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Spin-Polarized Generalization of the Concepts of Electronegativity and Hardness and the Description of Chemical Binding

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Abstract: The generalized spin-dependent electronegativity and hardness parameters for the up- and down-spin electrons, defined within the framework of spin-polarized density functional theory are calculated for atomic systems using self-interaction correction along with local spin-density approximation for the exchange correlation. Chemical binding in molecules is formulated in terms of (i) a two-way flow of unpaired electrons of opposite spin between the atoms governed by these parameters and also (ii) the accumulation of electron density at the bond center using the concepts of electronegativity and hardness for the bond region. The associated energy changes obtained by an electronegativity equalization procedure corresponding to these descriptions are shown to provide quite accurate estimates of bond energies for homonuclear as well as simple heteronuclear polyatomic molecules.

1. Introduction

The concept of electronegativity[1] is one of the most widely used concepts, quite successful for understanding chemical binding and reactivity in molecular systems. Since electronegativity is a measure of the electron attracting power of atoms in a molecule, the interatomic charge transfer and ionic binding are governed by the electronegativity difference and is usually estimated by making use of the well-known electronegativity equalization principle.[1] Consequently, this concept has been less useful for describing the properties of homonuclear molecules or covalent binding in general.

In recent years, however, attempts are being made[2–6] to understand covalent binding within the framework of electronegativity based theories. These approaches rest heavily on the work of Parr et al.[7] who have built a rigorous quantum mechanical foundation for this concept using the density functional theory[8,9] (DFT) of electronic structure. Since DFT uses the electron density as the basic variable and the molecule formation essentially involves a reorganization of the electron density of the atoms, DFT stands as the natural choice for developing concepts to discuss both covalent and ionic binding.

When the atoms approach to form a molecule, the electron density function over the whole space undergoes rearrangement. However, the major features in binding can be understood in terms of the density reorganizations in a few selected regions, where the density variations are most significant. Thus, there is an interatomic charge transfer in heternuclear molecules which is considered in the usual electronegativity based procedures for ionic binding. There is also a charge accumulation in the bond region, which should contribute to covalent binding in both homo- and heteronuclear molecules. Among the other important consequences of the density reorganization in atoms on molecule formation, an important factor that has not received proper attention[6] in the formulation of chemical binding using electronegativity and related concepts is concerned with the role played by the unpaired electrons of the atoms. The resulting effect that can be visualized is a two-way transfer of electrons of opposite spins between the atoms forming a chemical bond even in the absence of a net interatomic charge transfer. This picture is consistent with the concept of electron pair formation by the unpaired electrons of the open shell reactant atoms, even for homonuclear diatomics.

Thus, while ionic binding is a consequence of interatomic charge transfer, covalent binding can be formulated in terms of this spin transfer as well as the accumulation of the electron density in the bond region, both of which take place even in the case of a homonuclear molecule. The purpose of the present work is to develop a formalism for understanding chemical binding in terms of these two important effects, by invoking generalization of the concept of electronegativity to the case of spin-polarized systems[6,10] and also for regions other than the atomic sites. In what follows, we first discuss in section 2 the spin-polarized generalization of the electronegativity and related concepts and their calculation using a rigorous DFT procedure. In section 3, we provide a formulation of both covalent and ionic binding using the generalized electronegativity equalization procedure. Finally we discuss the results of numerical calculation of bond energies for a number of simple molecules in section 4, which is then followed by a few concluding remarks in section 5.

2. Spin-Polarized Density Functional Theory and the Concepts of Generalized Electronegativity and Hardness

The spin-polarized density functional theory employs the single particle up- and down-spin electron densities $\rho_\alpha(r)$ and $\rho_\beta(r)$ as basic variables to describe a many-particle system consisting of N_α and N_β up- and down-spin electrons, respectively. For a given external potential $v(r)$ characterizing the system, the energy can be written as the unique density functional[9]

