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Atomic Fukui function indices and local softness *ab initio*

Robert Balawender and Ludwik Komorowski^{a)}

*Institute of Physical and Theoretical Chemistry, Wrocław University of Technology,
Wyb. Wyspiańskiego 27, PL-50-370 Wrocław, Poland*

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The complete and original calculation scheme beyond the finite difference approximation, for the atomic (and orbital) Fukui function (FF) indices is proposed. The method explores an expansion for derivatives of LCAO coefficients, $\partial \mathbf{C} / \partial N = \mathbf{C} \mathbf{U}$. The separation scheme for the \mathbf{U} matrix has been elaborated at the *ab initio* level. Nucleophilic and electrophilic FF indices, as well as atomic softness, have been derived from the standard result of SCF HF *ab initio* calculations. The indices reproduce two effects; the change in orbital occupancy and the relaxation of the electronic system. The molecular hardness (softness) provided by this scheme explicitly includes these two effects.
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I. INTRODUCTION

Density functional theory (DFT) has offered formal justification of purely experimental description of the behavior of electrons in molecules,¹ as developed by chemists within the framework of the electronegativity concept. Based on theorems by Hohenberg and Kohn² this theory focuses on the electron density function $\rho(\mathbf{r})$, the fundamental quantity for a many-electron system, containing all information on atomic and molecular ground-state properties. This theory provided solid support for traditional chemical ideas of electronegativity³ and hardness,⁴ and also introduced new descriptors such as hardness and softness kernels,⁵ global and local softness,⁶ Fukui function.⁷ The Fukui function, as proposed by Parr and Yang, is related to the Fukui's concept of frontier molecular orbitals (FMO). The Fukui method predicts the site of electrophilic reaction in a molecule to be where the relative density of the HOMO is high and the position of nucleophilic reaction to be where the relative density of the LUMO is high.⁸ Even if widely used, the method can hardly be justified as a general tool, as it frequently leads to false conclusions, e.g., in the famous counterexample, pyridine. Li and Evans have recently suggested that the FMO description can be incorporated into the more general DFT principle; the hard and soft acids and bases.⁹

A number of elaborate methods for local (atomic) description of molecular properties have been proposed within the DFT. The most common atomic index remains the atomic charge. New methods for calculation of atomic charges on the ground of electronegativity equalization have been proposed by Gasteiger and Marsili,¹⁰ and by Mortier,¹¹ the later scheme has been further developed by Geerlings and co-workers.¹² Several attempts have been directed to obtain Fukui function (FF) indices numerically. Yang and Mortier proposed condensed FF indices by the crude finite difference approximation based on atomic charges.¹³ Nalewajski introduced atom-in-molecule (AIM) FF indices in an original, normal representation.¹⁴ Komorowski *et al.* calcu-

lated atomic and group FF indices (and hardness) by the semiempirical method.^{15,16} Balawender *et al.* introduced a similar scheme at the *ab initio* level.¹⁷ Liu and Parr proposed calculation of molecular hardness, softness, and Fukui indices by SCF calculations, however, the finite-difference approximation has been used throughout their work.¹⁸ The most profound, variational method for determining FF indices and chemical hardness proposed by Chattaraj *et al.* has not yet been developed into a workable calculation scheme.¹⁹

In this paper, a strictly nonfinite difference approximation is proposed for the energy and density derivatives with respect to the number of electrons within the Hartree-Fock SCF method. The LCAO MO scheme with integral occupations of molecular orbitals (MO) for the closed shell systems has been chosen as the most general model available to chemists, both on the operational and conceptual level. This present analysis is suitable for understanding effects directly included in the approach (relaxation), which could not be reproduced by finite-difference approximations. The proposed method is readily applicable to any calculation technique based on LCAO. Electronegativity equalization has been demonstrated as a natural property of this approximation.

II. LOCAL DESCRIPTORS IN THE DENSITY FUNCTIONAL THEORY OF CHEMICAL REACTIVITY

The electronegativity χ of an N -electron system in its ground state, is defined in terms of the chemical potential μ , as³

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)}, \quad (1)$$

where E is the total electronic energy and $v(r)$ is the external potential. The Mulliken formula²⁰ $\chi = \frac{1}{2}(I + A)$, where I is the ionization energy and A is the electron affinity, is just the finite-difference approximation for Eq. (1). Similarly, the global hardness is defined by⁴

^{a)} Author to whom correspondence should be addressed.

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(r)}. \quad (2)$$

The 1/2 factor has been conventionally introduced into the definition of hardness for symmetry reasons, and leads to $\eta = \frac{1}{2}(I-A)$ in the finite-difference approximation.¹ In consequence, a routinely used definition of global softness is

$$S = \left(\frac{\partial N}{\partial \mu} \right)_{v(r)} = \frac{1}{2\eta}. \quad (3)$$

The first functional derivative of E with respect to the local electron density $\rho(r)$ is formally the local value of the chemical potential (negative of the local electronegativity)^{1,3,21}

$$\mu(r) = \left(\frac{\delta E}{\delta \rho(r)} \right)_{v(r)} = -\chi(r). \quad (4)$$

In a global equilibrium state the electronegativity (chemical potential) is equalized throughout the whole system. This follows from the property of the Lagrangian multiplier, in accordance with the intuitive principle of Sanderson,^{21,22} $\mu(r) = \text{const.}$

The functional derivative of the chemical potential μ with respect to the density is the local hardness²³

$$\eta(r) = \frac{1}{2} \left(\frac{\delta \mu}{\delta \rho(r)} \right)_{v(r)}. \quad (5)$$

The local hardness $\eta(r)$ proved to be ill-defined; it may be arbitrarily set as equal to global hardness η , constant for any point in the system in the global equilibrium state.²³ No local information about the system is available from electronegativity or hardness.

