + b_2 \frac{E_{N+2} - 2E_N + E_{N-2}}{4} + c_2 \frac{E_{N+3} - 2E_N + E_{N-3}}{9} \\ &- \alpha_2 \left(\frac{\partial^2 E}{\partial N^2} \Big|_{N-1} + \frac{\partial^2 E}{\partial N^2} \Big|_{N+1} \right) - \beta_2 \left(\frac{\partial^2 E}{\partial N^2} \Big|_{N-2} + \frac{\partial^2 E}{\partial N^2} \Big|_{N+2} \right) \cong 2a_2 \frac{E_{N+1} - 2E_N + E_{N-1}}{2} + b_2 \frac{E_{N+2} - 2E_N + E_{N-2}}{4} \\ &+ c_2 \frac{E_{N+3} - 2E_N + E_{N-3}}{9} - \alpha_2 \left(2a_2 \frac{E_N - 2E_{N-1} + E_{N-2}}{2} + 2a_2 \frac{E_{N+2} - 2E_{N+1} + E_N}{2} \right) \\ &- \beta_2 \left(2a_2 \frac{E_{N-1} - 2E_{N-2} + E_{N-3}}{2} + 2a_2 \frac{E_{N+3} - 2E_{N+2} + E_{N+1}}{2} \right) \\ &= 2a_2(1 + 2a_2 - \beta_2) \frac{E_{N+1} + E_{N-1}}{2} + (8a_2\beta_2 + b_2 - 4a_2\alpha_2) \frac{E_{N+2} + E_{N-2}}{4} \\ &+ (c_2 - 9a_2\beta_2) \frac{E_{N+3} + E_{N-3}}{9} - \left(2a_2 + \frac{1}{2}b_2 + \frac{2}{9}c_2 + 2a_2\alpha_2 \right) E_N \quad (5) \end{aligned}$$

For practical computations the above formula has to be further expressed in terms of accessible energetic quantities as the ionization potentials and electron affinities of various orders. If the general definitions of ionization potential and electron affinity of i^{th} order are used

$$\begin{aligned} I_i &= E_{N-1} - E_{N-i+1} \\ A_i &= E_{N+i-1} - E_{N+i} \end{aligned} \quad (6)$$

the involved energetic differences become:

$$\begin{aligned} E_{N+1} + E_{N-1} &= (E_{N+1} - E_N) + (E_{N-1} - E_N) + 2E_N = (I_1 - A_1) \\ &+ 2E_N E_{N+2} + E_{N-2} = (E_{N+2} - E_{N+1}) + (E_{N+1} - E_N) + (E_{N-1} \\ &- E_N) + (E_{N-2} - E_{N-1}) + 2E_N = -A_2 - A_1 + I_1 + I_2 + 2E_N \\ &= (I_1 - A_1) + (I_2 - A_2) + 2E_N, E_{N+3} + E_{N-3} = (E_{N+3} - E_{N+2}) \\ &+ (E_{N+2} - E_{N+1}) + (E_{N+1} - E_N) + (E_{N-1} - E_N) + (E_{N-2} - E_{N-1}) \\ &+ (E_{N-3} - E_{N-2}) + 2E_N = -A_3 - A_2 - A_1 + I_1 + I_2 + I_3 + 2E_N \\ &= (I_1 - A_1) + (I_2 - A_2) + (I_3 - A_3) + 2E_N \quad (7) \end{aligned}$$

Table 2. HF, B3LYP, VWN, and BP86 Chemical Hardness Computations for the CN^- Ion, Using Orbital Energies and Vertical Ionization Potentials and the Electron Affinities Calculation, Respectively.

Schemes η (eV)	HF		B3LYP		VWN		BP86	
	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical
2C	18.0	15.3	8.8	15.8	6.4	15.7	6.4	15.4
4C	21.0	16.2	10.2	16.7	7.3	16.6	7.4	16.3
6C	14.9	10.2	7.2	10.5	5.1	10.4	5.1	10.2
SP	17.3	12.4	8.3	12.8	5.9	12.6	5.9	12.4
6T	22.9	17.8	11.2	18.3	8.0	18.2	8.1	17.9
8T	13.8	9.7	6.6	10.0	4.7	9.9	4.8	9.8
8P	13.4	10.5	6.5	10.8	4.6	10.8	4.7	10.6
10P	13.9	13.1	6.8	13.5	4.9	13.5	5.0	13.3
SLR	17.1	21.6	8.8	22.1	6.7	22.2	6.6	21.9

All the values are in eV.

Table 3. HF, B3LYP, VWN, and BP86 Chemical Hardness Computations for the CH_3S^- Ion, Using Orbital Energies and Vertical Ionization Potentials and the Electron Affinities Calculation, Respectively.

Schemes η (eV)	HF		B3LYP		VWN		BP86	
	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical
2C	13.0	11.4	6.1	11.1	4.4	11.1	4.4	10.9
4C	15.0	12.1	6.9	11.8	5.1	11.8	5.0	11.5
6C	10.6	7.6	4.8	7.4	3.5	7.4	3.5	7.2
SP	12.3	9.2	5.6	8.9	4.1	9.0	4.1	8.8
6T	16.4	13.3	7.6	12.9	5.6	12.9	5.5	12.7
8T	9.8	7.2	4.5	7.0	3.3	7.1	3.2	6.9
8P	9.6	7.8	4.4	7.6	3.2	7.6	3.2	7.4
10P	10.1	9.7	4.7	9.5	3.5	9.5	3.4	9.3
SLR	12.9	15.9	6.3	15.6	4.7	15.5	4.7	15.4

All the values are in eV.