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$$E[\rho_\alpha,\rho_\beta] = \int v(\mathbf{r})[\rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r})]d\mathbf{r} + F[\rho_\alpha,\rho_\beta] \quad (1)$$

which attains a minimum value when evaluated at the true density. The minimization of this energy functional with respect to the two density components lead to the Euler equations

$$\mu_\alpha = \delta E[\rho_\alpha,\rho_\beta]/\delta\rho_\alpha(\mathbf{r}) = v(\mathbf{r}) + \delta F[\rho_\alpha,\rho_\beta]/\delta\rho_\alpha(\mathbf{r}) \quad (2a)$$

$$\mu_\beta = \delta E[\rho_\alpha,\rho_\beta]/\delta\rho_\beta(\mathbf{r}) = v(\mathbf{r}) + \delta F[\rho_\alpha,\rho_\beta]/\delta\rho_\beta(\mathbf{r}) \quad (2b)$$

where μ_α and μ_β, the Lagrange multipliers for the normalization constraints $\int\rho_\alpha(\mathbf{r})d\mathbf{r} = N_\alpha$ and $\int\rho_\beta(\mathbf{r})d\mathbf{r} = N_\beta$, denote the chemical potentials corresponding to α- and β-spin components. One can also use the variables $\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r})$ and $s(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})$ representing, respectively, the total density and the spin density and thus define a spin potential μ_s as $[\delta E/\delta s(\mathbf{r})]$ along with the conventional chemical potential $\mu \equiv \mu_N = [\delta E/\delta\rho(\mathbf{r})]$, as considered earlier by Galvan et al.[10] Our objective here however is to develop a formalism for chemical binding and predict the bond energies, for which discussion in terms of μ_α and μ_β provides a more transparent picture.

In the spirit of the conventional definition of electronegativity, $\chi = -(\partial E/\partial N)$ denoting the energy derivative with respect to the number of electrons N, we define the two electronegativity parameters χ_α and χ_β as the partial derivatives

$$\chi_\alpha = -(\partial E/\partial N_\alpha); \qquad \chi_\beta = -(\partial E/\partial N_\beta) \quad (3)$$

corresponding to up- and down-spin electrons, respectively.

Following Parr et al.,[7] we can identify these electronegativities as negative of the chemical potentials μ_α and μ_β since

$$\chi_\alpha = -(\partial E/\partial N_\alpha) = -\int(\delta E/\delta\rho_\alpha(\mathbf{r}))(\partial\rho_\alpha(\mathbf{r})/\partial N_\alpha)\,d\mathbf{r} - \int(\delta E/\delta\rho_\beta(\mathbf{r}))(\partial\rho_\beta(\mathbf{r})/\partial N_\alpha)\,d\mathbf{r} = -\mu_\alpha\int(\partial\rho_\alpha(\mathbf{r})/\partial N_\alpha)\,d\mathbf{r} - \mu_\beta\int(\partial\rho_\beta(\mathbf{r})/\partial N_\alpha)\,d\mathbf{r} = -\mu_\alpha \quad (4)$$

and similarly $\chi_\beta = -\mu_\beta$. This identification enables one to calculate these parameters through a rigorous quantum mechanical procedure. Also since μ_α and μ_β as defined in eq 2 are independent of position (in spite of being the sum of position dependent terms), it is clear that on molecule formation each of the two electronegativity parameters should be equal in all the participating atoms. For an open-shell atom, since χ_α and χ_β have different values, there is a two-way transfer of electrons between the atoms even for a homonuclear case, arising from a tendency of this equalization.[6]

In the spirit of the work on chemical hardness[11] by Parr and Pearson,[12] we also define the hardness parameters, η_α and η_β, for up- and down-spin electrons, viz.

$$\eta_\alpha = (^1/_2)(\partial^2E/\partial N_\alpha^{\,2}); \qquad \eta_\beta = (^1/_2)(\partial^2E/\partial N_\beta^{\,2}) \quad (5)$$

and also the cross coefficient

$$\eta_{\alpha\beta} = (\partial^2E/\partial N_\alpha\partial N_\beta) \quad (6)$$

While these definitions are based on derivatives with respect to the global number of electrons, these hardness parameters can also be expressed in terms of the electron densities $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$ through the definition of a local hardness,[13] thus permitting a rigorous calculation of hardnesses through DFT.