The truly local density functional quantity is the Fukui function⁷

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)}. \quad (6)$$

The Fukui function indicates how the incoming or outgoing number of electrons is redistributed in regions of the molecule, hence it is of primary importance for a chemist. For the finite system, the derivative in Eq. (6) (and all derivatives with respect to the number of electrons) is discontinuous. Parr and Yang have proposed to associate $f(r)$ with reactivity indices.⁷ In nucleophilic attack (the increasing number of electrons)

$$f^+(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)}^+, \quad (7)$$

and in an electrophilic attack (decreasing number of electrons),

$$f^-(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)}^-, \quad (8)$$

where the superscripts (+/−) refer to right and left derivatives, respectively. For neutral reagents (a radical or species of similar electronegativity) the Fukui function has been proposed as the average of those two derivatives,

$$f^0(r) = \frac{1}{2}[f^+(r) + f^-(r)]. \quad (9)$$

In the finite difference approach $f^+(r)$ and $f^-(r)$ reduce to the original Fukui indices^{7,24}

$$f^+(r) \approx \rho_{N+1}(r) - \rho_N(r) \approx \rho_{\text{LUMO}}(r), \quad (10)$$

$$f^-(r) \approx \rho_N(r) - \rho_{N-1}(r) \approx \rho_{\text{HOMO}}(r), \quad (11)$$

where ρ_N , ρ_{N+1} , and ρ_{N-1} are electron density functions of N , $N+1$, and $N-1$ electron systems, respectively, at the same geometry. The $f^0(r)$ is then

$$f^0(r) \approx \frac{1}{2}[\rho_{N+1}(r) - \rho_{N-1}(r)] \\ \approx \frac{1}{2}[\rho_{\text{LUMO}}(r) - \rho_{\text{HOMO}}(r)]. \quad (12)$$

A condensed version of Eqs. (7)–(9) has been proposed by Yang and Mortier. Integration of the information contained in $f(r)$ in the neighborhood of a given atom A may be approximated by using the gross atomic charge q_A available from a Mulliken population analysis.²⁵ The condensed Fukui function index on the atom A is¹³

$$f_A^+ = q_A(N+1) - q_A(N), \quad (13)$$

$$f_A^- = q_A(N) - q_A(N-1), \quad (14)$$

$$f_A^0 = \frac{1}{2}[q_A(N+1) - q_A(N-1)]. \quad (15)$$

An alternative approximation of the Fukui function, entirely neglecting the discontinuity of the derivative at N has been used by Nalewajski,¹⁴

$$f(r) = \frac{\rho(r)}{N}. \quad (16)$$

The Fukui function is normalized to unity. Using Janak's formulation²⁶ of the Kohn–Sham theory,²⁷ Yang *et al.*^{7,28} have expressed $f(r)$ in terms of Kohn–Sham orbitals, $\phi(r)$. Here the electron coordinate x is comprised of a space coordinate r and a spin coordinate s , $x = (r, s)$. Yang *et al.* obtained relations

$$f^+(r) = \sum_s \left\{ |\phi_{N+1}(x)|^2 + \sum_{i=1}^N \left[\frac{\partial |\phi_i(x)|^2}{\partial N} \right]_{v(r)}^+ \right\} \quad (17)$$

and

$$f^-(r) = \sum_s \left\{ |\phi_N(x)|^2 + \sum_{i=1}^{N-1} \left[\frac{\partial |\phi_i(x)|^2}{\partial N} \right]_{v(r)}^- \right\}. \quad (18)$$

Another local quantity, potentially characterizing a +site in a molecule, is the local softness^{5,6}

$$s^\alpha(r) = \left[\frac{\partial \rho(r)}{\partial \mu} \right]_{v(r)}^\alpha = \left[\frac{\partial \rho(r)}{\partial N} \right]_{v(r)}^\alpha \left[\frac{\partial N}{\partial \mu} \right]_{v(r)}^\alpha = f^\alpha(r) S^\alpha, \quad (19)$$

where the superscript $\alpha = (+/-)$ indicates the one-sided derivative. The local softness s integrates to the global softness S , and appears as the key local descriptor at the DFT level. The Fukui function is now the normalized softness.

III. $\partial/\partial N$ DERIVATIVES IN THE LCAO MO APPROXIMATION

For a closed-shell, single-determinant, self-consistent-field (SCF) wave function in the typical LCAO MO approach,²⁹ the electronic energy is minimized with respect to variations of molecular orbital coefficients \mathbf{C} under the constraint of orthonormality,

$$\mathbf{C}^T \mathbf{S} \mathbf{C} = \mathbf{1}. \quad (20)$$

\mathbf{S} is the overlap matrix in the atomic orbital (AO) basis for the fixed external potential (i.e., the ‘‘frozen’’ nuclear positions). In the restricted Hartree–Fock (RHF) theory, the electronic energy for a single configuration closed-shell SCF wave function is

$$E = \text{tr } \mathbf{n}(\mathbf{H} + \frac{1}{2}\mathbf{G}), \quad (21)$$

where \mathbf{H} stands for one-electron integrals matrix (kinetic and electron–nuclei attraction energies) and \mathbf{G} is the two-electron integrals matrix in the molecular orbital (MO) basis. The elements of diagonal matrix \mathbf{n} contain MO occupations (2 for occupied MO and 0 for virtual MO). In RHF theory, the Fock operator for a single-configuration closed-shell SCF wave function is

$$\mathbf{F} = \mathbf{H} + \mathbf{G}. \quad (22)$$

The SCF energy is invariant to a unitary transformation within the occupied space and the diagonal Fock matrix (\mathbf{e}) defines the canonical molecular orbitals,³⁰

$$F_{ij} = \delta_{ij} e_i, \quad (23)$$

where e_i are orbital energies.

The derivative of the μ th coefficient of the i th MO with respect to the number of electrons may be expanded in the basis of unchanged MOs. Similar procedures have been successfully used for the derivatives over the geometrical coordinates,³⁰ and time,³¹

$$\left(\frac{\partial c_{\mu i}}{\partial N} \right)_{v(r)} = \sum_m^{\text{MO}} c_{\mu m} U_{mi} \quad \text{or} \quad \left(\frac{\partial \mathbf{C}}{\partial N} \right)_{v(r)} = \mathbf{C} \mathbf{U}. \quad (24)$$

For simplicity, the superscripts (+/–) are not shown, however, the derivative with respect to N is discontinuous. Hence, Eq. (24) must be written separately for (+) and (–) derivatives, and in fact defines two new matrices to be found, \mathbf{U}^+ and \mathbf{U}^- . Taking the derivative ($\partial/\partial N$) of the orthonormality condition of the molecular orbitals [Eq. (20)] reveals that the \mathbf{U} matrix is antisymmetric; this important property will be extensively explored throughout this work,

$$\mathbf{U}^T + \mathbf{U} = \mathbf{0}. \quad (25)$$

When the external potential is fixed (frozen nuclear positions) both one- and two-electron integrals of AOs are unchanged. The derivative of the \mathbf{H} matrix becomes

$$\left(\frac{\partial \mathbf{H}}{\partial N} \right)_{v(r)} = \mathbf{H} \mathbf{U} - \mathbf{U} \mathbf{H}. \quad (26)$$