Introducing these quantities into eq. (5) the general Compact Finite Difference expression for hardness in terms of ionization and electron affinities up to the third order is obtained:

$$\eta_{\text{CFD}} = \left[a_2(1 - \alpha_2 + 2\beta_2) + \frac{1}{4}b_2 + \frac{1}{9}c_2 \right] I_1 - A_1 + \left[\frac{1}{2}b_2 + \frac{2}{9}c_2 + 2a_2(\beta_2 - \alpha_2) \right] \frac{I_2 - A_2}{2} + \left[\frac{1}{3}c_2 - 3a_2\beta_2 \right] \frac{I_3 - A_3}{3} \quad (8)$$

When the second order central Compact Finite Difference Scheme (2C) is considered, corresponding to the following values of the coefficients $\{a_2 = 1, b_2 = c_2 = \alpha_2 = \beta_2 = 0\}$ (see Table 1), the generalized Compact Finite Difference formula of eq. (8) for hardness becomes the well-known

$$\eta_{\text{CFD}}^{(2C)} = I_1 - A_1 \quad (9)$$

Given an N -electron system with highest occupied and lowest virtual spin orbital energies ε_a and ε_r , Koopmans' theorem gives

a way for calculating approximate ionization potential and electron affinity just as $-\varepsilon_a$ and $-\varepsilon_r$. If the rough approximation of the "frozen orbitals" is applied also to the calculation of ionization potentials and electron affinities of i^{th} order, then from the same eq. (8) the following expression for hardness in terms of orbital energies is obtained

$$\eta_{\text{CFD}} = \left[a_2(1 - \alpha_2 + 2\beta_2) + \frac{1}{4}b_2 + \frac{1}{9}c_2 \right] \varepsilon_a - \varepsilon_r + \left[\frac{1}{2}b_2 + \frac{2}{9}c_2 + 2a_2(\beta_2 - \alpha_2) \right] \frac{\varepsilon_b - \varepsilon_s}{2} + \left[\frac{1}{3}c_2 - 3a_2\beta_2 \right] \frac{\varepsilon_c - \varepsilon_t}{3} \quad (10)$$

where b and c labels are used for occupied orbitals below a , and s and t are used for virtual orbitals above r . If the 2C is used the well known eq. (3) in terms of HOMO and LUMO orbital energies is obtained. The improved operational definitions of η , therefore, take into account contributions from orbitals beside HOMO and LUMO.

Table 4. HF, B3LYP, VWN, and BP86 Chemical Hardness Computations for the CH_3SH Molecule, Using Orbital Energies and Vertical Ionization Potentials and the Electron Affinities Calculation, Respectively.

Schemes η (eV)	HF		B3LYP		VWN		BP86	
	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical
2C	14.7	12.8	7.3	12.6	5.4	12.6	5.4	12.4
4C	16.8	13.5	8.2	13.4	6.1	13.4	6.0	13.1
6C	11.7	8.5	5.6	8.4	4.1	8.4	4.1	8.2
SP	13.7	10.3	6.6	10.2	4.9	10.2	4.8	9.98
6T	18.3	14.8	8.9	14.6	6.7	14.6	6.6	14.3
8T	10.9	8.1	5.2	8.0	3.9	8.0	3.8	7.8
8P	10.8	8.8	5.3	8.7	3.9	8.6	3.9	8.5
10P	11.5	11.0	5.8	10.9	4.4	10.8	4.4	10.7
SLR	14.9	18.2	7.9	17.9	6.2	17.6	6.2	17.5

All the values are in eV.

Table 5. HF, B3LYP, VWN, and BP86 Chemical Hardness Computations for the CH_3O^- Molecule, Using Orbital Energies and Vertical Ionization Potentials and the Electron Affinities Calculation, Respectively.

Schemes η (eV)	HF		B3LYP		VWN		BP86	
	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical
2C	14.4	11.3	6.4	11.9	4.6	12.2	4.6	11.9
4C	16.6	11.7	7.3	12.5	5.2	12.9	5.2	12.5
6C	11.7	7.1	5.0	7.7	3.6	8.0	3.6	7.7
SP	13.6	8.7	5.9	9.4	4.2	9.8	4.2	9.5
6T	18.1	12.9	8.0	13.8	5.8	14.2	5.7	13.7
8T	10.8	6.8	4.7	7.4	3.3	7.6	3.3	7.4
8P	10.7	7.6	4.7	8.1	3.4	8.3	3.3	8.1
10P	11.3	9.9	5.1	10.3	3.7	10.5	3.7	10.3
SLR	14.5	17.4	6.9	17.5	5.1	17.5	5.1	17.3

All the values are in eV.