Thus, μ_α and μ_β can in principle be calculated using eq 2, with a suitable form for the universal functional $F[\rho_\alpha,\rho_\beta]$, which consists of kinetic energy $T_s[\rho_\alpha,\rho_\beta]$, Coulomb energy $E_{\text{coul}}[\rho]$, and exchange-correlation (XC) energy $E_{\text{XC}}[\rho_\alpha,\rho_\beta]$ contributions. The exact density functional is however known only for the Coulomb energy, viz.

$$E_{\text{coul}}[\rho] = (^1/_2)\int\int d\mathbf{r}\,d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| \quad (7)$$

and hence one has to introduce approximations for T_s as well as E_{XC}. Conventionally, one can employ the Thomas–Fermi–Weizsacker type functional[14] for kinetic and a local spin-density (LSD) approximation[15] for XC, but the accuracy of this procedure for obtaining μ_α and μ_β is rather poor. Alternatively, one can employ an orbital-based prescription to evaluate T_s exactly with an LSD approximation for XC, which corresponds to solving the Kohn–Sham equation[16] to obtain the eigenvalues and orbital densities and hence the density and total energy of the system.

Although the so-called LSD approximation is widely used for E_{XC}, it does not exclude the effect of interaction of an electron with itself, and, as a result, unlike Hartree–Fock theory, the eigenvalues do not correspond to exact electron removal energies as demanded by Koopmans's theorem. Thus, there is a need to subtract this self-interaction correction[17] (SIC) term from the LSD energy functional to obtain the corrected energy functional. In this approach one finally solves the SIC incorporated Kohn–Sham equation

$$[-(^1/_2)\nabla^2 + v_{\text{eff}}^{i\sigma}(r,\{\rho_\sigma\})]\psi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma}^{\text{SIC}}\psi_{i\sigma}(\mathbf{r}) \quad (8)$$

where $\rho_\sigma(\mathbf{r}) = \sum\rho_{i\sigma}(\mathbf{r}) = \sum_i n_{i\sigma}|\psi_{i\sigma}(\mathbf{r})|^2$ with the occupation numbers $n_{i\sigma}$ satisfying $\sum_i n_{i\sigma} = N_\sigma$, and the spin and orbital dependent Kohn–Sham effective potential is given by

$$v_{\text{eff}}^{i\sigma}(\mathbf{r}) = v(\mathbf{r}) + \int d\mathbf{r}'[\rho(\mathbf{r}') - \rho_{i\sigma}(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| + \mu_{\text{XC}}^{\text{LSD}}(\mathbf{r};[\{\rho_\sigma\}]) - \mu_{\text{XC}}^{\text{LSD}}(\mathbf{r};[\rho_{i\sigma}]) \quad (9)$$

where $\mu_{\text{XC}}^{\text{LSD}}$ $(=\delta E_{\text{XC}}^{\text{LSD}}/\delta\rho_\sigma)$ denotes the XC potential within the LSD approximation. In this prescription, the total energy is given by the expression

$$E = \sum_i\sum_\sigma\epsilon_{i\sigma}^{\text{SIC}} - E_{\text{coul}}[\rho] + \sum_i\sum_\sigma E_{\text{coul}}[\rho_{i\sigma}] + E_{\text{XC}}^{\text{LSD}}[\{\rho_\sigma\}] - \sum_i\sum_\sigma E_{\text{XC}}^{\text{LSD}}[\rho_{i\sigma}] - \sum_\sigma\int d\mathbf{r}\,\mu_{\text{XC}}^{\text{LSD}}[\{\rho_\sigma\}]\rho_\sigma(\mathbf{r}) + \sum_i\sum_\sigma\int dr\mu_{\text{XC}}^{\text{LSD}}[\rho_{i\sigma}]\rho_{i\sigma}(\mathbf{r}) \quad (10)$$

By solving the Kohn–Sham equation (8), one thus obtains the eigenvalues as well as the orbitals and hence the total energies of any atom or its positive and stable negative ions, from which the ionization potential (IP) and electron affinity (EA) values corresponding to up- and down-spin can easily be obtained. Better accuracy can however be achieved by obtaining these quantities from the eigenvalues directly instead of as a difference of two large numbers. One can then employ a finite difference approximation to evaluate the parameters χ_σ and η_σ (for $\sigma = \alpha$ or β) defined in eqs 3 and 5 as $(I_\sigma + A_\sigma)/2$ and $(I_\sigma - A_\sigma)/2$, respectively, where I_σ and A_σ represent IP and EA of an electron

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of spin σ. The quantity $\eta_{\alpha\beta}$ can also be obtained in a similar manner, as $(I_\alpha - A_\beta)$, for example, and will be discussed later.