The two-electron MO integrals ($ij|kl$) for MO, are by definition,

$$(ij|kl) = \sum_{\mu\nu\rho\sigma}^{\text{AO}} c_{\mu i} c_{\nu j} c_{\rho k} c_{\sigma l} (\mu\nu|\rho\sigma). \quad (27)$$

The derivative can be expanded into a sum,

$$\left(\frac{\partial (ij|kl)}{\partial N} \right)_{v(r)} = \sum_m^{\text{MO}} \{ U_{mi} (mj|kl) + U_{mj} (im|kl) + U_{mk} (ij|ml) + U_{ml} (ij|km) \}. \quad (28)$$

For the \mathbf{G} matrix, differentiation with respect to the number of electrons gives

$$\left(\frac{\partial \mathbf{G}}{\partial N} \right)_{v(r)} = \mathbf{G} \mathbf{U} - \mathbf{U} \mathbf{G} + \mathbf{G}^f + \mathbf{G}^U. \quad (29)$$

The elements of \mathbf{G}^f and \mathbf{G}^U matrices are

$$G_{ij}^f = \sum_l^{\text{MO}} \left(\frac{\partial n_l}{\partial N} \right)_{v(r)} \left\{ (ij|ll) - \frac{1}{2}(il|jl) \right\} = \sum_l^{\text{MO}} f_l \left\{ (ij|ll) - \frac{1}{2}(il|jl) \right\}, \quad (30)$$

$$G_{ij}^U = \sum_l^{\text{MO}} \sum_m^{\text{MO}} (U_{ml} n_l - n_m U_{ml}) \left\{ (ij|lm) - \frac{1}{2}(im|jl) \right\}. \quad (31)$$

The analysis of the MO index f_l will follow in Sec. IV. Using Eqs. (22), (26), (29) for the \mathbf{F} matrix one gets

$$\left(\frac{\partial \mathbf{F}}{\partial N} \right)_{v(r)} = \mathbf{F} \mathbf{U} - \mathbf{U} \mathbf{F} + \mathbf{G}^f + \mathbf{G}^U. \quad (32)$$

IV. THE FUKUI FUNCTION INDICES

The probability $\sigma_{i\mu}$ of occupying the μ th AO in i th MO is defined,

$$\sigma_{i\mu} = c_{i\mu} \sum_\nu^{\text{AO}} c_{i\nu} S_{\mu\nu}. \quad (33)$$

The Mulliken population of μ th AO is²⁵

$$n_\mu = \sum_i^{\text{MO}} n_i \sigma_{i\mu}. \quad (34)$$

The summation over the AOs centered on nucleus A leads to the representation of this atom in the molecule. The atomic population,

$$n_A = \sum_{\mu \in A}^{\text{AO}} n_\mu = \sum_{\mu \in A}^{\text{AO}} \sum_i^{\text{MO}} n_i \sigma_{i\mu}. \quad (35)$$

Before proceeding to the AO Fukui function indices it is useful to find derivative expressions for the density matrix. The density matrix takes the form

$$\mathbf{P} = \mathbf{C} \mathbf{n} \mathbf{C}^T, \quad (36)$$

and its derivative,

$$\begin{aligned} \left(\frac{\partial \mathbf{P}}{\partial N}\right)_{v(r)} &= \mathbf{C} \left(\frac{\partial \mathbf{n}}{\partial N}\right)_{v(r)} \mathbf{C}^T + \left(\frac{\partial \mathbf{C}}{\partial N}\right)_{v(r)} \mathbf{n} \mathbf{C}^T \\ &+ \mathbf{C} \mathbf{n} \left(\frac{\partial \mathbf{C}^T}{\partial N}\right)_{v(r)}. \end{aligned} \quad (37)$$

Equations (24), (25) are now used to yield

$$\left(\frac{\partial \mathbf{P}}{\partial N}\right)_{v(r)} = \mathbf{C} \mathbf{f} \mathbf{C}^T + \mathbf{C} (\mathbf{U} \mathbf{n} - \mathbf{n} \mathbf{U}) \mathbf{C}^T, \quad (38)$$

where $\mathbf{f} = \partial \mathbf{n} / \partial N$ is the diagonal matrix of MO Fukui function indices. The integral population of molecular orbitals requires that Fukui function indices for MOs simply be

$$f_i^+ = \left(\frac{\partial n_i}{\partial N}\right)_{v(r)}^+ = \begin{cases} 0, & i \neq \text{LUMO} \\ 1, & i = \text{LUMO} \end{cases} \quad (39)$$

$$f_i^- = \left(\frac{\partial n_i}{\partial N}\right)_{v(r)}^- = \begin{cases} 0, & i \neq \text{HOMO} \\ 1, & i = \text{HOMO} \end{cases}$$

The derivative of the population of the μ th AO [Eq. (34)] with respect to N can now be written as

$$\begin{aligned} \left(\frac{\partial n_\mu}{\partial N}\right)_{v(r)} &= \left(\frac{\partial (\mathbf{P}\mathbf{S})_{\mu\mu}}{\partial N}\right)_{v(r)} \\ &= (\mathbf{C} \mathbf{f} \mathbf{C}^T \mathbf{S})_{\mu\mu} + (\mathbf{C} (\mathbf{U} \mathbf{n} - \mathbf{n} \mathbf{U}) \mathbf{C}^T \mathbf{S})_{\mu\mu}. \end{aligned} \quad (40)$$

The diagonal elements of $\mathbf{P}\mathbf{S}$ matrix are simply the Mulliken populations and \mathbf{S} is constant for the frozen geometry and the basis set. Using the antisymmetric property of the \mathbf{U} matrix, the AO FF index,

$$\begin{aligned} f_\mu &= \left(\frac{\partial n_\mu}{\partial N}\right)_{v(r)} = \sum_i f_i \sigma_{i\mu} + \sum_i n_i \left(\frac{\partial \sigma_{i\mu}}{\partial N}\right)_{v(r)} \\ &= f_{1,\mu} + f_{2,\mu}. \end{aligned} \quad (41)$$