The predictions of the HSAB principle for some chemical reactions have been used to test the performance of the new hardness formulations. Indeed, if the “preference” for hard-hard and soft-soft interactions, providing that other quantities such as strength remain unaltered, is the driving force of the reactions between acids and bases, the corresponding reaction energies have to assume values in agreement with this behavior. Thus, the exchange reactions in gas-phase between two acid-base complexes have been considered and the reaction energy is assumed as a measure of the stabilization of hard-hard and soft-soft adducts in comparison to the corresponding hard-soft and soft-hard counterparts. The general scheme, which we have already used⁶¹ for the acid-base reactions during which a base (X), bonded to the hard acid (H^+), removes a hard base (OH^-) from a soft acid, (HO^+) is



and to determine which reaction is more favorable the corresponding reaction energies are compared. Indeed, the more negative the reaction energy the softer the base X would be.

Computational Details

Quantum chemical computations were performed at *ab initio* Hartree-Fock, and, to include correlation effects, local-DF VWN,⁶² gradient corrected-DF BP86,^{63,64} and hybrid-DF B3LYP^{63,65,66} levels of theory together with the standard 6-31+G* basis set were also used. Several DF approaches were used to test if possible differences in behaviors could be ascribed to the method used. Geometries were fully optimized to evaluate global hardness values for all the bases X that were: CN^- , CH_3S^- , CH_3SH , CH_3O^- , NH_3 , and H_2O . Structures of all the adducts involved in the considered acid-base reactions were also optimized without constraints to evaluate reaction energies, which were corrected for zero point energy (ZPE) and thermal corrections to obtain free reaction energies. All the computations were performed using the GAUSSIAN98 program.⁶⁷ Global hardness values were calculated using both general eqs. (8) and (10) and appropriate coefficients for each approximation level.

Table 6. HF, B3LYP, VWN, and BP86 Chemical Hardness Computations for the NH_3 Molecule, Using Orbital Energies and Vertical Ionization Potentials and the Electron Affinities Calculation, Respectively.

Schemes η (eV)	HF		B3LYP		VWN		BP86	
	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical
2C	16.9	14.6	8.3	14.7	6.3	14.8	6.4	14.5
4C	18.9	15.1	9.1	15.3	6.6	15.5	6.7	15.1
6C	12.8	9.2	5.7	9.4	4.1	9.5	4.1	9.2
SP	15.1	11.3	6.9	11.5	4.9	11.7	5.0	11.3
6T	20.4	16.6	9.5	16.9	7.0	17.1	7.1	16.7
8T	11.9	8.8	5.4	8.9	3.9	9.1	3.9	8.8
8P	12.3	9.8	5.8	9.9	4.4	10.0	4.4	9.8
10P	13.8	12.8	7.1	12.8	5.6	12.9	5.6	12.7
SLR	19.4	22.1	11.2	21.9	9.3	21.9	9.3	21.8

All the values are in eV.

Table 7. HF, B3LYP, VWN, and BP86 Chemical Hardness Computations for the H₂O Molecule, Using Orbital Energies and Vertical Ionization Potentials and the Electron Affinities Calculation, Respectively.

Schemes η (eV)	HF		B3LYP		VWN		BP86	
	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical	Orbital	Vertical
2C	19.2	16.3	9.3	16.7	13.9	16.8	7.1	16.5
4C	22.1	17.1	10.5	17.5	15.6	17.8	7.9	17.3
6C	15.4	10.5	7.2	10.8	10.5	11.0	5.3	10.7
SP	17.9	12.9	8.5	13.1	12.4	13.4	6.3	13.0
6T	24.5	18.8	11.9	19.2	17.8	19.6	9.0	19.1
8T	14.2	10.0	6.7	10.3	9.7	10.4	4.9	10.2
8P	14.0	11.1	6.6	11.3	9.7	11.4	4.9	11.2
10P	14.9	14.2	7.3	14.5	10.9	14.6	5.6	14.3
SLR	19.7	24.1	10.4	24.4	16.3	24.6	8.2	24.3

All the values are in eV.

Results and Discussion

With the aim to test the above expanded second derivative compact difference schemes for chemical hardness calculation, in Tables 2–7 are reported the hardness values for the bases (X = CN[−], CH₃S[−], CH₃SH, CH₃O[−], NH₃, and H₂O) involved in the acid-base reaction eq. (11). For each level of theory are reported two columns that are labeled *orbital* and *vertical*. *Orbital* values are obtained introducing orbital energies into working eq. (10), whereas *vertical* values are obtained using calculated vertical I_1 and A_1 into eq. 8.

Some general conclusions can be drawn from the reported results. For each scheme *orbital* hardness values are about two times smaller than the *vertical* ones in all cases, except when the HF/6-31+G* computational protocol is adopted. In this latter case the differences are less pronounced and, on the contrary, the *vertical* values are smaller than the *orbital* ones. Results obtained at local VWN and nonlocal BP86 levels are coincident and in some cases differences are negligible also with respect to the B3LYP values. The HF values are completely different when the *orbital* operational definition of hardness is used, whereas *vertical* values are very close to those obtained at all the other levels of theory. The observed similarities indicate that the results do not strongly depend on the theoretical level used, except the remarkable dif-

ference between *orbital* values calculated at HF level and all DF *orbital* values, due to already underlined different meanings of orbital energies within the two approaches.