3. Generalized Electronegativity Equalization Procedure and Chemical Binding

When a molecule is formed from isolated atoms, the atomic electron densities are redistributed and the associated energy change obtained through a Taylor series expansion of the energy density functional of eq 1 provides an estimate of the bond energy. Within a semilocal or regional description, the molecule is divided into regions, and one considers the changes in the integrated values of the electron densities in these regions. In a nonequilibrium situation when the unperturbed atoms are placed at appropriate positions corresponding to the equilibrium configuration, there results a two-way flow of the up- and down-spin densities between each pair of bonded atoms and also a charge accumulation in the corresponding bond region. The resulting energy change can be expressed as a second-order perturbation expansion in terms of changes in the average number of electrons corresponding to these three regions, viz. the two atomic sites and the bond region.

For simplicity, we consider the molecule formation as a two-step process, viz. the equilibration of spin leading to a reorganization of the up- and down-spin densities of the constituent atoms and the second step involving charge equilibration corresponding to the accumulation of electron density at each bond region. The energy change due to the first step for the formation of an AB_n type molecule where each of the B species is placed at a distance R_{AB} (the equilibrium A–B bond length) from A, can be expressed as

$$\begin{aligned}\Delta E = {} & \mu_\alpha^{A}\Delta N_\alpha^{A} + \mu_\beta^{A}\Delta N_\beta^{A} + n\mu_\alpha^{B}\Delta N_\alpha^{B} + n\mu_\beta^{B}\Delta N_\beta^{B} + \\ & \eta_\alpha^{A}(\Delta N_\alpha^{A})^2 + \eta_\beta^{A}(\Delta N_\beta^{A})^2 + n\eta_\alpha^{B}(\Delta N_\alpha^{B})^2 + n\eta_\beta^{B}(\Delta N_\beta^{B})^2 + \\ & \eta_{\alpha\beta}^{A}(\Delta N_\alpha^{A})(\Delta N_\beta^{A}) + n\eta_{\alpha\beta}^{B}(\Delta N_\alpha^{B})(\Delta N_\beta^{B}) + \\ & n\eta_{\alpha\alpha}^{A,B}(\Delta N_\alpha^{A})(\Delta N_\beta^{B}) + n\eta_{\beta\beta}^{A,B}(\Delta N_\beta^{A})(\Delta N_\beta^{B}) + \\ & n\eta_{\alpha\beta}^{A,B}(\Delta N_\alpha^{A})(\Delta N_\beta^{B}) + n\eta_{\beta\alpha}^{A,B}(\Delta N_\beta^{A})(\Delta N_\alpha^{B})\end{aligned} \tag{11}$$

where (ΔN_α^{A}) and (ΔN_β^{A}) represent the change in the number of up- and down-spin electrons of atom A. The cross coefficient $\eta_{\alpha\beta}^{A,B}$ represents the atom–atom hardness due to the up- and down-spin electrons of atoms A and B, respectively. Corresponding to this energy expression, the effective up- and down-spin chemical potentials of the atoms A and B are given by

$$\mu_\alpha^{A}(\mathrm{eff}) = \mu_\alpha^{A} + 2\eta_\alpha^{A}(\Delta N_\alpha^{A}) + \eta_{\alpha\beta}^{A}(\Delta N_\beta^{A}) + n\eta_{\alpha\alpha}^{A,B}(\Delta N_\alpha^{B}) + n\eta_{\alpha\beta}^{A,B}(\Delta N_\beta^{B}) \tag{12a}$$

$$\mu_\alpha^{B}(\mathrm{eff}) = \mu_\alpha^{B} + 2\eta_\alpha^{B}(\Delta N_\alpha^{B}) + \eta_{\alpha\beta}^{B}(\Delta N_\beta^{B}) + \eta_{\alpha\alpha}^{A,B}(\Delta N_\alpha^{A}) + \eta_{\beta\alpha}^{A,B}(\Delta N_\beta^{A}) \tag{12b}$$