Summing over the AOs centered on nucleus A, and considering one side derivatives, $\alpha = (+/-)$, the following is obtained for the atomic FF index:

$$\left(\frac{\partial n_A}{\partial N}\right)_{v(r)}^\alpha = f_{1,A}^\alpha + f_{2,A}^\alpha, \quad (42)$$

where

$$f_{1,A}^\alpha = \sum_{\mu \in A}^{\text{AO}} \sum_{\nu}^{\text{AO}} c_{\text{FMO}\mu}^\alpha c_{\text{FMO}\nu} S_{\mu\nu},$$

and

$$f_{2,A}^\alpha = 2 \sum_k^{\text{vir}} \sum_i^{\text{occ}} U_{ki}^\alpha \sum_{\mu \in A}^{\text{AO}} \sum_{\nu}^{\text{AO}} (c_{k\mu} c_{i\nu} + c_{i\mu} c_{k\nu}) S_{\mu\nu}.$$

$f_{1,A}$ accounts for the effect of changing MO occupations; its form is identical to the previously described.^{15,17} The second term $f_{2,A}$ represents the MO relaxation contribution for the frozen MO occupations; it is an original result of this work. Quite interestingly, the contributions from the occupied-occupied and virtual-virtual orbital interactions vanish due to the antisymmetric property of the \mathbf{U} matrix.

V. THE DERIVATIVES OF THE ELECTRONIC ENERGY

From the definition of the electronegativity χ for an N -electron system in its ground state we have [Eqs. (26), (32)],

$$\begin{aligned} \left(\frac{\partial E}{\partial N}\right)_{v(r)} &= \left(\frac{\partial}{\partial N} \text{tr} \frac{1}{2} \mathbf{n} (\mathbf{H} + \mathbf{F})\right)_{v(r)} \\ &= \text{tr} \frac{1}{2} \mathbf{f} (\mathbf{H} + \mathbf{F}) + \text{tr} \frac{1}{2} \mathbf{n} [(\mathbf{H} + \mathbf{F}) \mathbf{U} - \mathbf{U} (\mathbf{H} + \mathbf{F})] \\ &+ \text{tr} \frac{1}{2} \mathbf{n} (\mathbf{G}^f + \mathbf{G}^U). \end{aligned} \quad (43)$$

From the detailed form of \mathbf{G} , \mathbf{G}^f , and \mathbf{G}^U matrices [Eqs. (27)–(31)] the following identity may be demonstrated:

$$\text{tr} \frac{1}{2} \mathbf{n} (\mathbf{G}^f + \mathbf{G}^U) = \text{tr} \frac{1}{2} (\mathbf{f} + \mathbf{U} \cdot \mathbf{n} - \mathbf{n} \cdot \mathbf{U}) \mathbf{G}. \quad (44)$$

Applying Eq. (44) and Eq. (22) in Eq. (43) leads to

$$\left(\frac{\partial E}{\partial N}\right)_{v(r)} = \text{tr} \mathbf{f} \mathbf{F} + \text{tr} \mathbf{U} (\mathbf{n} \cdot \mathbf{F} - \mathbf{F} \cdot \mathbf{n}). \quad (45)$$

The Fock matrix commutes with the \mathbf{n} matrix, and the second term vanishes identically. For canonical orbitals [Eq. (23)], the global electronegativity χ becomes

$$\chi = - \left(\frac{\partial E}{\partial N}\right)_{v(r)} = - \text{tr} \mathbf{f} \cdot \mathbf{e} = \begin{cases} \chi^+ = -e_{\text{LUMO}} \\ \chi^- = -e_{\text{HOMO}} \end{cases}. \quad (46)$$

The electronegativity of the X fragment can now be analyzed in the same fashion. If n_X is the electron population of the fragment and $n_R = N - n_X$ the population of the rest of the molecule, a consistent definition for the electronegativity of the fragment X is

$$\chi_X = - \left(\frac{\partial E}{\partial n_X}\right)_{v(r), n_R}. \quad (47)$$

Using Eqs. (26)–(32) and (45) for the derivatives written with respect to the population of the X molecular fragment yields (the U_X matrix for the fragment must be used instead of the global U matrix)

$$\left(\frac{\partial E}{\partial n_X}\right)_{v(r), n_R} = \text{tr} \left(\frac{\partial \mathbf{n}}{\partial n_X}\right)_{v(r), n_R} \mathbf{e}. \quad (48)$$

Due to the extreme MO occupation in the HF approximation, we have

$$\left(\frac{\partial \mathbf{n}}{\partial n_X}\right)_{v(r), n_R} = \left(\frac{\partial \mathbf{n}}{\partial N}\right)_{v(r)} = \mathbf{f}. \quad (49)$$

Hence, the principle of electronegativity equalization holds for any chosen fragment X ,

$$\hat{\chi} \chi_X = - \left(\frac{\partial E}{\partial n_X}\right)_{v(r), n_R} = - \left(\frac{\partial E}{\partial N}\right)_{v(r)} = - \text{tr} \mathbf{f} \cdot \mathbf{e} = \chi. \quad (50)$$

The analysis of hardness must start with the global hardness η [Eq. (2)]. Using Eqs. (26)–(32), (44), and (45), the following expression results:

$$\eta = \frac{1}{2} \text{tr} \left(\frac{\partial \mathbf{f}}{\partial N}\right)_{v(r)} \mathbf{e} + \frac{1}{2} \text{tr} (\mathbf{f} + \mathbf{U} \cdot \mathbf{n} - \mathbf{n} \cdot \mathbf{U}) \mathbf{G}^f. \quad (51)$$

Using the approximation proposed for the molecular FF index f_l [Eq. (39)], G^f matrix elements introduced by Eq. (30) is reduced to

$$G_{ij}^f = (i, j | \text{FMO}, \text{FMO}) - \frac{1}{2}(i, \text{FMO} | j, \text{FMO}). \quad (52)$$

The detailed form of the final expression for the global hardness η depends on the approximation applied to the derivative $\partial f / \partial N$. The choice $\partial f_{\text{MO}} / \partial N = 0$, though not unique, is consistent with the argument given in Eq. (39) for integral occupancies of molecular orbitals. This leads to the global hardness for the molecule as seen in the nucleophilic ($\alpha = \{+\}$, FMO=LUMO) and electrophilic attack ($\alpha = \{-\}$, FMO-HOMO),

$$\eta^\alpha = \frac{1}{4} J_{\text{FMO}} + \sum_i^{\text{vir}} \sum_j^{\text{occ}} U_{ij}^\alpha [2(i, j | \text{FMO}, \text{FMO}) - (i, \text{FMO} | j, \text{FMO})],$$

where

$$J_{\text{FMO}} = (\text{FMO}, \text{FMO} | \text{FMO}, \text{FMO}). \quad (53)$$

The global softness S^α can be obtained directly from its definition, Eq. (3).