Concerning the trend of values along each column, as the second derivative computational scheme is varied, no regular increasing or decreasing can be observed. It is noteworthy that when the *orbital* operational definition is used the first, 2C, and the last, SLR, values are close to each other, whereas a difference of at least 2 eV exists between the same *vertical* values. The hardness values for water and ammonia obtained by introducing available experimental values of I and A into eq. (2) are 19.0 and 18.4 eV, respectively. These “experimental” values compare very well with the corresponding *orbital* 2C values calculated at HF level and, as a consequence, with *orbital* SLR values at the same level of theory. It seems that when the operational definition of eq. (3), in terms of HOMO and LUMO energies, is applied within the level of theory for which the use of Koopmans’ theorem is justified, it is pointless to make use of more precise approximations. On the contrary, 2C *vertical* values at all the considered levels of theory are close to the numbers obtained through the use of the “experimental” values of I and A , while data obtained applying more precise schemes cover a wider range. In this latter case, improved computational schemes should represent alternative operational recipes if they work better in ordering molecules by hardness according to their chemical behavior. Indeed, because the “experimental” ordering is based on hardness evaluation through eq. (2), which is an approximation to the exact definition of eq. (1), the matching of the “experimental” values cannot be used to assess the goodness of the obtained data.

In Table 8 the free reaction energies (ΔG) are given for each of the probe bases used in the exchange reaction eq. (11). The DF values of free reaction energies calculated employing different functionals are similar among them and only B3YP ones have been reported. Although values of ΔG calculated at HF level differ with respect to the DF ones the trend remains unaltered. The bases have been chosen according to their general classification as hard (CH₃O[−], NH₃, H₂O) or soft (CN[−], CH₃S[−], CH₃SH) and the reported values of reaction free energies correspond to their expected behavior. Because the more negative the ΔG the softer the

Table 8. HF and B3LYP Free Reaction Energies (in kJ/mol) for Each of the Probe Bases Involved in the Test Exchange Acid-Base Reaction.

Species	ΔG	
	B3LYP	HF
CN [−]	−190.8	−216.7
CH ₃ S [−]	−150.2	−181.2
CH ₃ SH	−128.0	−78.7
CH ₃ O [−]	−27.2	−23.4
NH ₃	6.7	−17.2
H ₂ O	71.1	61.5

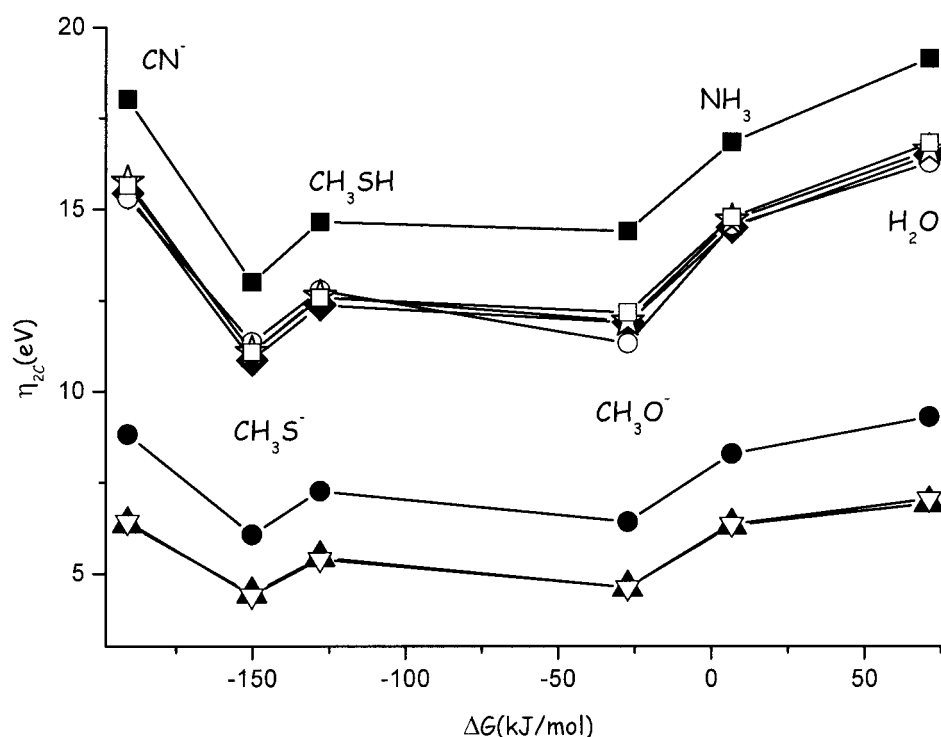


Figure 1. Hardness values (in eV) for the probe bases calculated through the second order central (2C) scheme as a function of free reaction energies (in kJ/mol) for orbital HF: ■, B3LYP: ●, VWN: ▲, BP86: ▽ and vertical BP86: ◆, HF: ○, B3LYP: ☆, and VWN: □ computations.