$$\mu_\beta^{A}(\mathrm{eff}) = \mu_\beta^{A} + 2\eta_\beta^{A}(\Delta N_\beta^{A}) + \eta_{\alpha\beta}^{A}(\Delta N_\alpha^{A}) + n\eta_{\beta\beta}^{A,B}(\Delta N_\beta^{B}) + n\eta_{\beta\alpha}^{A,B}(\Delta N_\alpha^{B}) \tag{12c}$$

$$\mu_\beta^{B}(\mathrm{eff}) = \mu_\beta^{B} + 2\eta_\beta^{B}(\Delta N_\beta^{B}) + \eta_{\alpha\beta}^{B}(\Delta N_\alpha^{B}) + \eta_{\beta\beta}^{A,B}(\Delta N_\beta^{A}) + \eta_{\alpha\beta}^{A,B}(\Delta N_\alpha^{A}) \tag{12d}$$

Equating these effective spin-polarized electronegativities of the two atoms A and B for each spin subject to the charge conservation condition $(\Delta N_\sigma^{A} + n\Delta N_\sigma^{B}) = 0$ for $\sigma = \alpha$ as well as β, we now obtain the expressions for ΔN_α^{A} and ΔN_β^{A} as

$$\begin{aligned}\Delta N_\alpha^{A} = {} & [(\mu_\beta^{A} - \mu_\beta^{B})(\eta_{\alpha\beta}^{A} + \eta_{\alpha\beta}^{B}/n - \eta_{\alpha\beta}^{A,B} - \eta_{\beta\alpha}^{A,B}) - \\ & (\mu_\alpha^{A} - \mu_\alpha^{B})(2\eta_\beta^{A} + 2\eta_\beta^{B}/n - 2\eta_{\beta\beta}^{A,B})]/[(2\eta_\alpha^{A} + 2\eta_\alpha^{B}/n - \\ & 2\eta_{\alpha\alpha}^{A,B})(2\eta_\beta^{A} + 2\eta_\beta^{B}/n - 2\eta_{\beta\beta}^{A,B}) - (\eta_{\alpha\beta}^{A} + \eta_{\alpha\beta}^{B}/n - \eta_{\alpha\beta}^{A,B} - \eta_{\beta\alpha}^{A,B})^2]\end{aligned} \tag{13a}$$

$$\begin{aligned}\Delta N_\beta^{A} = {} & [(\mu_\alpha^{A} - \mu_\alpha^{B})(\eta_{\alpha\beta}^{A} + \eta_{\alpha\beta}^{B}/n - \eta_{\alpha\beta}^{A,B} - \eta_{\beta\alpha}^{A,B}) - \\ & (\mu_\beta^{A} - \mu_\beta^{B})(2\eta_\alpha^{A} + 2\eta_\alpha^{B}/n - 2\eta_{\alpha\alpha}^{A,B})]/[(2\eta_\alpha^{A} + 2\eta_\alpha^{B}/n - \\ & 2\eta_{\alpha\alpha}^{A,B})(2\eta_\beta^{A} + 2\eta_\beta^{B}/n - 2\eta_{\beta\beta}^{A,B}) - (\eta_{\alpha\beta}^{A} + \eta_{\alpha\beta}^{B}/n - \eta_{\alpha\beta}^{A,B} - \eta_{\beta\alpha}^{A,B})^2]\end{aligned} \tag{13b}$$

The total energy change involved in this spin-transfer process (i.e., the first step) is obtained by substituting eqs 13a and 13b in eq 11 and is given by

$$\Delta E^{I}(AB_n) = (^1/_2)[(\mu_\alpha^{A} - \mu_\alpha^{B})\Delta N_\alpha^{A} + (\mu_\beta^{A} - \mu_\beta^{B})\Delta N_\beta^{A}] \tag{14}$$

The amount of spin transfer in the process can also be used to obtain an estimate of the chemical valency and the bond order of the A–B bond.