VI. THE U MATRIX SEPARATION SCHEME

The differentiation of the variational condition for the RHF close-shell SCF [Eq. (23)] with respect to a number of electrons for the fixed external potential leads, for any pair of canonical orbitals i, j ,

$$\left(\frac{\partial F_{ij}}{\partial N} \right)_{v(r)} = \delta_{ij} e'_i. \quad (54)$$

Due to the antisymmetric property of the \mathbf{U} matrix, its diagonal elements vanish identically, $U_{ii} = 0$ and the situation $i = j$ will not concern us any further. Rewriting Eq. (32) for $i \neq j$ we have

$$\sum_k (U_{ki} F_{kj} + U_{kj} F_{ik}) + \frac{1}{2} \sum_{kl} U_{kl} n_l [4(ij|kl) - (ik|jl) - (il|jk)] + \sum_l f_l [(ij|ll) - \frac{1}{2}(il|jl)] = 0. \quad (55)$$

To abbreviate the notation, a symmetric τ matrix will be defined by its elements

$$\tau_{ijkl} = 4(ij|kl) - [(ik|jl) + (il|jk)]. \quad (56)$$

Considering the diagonal nature of the \mathbf{F} matrix [Eq. (23)] and the antisymmetry of the \mathbf{U} matrix reduces Eq. (55) to

$$U_{ij}(e_j - e_i) - \frac{1}{2} \sum_{kl} U_{kl} n_l \tau_{ijkl} = \sum_l f_l [(ij|ll) - \frac{1}{2}(il|jl)]. \quad (57)$$

The second term in the left-hand side of Eq. (57) may be further manipulated in the following way. Using the antisymmetric property of the \mathbf{U} matrix and orbital populations n_i equal 2 and 0 for the occupied and virtual orbitals, gives

$$\begin{aligned} \sum_{kl} U_{kl} n_l \tau_{ijkl} &= \sum_{k>l} U_{kl} n_l \tau_{ijkl} + \sum_{k>l} U_{lk} n_k \tau_{ijkl} \\ &= \sum_{k>l} U_{kl} n_l \tau_{ijkl} - \sum_{k>l} U_{kl} n_k \tau_{ijkl} \\ &= \sum_{k>l} U_{kl} (n_l - n_k) \tau_{ijkl} \\ &= 2 \sum_k^{\text{vir}} \sum_l^{\text{occ}} U_{kl} \tau_{ijkl}. \end{aligned} \quad (58)$$

Hence,

$$U_{ij}(e_j - e_i) - \sum_k^{\text{vir}} \sum_l^{\text{occ}} U_{kl} \tau_{ijkl} = \sum_l f_l [(ij|ll) - \frac{1}{2}(il|jl)]. \quad (59)$$

Introducing the f_l as given by Eq. (39) one finally gets

$$\begin{aligned} U_{ij}^\alpha (e_j - e_i) - \sum_k^{\text{vir}} \sum_l^{\text{occ}} U_{kl}^\alpha \tau_{ijkl} \\ = (ij | \text{FMO}, \text{FMO}) - \frac{1}{2}(i, \text{FMO} | j, \text{FMO}). \end{aligned} \quad (60)$$

The set of such equations potentially allows calculation of the nondiagonal elements of the \mathbf{U} matrix. However, the procedure must proceed in two steps, separately for the two bodies of MO pairs i, j . When i is an occupied MO and j is virtual MO (or symmetrically), the pair will be labeled independent. Otherwise the i, j pair is nonindependent. When i, j are independent pairs of MOs, the sum over virtual and occupied MOs (kl) contains exactly one term identical to U_{ij} . Hence, the set of such equations for all ij being the independent pairs is directly solvable for U_{ij} . The elements of the \mathbf{U} matrix for the independent pairs are sufficient for the calculation of the FF indices [Eq. (42)] and the global hardness [Eq. (53)]. Nevertheless, the U_{ij}^α elements for the remaining nonindependent pairs of MOs may also be found subsequently from Eq. (60), once the sum $\sum_k^{\text{vir}} \sum_l^{\text{occ}} U_{kl}^\alpha \tau_{ijkl}$ for the independent pairs is known.

When molecular orbital degeneracy occurs in the system, the MOs must be subjected to a unitary transformation within unique shells using the averaged Fock operator in Eq. (22),

$$F_{ij}^{\text{av}} = H_{ij} + \sum_l^{\text{all}} \frac{p_l}{m_l} \left[(ij|ll) - \frac{1}{2}(il|jl) \right], \quad (61)$$

where p_l is the shell population and m_l stands for its orbital degeneracy. Employing these redefined molecular orbitals, the elements of the \mathbf{U} matrix can be found.

VII. RESULTS AND DISCUSSION

The method described above has been tested on the selection of simple molecules. Calculations have been performed by the RHF method using the GAMESS (Ref. 32) program and the 6-31G* basis set with geometry optimization. Condensed FF indices have also been calculated for bonded

TABLE I. Hardness of the molecule as calculated by various approaches (V/e).