base X, that is, the easier it is to remove the hard base OH^- from the soft acid HO^+ , in Table 8 bases are arranged from the softest, CN^- , to the hardest, H_2O , ones. Consequently, the calculated hardness values would satisfy this requirement and according to ΔG values the hardness order would be $\text{CN}^- < \text{CH}_3\text{S}^- < \text{CH}_3\text{SH} < \text{CH}_3\text{O}^- < \text{NH}_3 < \text{H}_2\text{O}$. In Figure 1 and 2 B3LYP reaction free energies are plotted as a function of the hardness. In particular, in Figure 1 are reported hardness values calculated employing the coefficients corresponding to 2C scheme, for both the *orbital* and *vertical* approaches, whereas in Figure 2 η values computed using all the other schemes are plotted versus ΔG values. At a first glance it appears that none of the applied scheme is able to provide hardness values in agreement with the trend of reaction energies. The classification of the chosen bases as hard for CH_3O^- , NH_3 , H_2O , and soft for CH^- , CH_3S^- , CH_3SH , does not correspond to the calculated hardness values, whatever the used level of theory and the computational scheme are. It is noteworthy that the hardness for the hardest base, H_2O , is comparable to that of the softest one, CN^- . All the effects due to: the different values of orbital energies calculated at HF and DF levels; correlation; improved computational schemes for the second order derivatives; and the use of *orbital* and *vertical* energies seem to not influence at all the final result. In spite of the differences in hardness values due to the adoption of computational schemes that improve the approximate calculation of second order derivatives, the final trend is practically the same. The computational scheme corresponding to the lowest level of approximation as well as the highest one

gives hardness values that do not support the “preference” for the formation of hard-hard and soft-soft adducts. Further work has to be devoted to the introduction of a more refined working formula, which takes into account of the nature of the examined compounds and of the particular physical situation⁷ that defines the curve of the energy $E(N)$.

Finally, the results of this work have been used to check the parabolic behavior of the energy as a function of the electron number, $E(N)$, which is the limiting assumption for the use of the operational definitions of eqs. (2) and (3). In Figure 3 are reported the plots of the energy as a function of N for each probe base for all the employed levels of theory in the range from $N - 3$ to $N + 3$. It clearly appears that the energy behavior is parabolic and hardness correctly represents the curvature of the plot. The use of rough approximations for the hardness computation appears to be justified and the origin of the discrepancies, more and more numerous (see for example refs. 47, 48, 52b, 52d, 61, 68), between HSAB predictions and experimental and theoretical results has to be found elsewhere.

Conclusions

The focus of this work was to check whether the quantitative applicability of the HSAB principle can be limited by the use of hardness evaluation of working formula, which is only finite difference approximation to the rigorous definition of chemical