Unlike for the case of an isolated atom where the spin direction is arbitrary, for pairing to occur between the electrons of atoms involved in binding, the unpaired electron in atom A is considered to be of α-spin, while that of atom B as β-spin and vice versa, which implies that if $N_\alpha^{A} > N_\beta^{A}$ then $N_\alpha^{B} < N_\beta^{B}$. For a homonuclear diatomic molecule A_2, eqs 13 and 14 simplify, respectively, to

$$\Delta N_\alpha^{A} = -\Delta N_\beta^{A} = -(\mu_\alpha^{A} - \mu_\beta^{A})/(2\eta_\alpha^{A} + 2\eta_\beta^{A} - 2\eta_{\alpha\beta}^{A}) \tag{15}$$

and

$$\Delta E_{AA}^{I} = (\mu_\alpha^{A} - \mu_\beta^{A})\Delta N_\alpha^{A} \tag{16}$$

We now consider the second step, where we divide the molecule into $(n+1)$ atomic regions and n bond regions to take into account the charge accumulation in the bond region. The energy change in this step is expressed as an expansion in terms of the changes in the average number of electrons (ΔN) in these atomic and bond regions, viz.

$$\begin{aligned}\Delta E^{II}(AB_n) = {} & \bar{\mu}_A\Delta N_A + n\bar{\mu}_B\Delta N_B + n\mu_{AB}\Delta N_{AB} + \\ & \bar{\eta}_A(\Delta N_A)^2 + n\bar{\eta}_B(\Delta N_B)^2 + n\eta_{AB}(\Delta N_{AB})^2 + n\eta_{A,B}\Delta N_A\Delta N_B + \\ & n\eta_{A,AB}\Delta N_A\Delta N_{AB} + n\eta_{B,AB}\Delta N_B\Delta N_{AB}\end{aligned} \tag{17}$$

where the quantities $\bar{\mu}_A$ and $\bar{\eta}_A$ refer to the average chemical potential and average hardness parameters of atom A after the spin-transfer process and are assumed to be given by

$$\bar{\mu}_A = (^1/_2)[\mu_\alpha^{A}(\mathrm{eff}) + \mu_\beta^{A}(\mathrm{eff})] \tag{18}$$

$$\bar{\eta}_A = (^1/_2)[\eta_\alpha^{A} + \eta_\beta^{A}] \tag{19}$$

The quantities μ_{AB} and η_{AB} here correspond to the chemical potential and hardness parameters characterizing the bond region.[2-4] The cross coefficients $\eta_{A,B}$ and $\eta_{A,AB}$ denoting the atom–atom and atom–bond mutual hardness parameters, respectively, are analogous to similar quantities studied[18,19] earlier and include the effects of the modified external potential experienced by the electrons.

The effective chemical potentials of the atomic and bond regions corresponding to eq 17 are given by

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(18) See, for example; Nalewajski, R. F.; Korchowiec, J.; Zhou, Z. *Int. J. Quant. Chem. Symp.* **1988**, *22*, 349.

(19) For a recent calculation, see: Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1993**, *115*, 1084.

$$\mu_{A}^{\text{eff}} = \bar{\mu}_{A} + 2\bar{\eta}_{A}\Delta N_{A} + n\eta_{A,B}\Delta N_{B} + n\eta_{A,AB}\Delta N_{AB} \quad (20a)$$

$$\mu_{B}^{\text{eff}} = \bar{\mu}_{B} + 2\bar{\eta}_{B}\Delta N_{B} + \eta_{B,A}\Delta N_{A} + \eta_{B,AB}\Delta N_{AB} \quad (20b)$$

$$\mu_{AB}^{\text{eff}} = \mu_{AB} + 2\eta_{AB}\Delta N_{AB} + \eta_{A,AB}\Delta N_{A} + \eta_{B,AB}\Delta N_{B} \quad (20c)$$

and are equalized using the charge conservation condition $\Delta N_A + n\Delta N_B + n\Delta N_{AB} = 0$, to obtain

$$\Delta N_{A} = n[(\mu_{AB} - \bar{\mu}_{A})(2\bar{\eta}_{B} + 2\eta_{AB} - 2\eta_{B,AB}) - (\mu_{AB} - \bar{\mu}_{B})(2\eta_{AB} + \eta_{A,B} - \eta_{A,AB} - \eta_{B,AB})]/[(2n\bar{\eta}_{A} + 2\eta_{AB} - 2n\eta_{A,AB})(2\bar{\eta}_{B} + 2\eta_{AB} - 2\eta_{B,AB}) - (2\eta_{AB} + \eta_{A,B} - \eta_{A,AB} - \eta_{B,AB})^{2}] \quad (21a)$$