Molecule	$\frac{1}{2}(I-A)$	$\frac{1}{2}(e_L - e_H)$	$\frac{1}{2}(\eta^+ + \eta^-)$	η^+	η^-	$\frac{1}{4}J_{\text{LUMO}}$	$\frac{1}{4}J_{\text{HOMO}}$
BCl ₃	6.537	7.294	1.566	1.561	1.570	2.430	2.024
BF ₃	10.242	11.677	2.202	2.162	2.243	2.634	3.192
BH ₃	7.192	7.973	2.285	2.041	2.530	2.631	3.221
C ₂ H ₂	7.610	8.509	2.088	1.983	2.192	2.558	3.299
C ₂ H ₄	6.549	7.569	1.864	1.820	1.909	2.578	3.095
C ₂ H ₆	9.501	9.943	1.649	1.428	1.871	1.586	2.586
CF ₃ ⁻	4.944	5.735	2.143	1.878	2.408	2.850	3.523
CF ₃ ⁺	9.576	11.388	2.466	2.516	2.416	3.551	3.348
CH ₃ ⁻	5.700	6.501	1.916	1.706	2.126	1.951	3.406
CH ₃ ⁺	8.021	9.071	2.574	2.256	2.892	3.178	3.809
CN ⁻	8.149	9.198	2.272	2.102	2.442	2.701	3.549
CNO ⁻	8.386	9.336	1.974	1.984	1.964	2.718	3.201
H ₂ O	7.443	9.098	2.122	2.066	2.177	2.373	5.217
H ₂ S	6.856	7.573	2.028	1.828	2.227	2.191	3.146
NCO ⁻	8.386	9.336	2.068	2.049	2.087	2.759	3.084
NH ₂ ⁻	5.958	7.098	2.060	1.918	2.202	2.185	4.148
NH ₃	7.237	8.308	2.143	1.797	2.489	1.964	4.319
NH ₄ ⁺	12.021	12.851	2.150	1.735	2.566	1.891	4.006
PH ₂ ⁻	5.352	5.906	1.793	1.659	1.928	1.969	2.578
PH ₃	5.746	6.331	1.900	1.733	2.068	2.089	2.727
PH ₄ ⁺	10.025	10.464	1.920	1.673	2.167	1.942	2.732
OH ⁻	6.761	8.176	2.441	2.345	2.537	2.748	4.946
HS ⁻	6.437	7.159	1.967	1.851	2.083	2.230	2.974
SO ₂	6.224	7.012	2.012	1.977	2.046	2.627	2.869
SO ₃	7.004	8.192	1.955	1.938	1.973	2.626	2.833
CO	8.579	9.715	2.684	2.373	2.994	3.049	4.149
H ₂ CO	6.299	7.908	2.066	2.073	2.060	3.004	3.560
SCN ⁻	6.780	7.619	1.638	1.503	1.772	2.192	2.553

atoms. The results of other authors²⁴ for H₂CO, SCN, and CO have been reproduced with high accuracy when the identical basis set was employed.

The list of molecules is indicated in Table I, where the results for the global hardness are shown. Three measures of global hardness have been obtained within the same calculation scheme and identical basis set; the absolute hardness (classical finite difference approximation), $\frac{1}{2}(I-A)$, the Koopmans approximation, $\frac{1}{2}(e_{\text{LUMO}} - e_{\text{HOMO}})$, and the average global hardness from Eq. (53), $\eta = \frac{1}{2}(\eta^+ + \eta^-)$. While the two former measures of hardness are very well correlated, the latter obviously represents a different approach, being consistently smaller in all molecules under study. The value of global hardness is beyond experimental verification; the only reasonable judgment can be built by confrontation with the absolute hardness of free atoms. While the absolute and Koopmans approaches (Table I, column 1 and 2) give the molecular hardness in the identical range as it is known for free atoms, the average hardness calculated from Eq. (53) tends to suggest that molecules are considerably softer than free atoms.

The problem of units for hardness and softness has not yet been definitely resolved. In this work, the convention is used as developed earlier in this laboratory.³³ Since electrons are charged particles, taking the derivative over the number of electrons $\partial/\partial N$ invariably involves changing the charge. Hence the conventional units are [volt] for electronegativity, [volt/electron] for hardness, and [electron/volt] for softness.

Two terms contribute to the hardness of the molecule. The first is identical to the result reported in our previous

papers.^{15,17} The second term in Eq. (53) is an entirely new contribution introduced by this work and is based on the result for the **U** matrix. This part may be interpreted as a result of the relaxation of the electronic structure upon ionization. Its role is quite important, as proved by the comparison of hardness with $\frac{1}{4}J_{\text{HOMO}}$, $\frac{1}{4}J_{\text{LUMO}}$, the last two entries in Table I. The relaxation term is always negative.

The classical term $(I-A)$ no longer appears in the expression for the global hardness of the molecule. Instead, by neglecting the exchange integrals and the contribution from the relaxation (**U**=0) the present result may be reduced to $\eta^\alpha \cong \frac{1}{2}J_{\text{FMO}}$. An identical expression for global hardness has been obtained earlier within a simplified HF analysis in previous work from this laboratory¹⁷ (see also references therein) and has also been proposed by other authors.³⁴ A distant relation between the global hardness ($\eta^\alpha \cong \frac{1}{2}J_{\text{FMO}}$) and the absolute hardness $\frac{1}{2}(I-A)$ can be explained tentatively by means of the Pariser approximation for the Coulomb integrals ($J \cong I-A$). However, this relation has been proposed for atoms, and as a working approach only; its extension to molecules would be unfounded.³⁵

Review of the results in Table I raises the question: which is the more realistic measure of the global hardness of a molecule: the absolute hardness $\frac{1}{2}(I-A)$, or the Hartree–Fock result [Eq. (53)]? Both represent only an approximation to the derivative $\eta = \frac{1}{2}(\partial^2 E/\partial N^2)_{v(r)}$. The absolute hardness is obtained by a crude finite-difference approximation to the energy function $E(N)$. The approach introduced in this work is more refined, albeit not accurate. It is subject to the limitation of the Hartree–Fock formalism, in particular the inte-