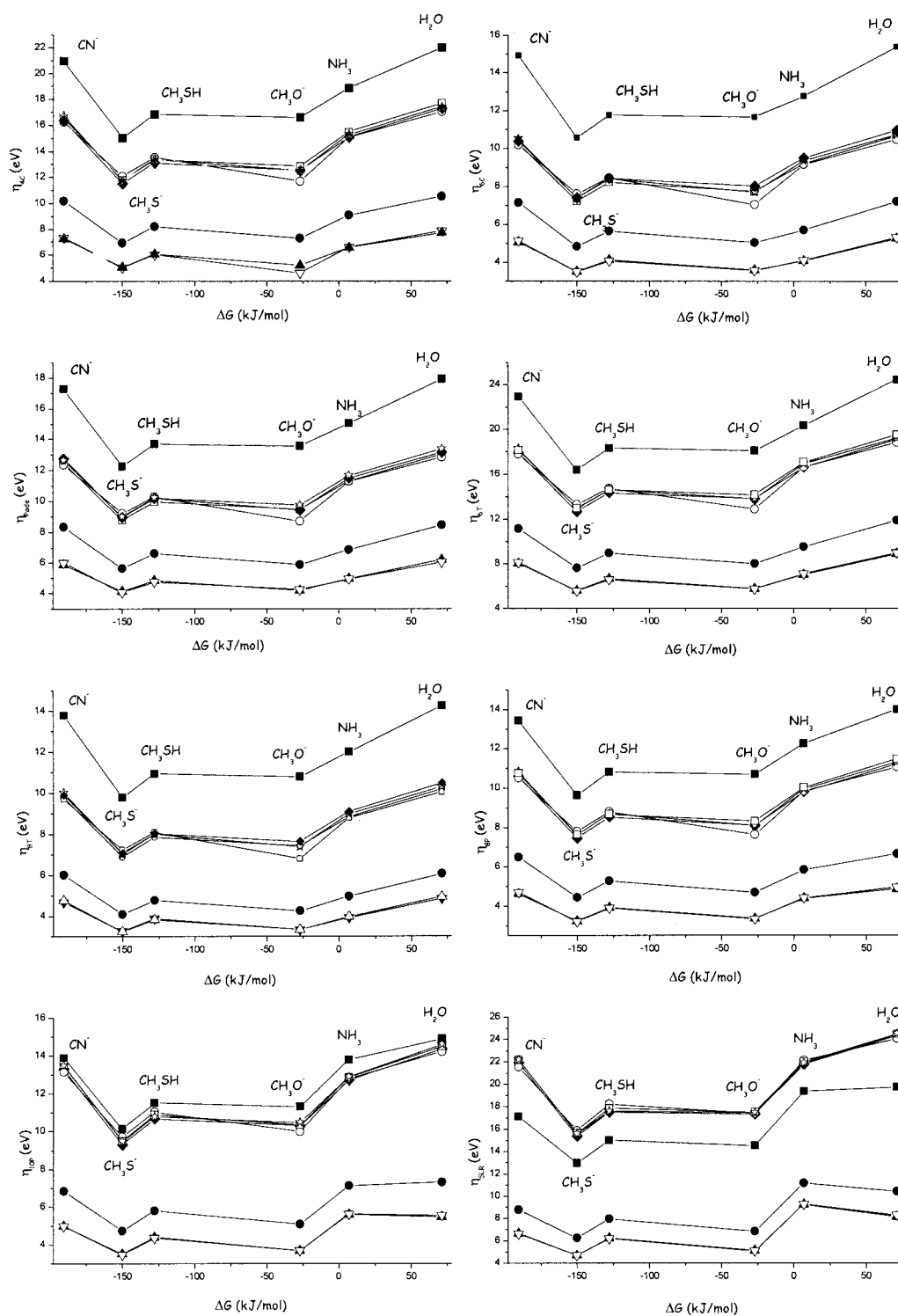


Figure 2. Hardness values (in eV) for the probe bases calculated through the fourth (4C)- and sixth (6C)-order central differences; standard Padé (SP) schemes; sixth (6T)- and eighth (8T)-order tridiagonal schemes; eighth (8P)- and tenth (10P)-order pentadiagonal schemes; and spectral-like resolution (SLR) scheme as a function of free reaction energies (in kJ/mol) for orbital HF: ■, B3LYP: ●, VWN: ▲, BP86: ▽ and vertical BP86: ◆, HF: ○, B3LYP: ☆, and VWN: □ computations.

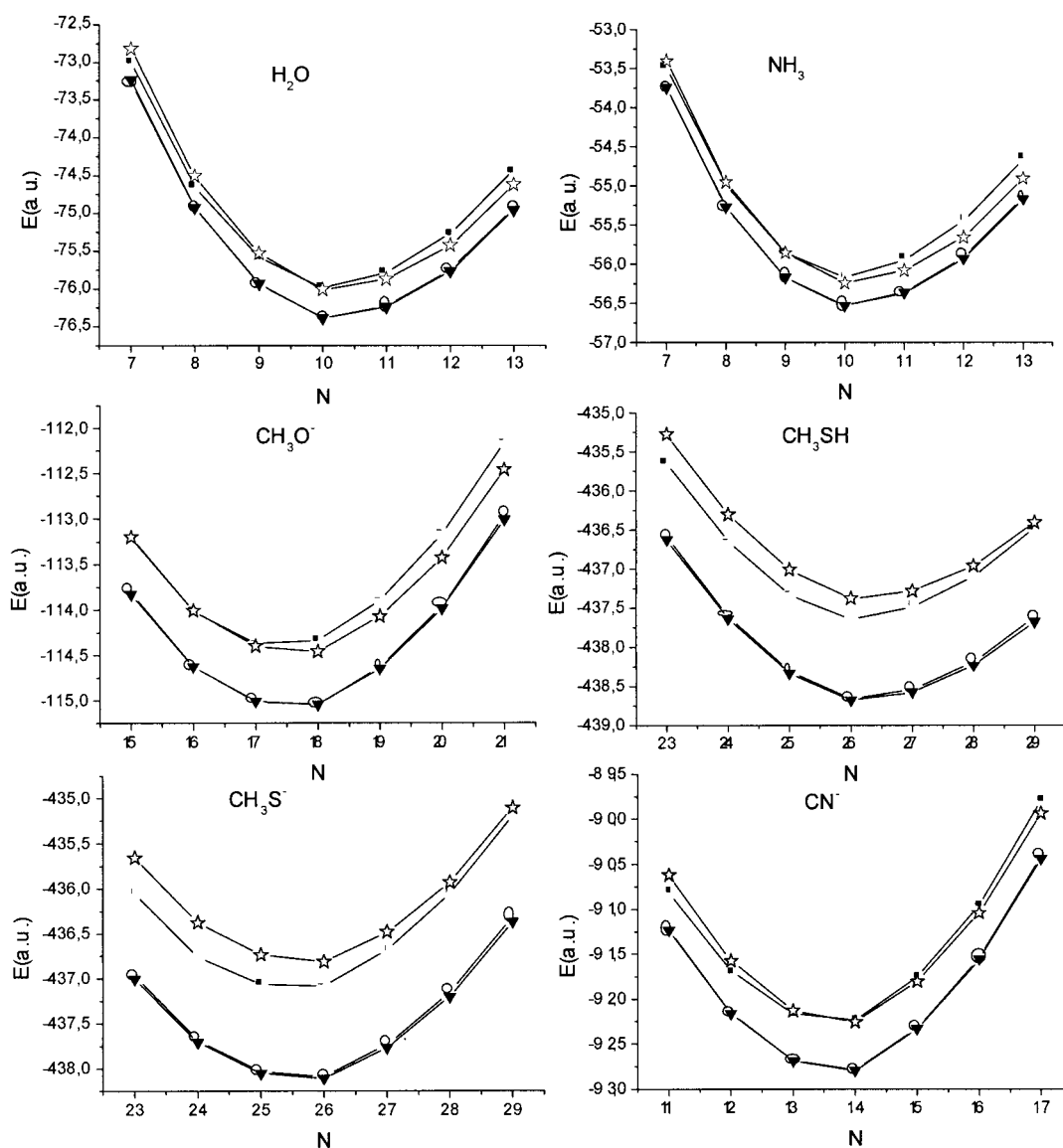


Figure 3. Plots of the HF: ■, B3LYP: ○, VWN: ☆, and BP86: ▼ total energies (in a.u.) as a function of the number of electrons (N), in the range between $N - 3$ and $N + 3$ for each base used in the test exchange acid-base reactions.

hardness as the second order derivative of the energy with respect to the electron number. To this aim Compact Finite Difference Schemes with SLR have been employed for a less rough estimate of the analytical definition of hardness, and the chemical hardness of a series of probe bases has been calculated using computational schemes of increasing complexity. The bases have been chosen on the basis of their traditional classification as hard or soft and the obtained values have been used to test the predictions of the HSAB principle for exchange reactions during which the base, bonded to a hard acid, removes a hard base from a soft acid. The reaction energy was assumed as a measure of the stabilization of the product adducts. No adopted computational scheme, whatever the employed level of theory, has given hardness values in agreement

with the proper order of preference for the examined acid-base reactions.

References

1. Pearson, R. G. *J Am Chem Soc* 1963, 85, 3533.
2. Pearson, R. G. *Science* 1966, 151, 172.
3. Pearson, R. G. *J Chem Educ* 1968, 45, 581.
4. Pearson, R. G. *J Am Chem Soc* 1985, 107, 6801.
5. Pearson, R. G. *Acc Chem Rec* 1993, 26, 250.
6. Pearson, R. G. *J Chem Educ* 1987, 64, 561.
7. Parr, R. G.; Pearson, R. G. *J Am Chem Soc* 1983, 105, 7512.

8. Pearson, R. G. *Struct Bonding* 1993, 80, 1.
9. (a) Kohn, W.; Becke, A. D.; Parr, R. G. *J Phys Chem* 1996, 100, 1274; (b) Ayers, P. W.; Parr, R. G. *J Am Chem Soc* 2000, 122, 2010; (c) Ayers, P. W.; Parr, R. G. *J Am Chem Soc* 2001, 123, 2007.
10. Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
11. (a) Cohen, M. H. In *Theory of Chemical Reactivity*. Topics in Current Chemistry, Vol. 183; Nalewajski, R. F., Ed.; Springer-Verlag: Berlin, 1996, p 143; (b) Cohen, M. H.; Ganduglia-Pirovano, M. V.; Kudrnosky, J. *J Chem Phys* 1995, 103, 3543; (c) Cohen, M. H.; Ganduglia-Pirovano, M. V.; Kudrnosky, J. *J Chem Phys* 1994, 101, 8988.
12. Mineva, T.; Neshev, N.; Russo, N.; Sicilia, E.; Russo, N. *Adv Quantum Chem* 1999, 33, 273.
13. Nalewajski, R. F. *J Am Chem Soc* 1984, 106, 944.
14. (a) Komorowski, L. *Chem Phys Lett* 1987, 134, 536; (b) Komorowski, L. *Chem Phys* 1987, 114, 55.
15. Grigorov, M.; Weber, J.; Chermette, H.; Tronchet, J. M. *J Int J Quantum Chem* 1997, 61, 551.
16. *Chemical Hardness Structure and Bonding*, Vol. 80; Sen, K. D., Ed.; Springer-Verlag: Berlin, 1993.
17. Mortier, W. J.; Gosh, S. K.; Shankar, S. *J Am Chem Soc* 1986, 108, 4315.
18. Galvan, M.; Dal Pino, A.; Joannopoulos, J. D. *Phys Rev Lett* 1993, 70, 21.
19. Liu, G. H. *J Chem Phys* 1997, 106, 165.
20. Chattaraj, P. K.; Cedillo, A.; Parr, R. G. *J Chem Phys* 1995, 103, 7645.
21. Liu, S.; De Proft, F.; Parr, R. G. *J Phys Chem A* 1997, 101, 6991.
22. Torrent-Sucarrat, M.; Duran, M.; Sola, M. *J Phys Chem A* 2002, 106, 4632.
23. Parr, R. G.; Chattaraj, P. K. *J Am Chem Soc* 1991, 113, 1854.
24. Mineva, T.; Russo, N.; Sicilia, E. *J Am Chem Soc* 1998, 120, 9053.
25. Sicilia, E.; Russo, N.; Mineva, T. *J Phys Chem A* 2001, 105, 442.
26. Chattaraj, P. K.; Lee, H.; Parr, R. G. *J Am Chem Soc* 1991, 113, 1855.
27. De Proft, F.; Langeneaker, W.; Geerlings, P. *J Phys Chem* 1993, 97, 1826.
28. Chattaraj, P. K.; Nath, S.; Sannigrahi, A. B. *Chem Phys Lett* 1993, 212, 223.
29. Datta, D. *J Phys Chem* 1992, 96, 2409.
30. Pal, N.; Vaval, N.; Roy, S. *J Phys Chem* 1993, 97, 4404.
31. Chattaraj, P. K.; Nath, S.; Sannigrahi, A. B. *J Phys Chem* 1994, 98, 9143.
32. Cardenas-Jirón, G. I.; Toro-Labbé, A. *J Phys Chem* 1995, 99, 12730.