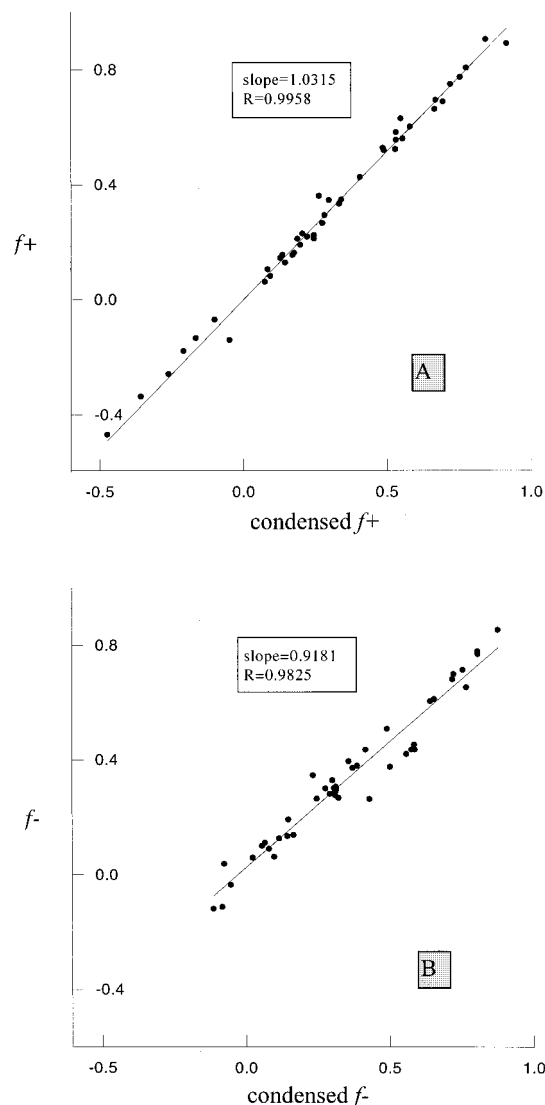


FIG. 1. Fukui function indices calculated by means of Eq. (42) against the condensed indices [Eqs. (13), (14)] for atoms other than hydrogen. (A) Electron accepting process; (B) electron donating process. All atoms in all molecules listed in Table I are included. Calculated slope and correlation coefficient is given in the box.

gral occupation of the molecular orbitals. Equation (53) for hardness seems to be a limit achievable by the rigorous Hartree–Fock treatment. Further application of this new measure of hardness provides additional support to the proposed new measure of hardness.

The principal result of this work are the *ab initio* FF indices calculated from Eq. (42). They have been tested against the condensed FF indices [Eq. (13) and (14)] calculated by the same RHF method and the identical basis set. Results are shown in Fig. 1 for the collection of bonded atoms other than hydrogen, and in Fig. 2 for the bonded hydrogen atoms. Correlation coefficients (R) prove a very good match between the two sets of data; both seem to contain the same information. This fact is significant. The condensed indices are obtained in two independent Hartree–Fock calculation runs for the ion and for the neutral molecule. The *ab initio* FF indices are the result of one single SCF run for a given molecule. The close match be-

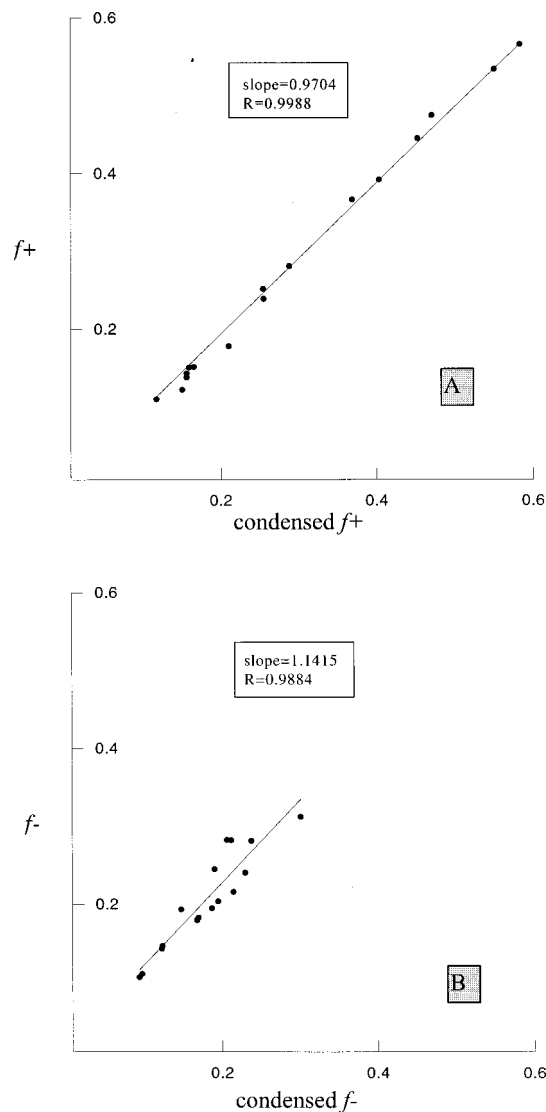


FIG. 2. Fukui function indices calculated by means of Eq. (42) against the condensed indices [Eqs. (13), (14)] for the hydrogen. (A) Electron accepting process; (B) electron donating process. All hydrogen atoms in all hydrogen containing molecules listed in Table I are included. Calculated slope and correlation coefficient is given in the box.

tween the two sets of data indicates that the proposed approximation for the derivative $\partial C/\partial N$ [Eq. (24)] very accurately predicts also the change in atomic charges upon ionization. The *ab initio* FF indices introduced in this work are superior over the condensed ones in one more point; they are independent of the definition of atomic charges, essential for the calculation of the condensed indices.

The analysis of two contributions to the *ab initio* FF indices, f_1 and f_2 [Eq. (42)] is instructive. The first (f_1) is a direct result of changing the orbital population at the HOMO/LUMO level, and is identical to the result obtained earlier by this group.¹⁶ The second (f_2) appears in this present work as the consequence of the proposed approximation for $\partial C/\partial N$ [Eq. (24)]. f_2 contains contributions from MO other than HOMO/LUMO and may be interpreted as a relaxation term due to the change of all MOs due to the ionization process. It also contains the elements of the U matrix and thus f_2 reflects the quality of the approximation

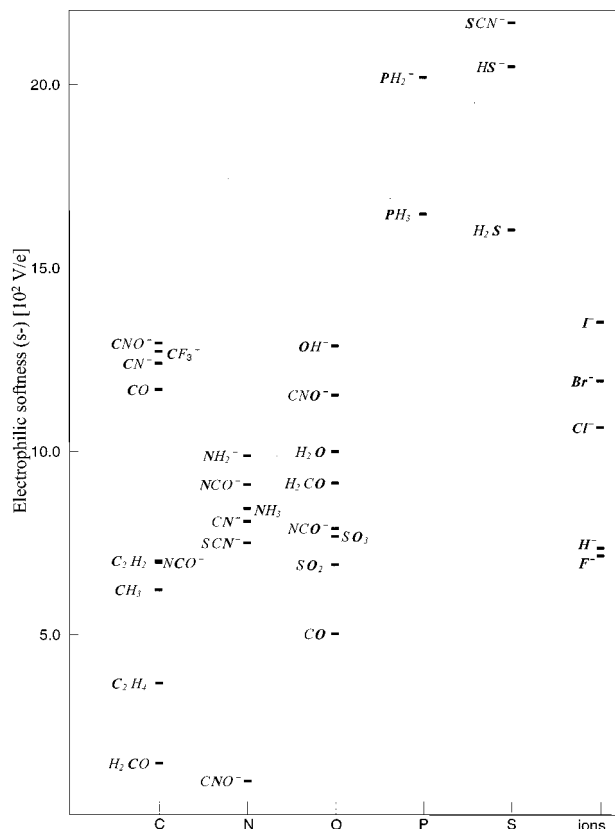


FIG. 3. The diagram of atomic softness for the reaction with an electrophile. Atoms are indicated in boldface. Softness of halogen ions (the last column) has been calculated from their absolute hardness [Eq. (3)] as proposed in Ref. 4.