33. Kar, T.; Scheiner, S. *J Phys Chem* 1995, 99, 8121.
34. Ghanty, T. K.; Ghosh, S. K. *J Phys Chem* 1996, 100, 12295.
35. Cardenas-Jirón, G. I.; Gutierrez-Oliva, S.; Melin, J.; Toro-Labbé, A. *J Phys Chem* 1997, 101, 4621.
36. Kar, T.; Scheiner, S.; Sannigrahi, A. B. *J Phys Chem* 1998, 102, 5967.
37. Chandra, A. K.; Nguyen, M. T. *J Phys Chem* 1998, 102, 6181.
38. Cardenas-Jirón, G. I.; Gutierrez-Oliva, S.; Letelier, J. R.; Toro-Labbé, A. *Mol Phys* 1999, 96, 61.
39. Le, T. N.; Nguyen, L. T.; Chandra, A. K.; De Proft, F.; Geerlings, P.; Nguyen, M. T. *J Chem Soc Perkin Trans 2* 1999, 1249.
40. Nguyen, L. T.; Le, T. N.; De Proft, F.; Chandra, A. K.; Langeneaker, W.; Nguyen, M. T.; Geerlings, P. *J Am Chem Soc* 1999, 121, 5992.
41. Chattaraj, P. K.; Fuentealba, P.; Gomez, B.; Contreras, R. *J Am Chem Soc* 2000, 122, 348.
42. Toro-Labbé, A. *J Phys Chem* 1999, 103, 4398.
43. Pérez, P.; Toro-Labbé, A.; Contreras, R. *J Phys Chem* 1999, 103, 11246.
44. Ghanty, T. K.; Ghosh, S. K. *J Phys Chem* 2000, 104, 2975.
45. Sebastian, L. *Chem Phys Lett* 1994, 231, 40.
46. Parr, R. G.; Yang, W. *Annu Rev Phys Chem* 1995, 46, 701.
47. Skancke, A.; Skancke, P. N. *J Phys Chem* 1996, 100, 15079.
48. Chattaraj, P. K.; Schleyer, P. V. R. *J Am Chem Soc* 1994, 116, 1067.
49. Chattaraj, P. K.; Gomez, B.; Chamorro, E.; Santos, J.; Fuentealba, P. *J Phys Chem A* 2001, 105, 8815.
50. (a) Mendez, F.; Gazquez, J. L. *J Am Chem Soc* 1994, 116, 9298; (b) Gazquez, J. L.; Mendez, F. *J Phys Chem* 1994, 98, 4591.
51. Chattaraj, P. K. *J Phys Chem A* 2001, 105, 8815.
52. (a) Drago, R. S. *Struct Bonding* 1973, 15, 73; (b) Drago, R. S.; Kabler, R. A. *Inorg Chem* 1972, 11, 3144; (c) Drago, R. S. *Inorg Chem* 1973, 12, 21; (d) Shoeib, T.; Gorelsky, S. I.; Lever, A. B. P.; Siu, K. W. M.; Hopkinson, A. C. *Inorg Chim Acta* 2001, 315, 236.
53. (a) Jonas, V.; Frenking, G.; Reetz, M. T. *J Am Chem Soc* 1994, 116, 8741; (b) Anane, H.; Boutalib, A.; Nebot-Gil, I.; Tomas, F. *J Phys Chem A* 1998, 102, 7070; (c) Anane, H.; Boutalib, A.; Nebot-Gil, I.; Tomas, F. *Chem Phys Lett* 1998, 287, 575.
54. See e.g.: (a) Mendez, F.; Gazquez, J. L. *J Am Chem Soc* 1994, 116, 9298; (b) Gazquez, J. L.; Mendez, F. *J Phys Chem* 1994, 98, 4591; (c) Li, Y.; Evans, J. N. S. *J Am Chem Soc* 1995, 117, 7756; (d) Nguyen, L. T.; Le, T. N.; De Proft, F.; Chandra, A. K.; Langeneaker, W.; Nguyen, M. T.; Chandrakumar, K. R. S. *J Am Chem Soc* 2000, 122, 4145 and references therein; (e) Perez, P.; Simon-Manso, Y.; Aizman, A.; Fuentealba, P.; Contreras, R. *J Am Chem Soc* 2000, 122, 4756 and references therein.
55. Klopman, G. *J Am Chem Soc* 1968, 90, 223.
56. Chattaraj, P. K. *J Phys Chem A* 2001, 105, 511 and references therein.
57. Chermette, H. *J Comput Chem* 1999, 20, 129.
58. Geerlings, P.; De Proft, F.; Langeneaker, W. *Chem Rev* 2003, 103, 1793.
59. Lele, S. K. *J Comp Phys* 1992, 103, 16.
60. Rubin, S. G.; Khosla, P. K. *J Comp Phys* 1977, 24, 217.
61. De Luca, G.; Sicilia, E.; Russo, N.; Mineva, T. *J Am Chem Soc* 2002, 124, 1494.
62. Vosko, S. H.; Wilk, L.; Nusair, M. *Can J Phys* 1980, 58, 1200.
63. Becke, A. D. *Phys Rev A* 1988, 38, 3098.
64. Perdew, J. P. *Phys Rev B* 1986, 33, 8822.
65. Becke, A. D. *J Chem Phys* 1993, 98, 5648.
66. Lee, C.; Yang, W.; Parr, R. G. *Phys Rev B* 1988, 37, 785.
67. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheesman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
68. Shoeib, T.; Aribi, H. E.; Siu, K. W. M.; Hopkinson, A. C. *J Phys Chem* 2001, 105, 710.