introduced by this present work. The f_2 term is in most cases smaller than f_1 . In few molecules $f_1=0$ for the hydrogen (BH_3 , C_2H_4 , C_2H_2 , H_2CO) for the symmetry reason. f_2 may be positive or negative, in contrast to f_1 being positive for but a few of the molecules studied (nitrogen in NH_3 , NH_2^- , NH_4^+). An approximation limited to the HOMO/LUMO occupancy proved to be insufficient, except when $f_2 \cong 0$ which is exceptional, in view of the calculated data.

The local (atomic) softness is potentially the most interesting result from the chemical point of view. The fact that bonded atoms show various softnesses belongs to the classics of chemistry (the doubts concerning the definition of the local hardness in DFT represent only the difficulty of describing this fact by the tools of the theory). The ambidental base SCN^- is the best known example. SCN^- shows two kinds of preferences; to the hard external atom (Si) it binds by the hard end (N), to the soft external atom (Pt) if it is bound by the soft end (S).³⁶ The local softness index derived here provides clear quantification of this effect in this molecule and for other similar examples on the list, CO , CN^- , CNO^- , NCO^- .

An important new feature discovered here is the substantial difference between the softness against an electrophile (s^-) and the softness against a nucleophile (s^+). Therefore, separate analysis has been performed for the two sets of data. They have been collected in Fig. 3 (s^-) and Fig. 4 (s^+). Several observations on the diagrams confirm very rational-

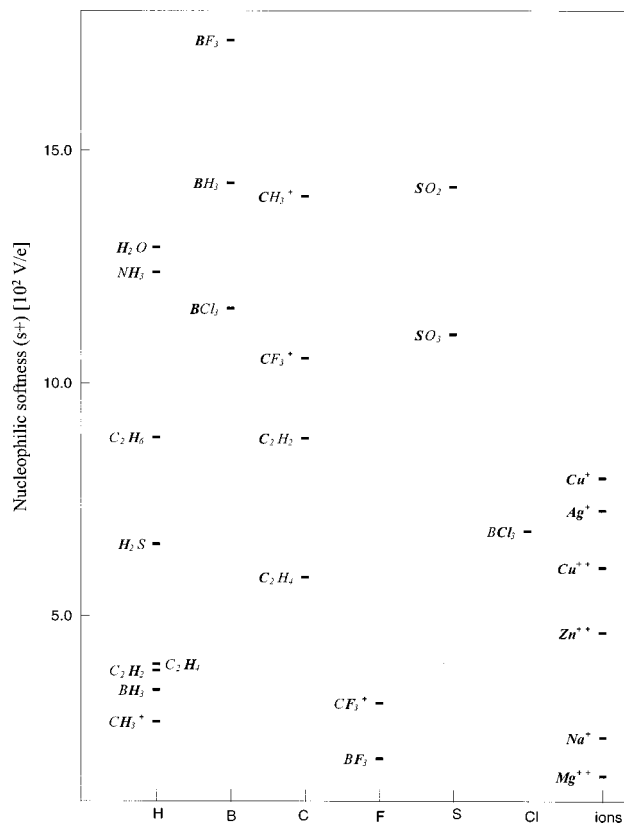
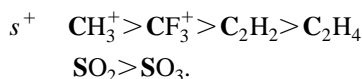
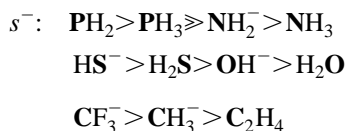


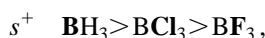
FIG. 4. The diagram of atomic softness for the reaction with a nucleophile. Atoms are indicated in boldface. Softness of simple cations (the last column) has been calculated from their absolute hardness [Eq. (3)] as given in Ref. 4.

character of the proposed atomic softness indices.

- (i) Electrophilic softness (s^-) for the terminal atoms in pseudohalogen ions covers the same range as softness for halogen ions [calculated from absolute hardness by Eq. (3)]. Carbon in CNO^- appears as soft as iodine anion I^- , while nitrogen in CN^- , SCN^- is as hard as fluorine F^- (Fig. 3). Similar correspondence is found for s^+ . Carbon in acetylene is as soft as the Cu^+ and Ag^+ ions, while fluorine in CF_3^+ is as hard as, e.g., Na^+ or Mg^{++} .
- (ii) A number of experimentally well established trends are properly reproduced by the atomic softness (atom in boldface),



However, the classical sequence for boron containing Lewis acids BX_3 is apparently not reproduced by the s^+ of the boron atom (Fig. 4). It is recovered in the form

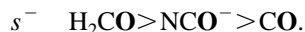


which suggests that acidic character of the boron trifluoride (very hard) and boron chloride (hard) is predominantly determined by the halogens (large), whereas small hydrogen atom in boron hydride does not shield the boron atom from playing a role in acidic action in BH_3 .

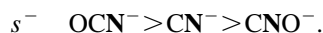
- (iii) Interesting new relations have been disclosed through the data given in Fig. 3 and Fig. 4.



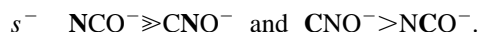
Attaching atoms to the carbon in CO reduces its softness, the more so, the harder atom is attached. This behavior has long been known as the "symbiosis,"³⁷



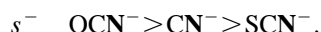
The softness of the terminal oxygen increases upon substitution at the vicinal carbon atom, in reverse order to the former sequence. The two previous observations are confirmed for the nitrogen atom in



Also,



In general, atoms appear softer when bonded in the terminal position than in the chain. An interesting role of electronegativity of the substituting atom can be found on the following example:



An electron withdrawing oxygen atom added to CN^- softens the terminal nitrogen, while an electron donating sulfur atom at the same position makes it harder.

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