$$\Delta N_{B} = [(\mu_{AB} - \bar{\mu}_{B})(2n\bar{\eta}_{A} + 2\eta_{AB} - 2n\eta_{A,AB}) - (\mu_{AB} - \bar{\mu}_{A})(2\eta_{AB} + n\eta_{A,B} - \eta_{A,AB} - n\eta_{B,AB})]/[(2n\bar{\eta}_{A} + 2\eta_{AB} - 2n\eta_{A,AB})(2\bar{\eta}_{B} + 2\eta_{AB} - 2\eta_{B,AB}) - (2\eta_{AB} + \eta_{A,B} - \eta_{A,AB} - \eta_{B,AB})^{2}] \quad (21b)$$

$$\Delta N_{AB} = -[\Delta N_{A}/n + \Delta N_{B}] \quad (21c)$$

For a homonuclear diatomic molecule $\Delta N_A = \Delta N_B$ and one has the simplified result

$$\Delta N_{AA} = -2\Delta N_{A} = \frac{2[\bar{\mu}_{A} - \mu_{AA}]}{[2\bar{\eta}_{A} + 4\eta_{AA} + \eta_{A,A} - 4\eta_{A,AA}]} \quad (22)$$

Equations 17 and 21 lead to the expression for the energy change in the second step given by

$$\Delta E^{\text{II}}(\text{AB}_{n}) = (^{1}/_{2})[\bar{\mu}_{A}\Delta N_{A} + n\bar{\mu}_{B}\Delta N_{B} + n\mu_{AB}\Delta N_{AB}] \quad (23)$$

The net bond energy of an A–B bond in the AB_n molecule, obtained from the sum of contributions from eqs 14 and 23, is given by

$$D_{AB} = -(1/2n)[(\mu_{\alpha}^{A} - \mu_{\alpha}^{B})\Delta N_{\alpha}^{A} + (\mu_{\beta}^{A} - \mu_{\beta}^{B})\Delta N_{\beta}^{A} + \bar{\mu}_{A}\Delta N_{A} + n\bar{\mu}_{B}\Delta N_{B} + n\mu_{AB}\Delta N_{AB}] \quad (24)$$

which simplifies for a homonuclear diatomic molecule to

$$D_{AA} = -[(\mu_{\alpha}^{A} - \mu_{\beta}^{A})\Delta N_{\alpha}^{A} + (\bar{\mu}_{A} - \mu_{AA})\Delta N_{A}] \quad (25)$$

The bond energy is thus contributed by spin transfer arising from the difference between the up- and down-spin electronegativities of the atoms and also the electron density accumulation in the bond region. For heteronuclear molecules, the first step includes a net interatomic charge transfer as well.

4. Results and Discussion

We have calculated the bond energies of several homonuclear diatomic and simple heteronuclear polyatomic molecules involving hydrogen and a number of alkali, alkaline earth, and halogen atoms, using eqs 25 and 24, respectively. The atomic parameters χ_α ($= -\mu_\alpha$), χ_β, η_α, η_β, and $\eta_{\alpha\beta}$ used for this purpose have been obtained through a density functional calculation, while those involving interatomic or bond contributions are obtained through suitable modeling. For calculating atomic χ and η parameters, using a finite difference approximation, one requires knowledge of the IP and EA for each spin i.e., (I_α, I_β) and (A_α, A_β). To obtain these quantities, we have solved the self-interaction corrected Kohn–Sham equation (eq 8) for the atoms concerned using Ceperley parametrization[20] for the XC energy within the LSD approximation.

Although both IP and EA can be calculated from the total energy of an atom and the corresponding positive and negative ions, for better accuracy, we have obtained the IP for up- as well as down-spin electrons from the eigenvalues of the highest occupied (HOMO) levels corresponding to the calculation for the neutral atom, by using Koopmans' theorem, viz., $I_\alpha = -\epsilon_{\text{HOMO}}^{\alpha}$ and $I_\beta = -\epsilon_{\text{HOMO}}^{\beta}$. This has been possible since the eigenvalues calculated from DFT using LSD approximation with SIC agree very well with the experimental values of electron removal energies. We consider $N_\alpha > N_\beta$ without loss of generality and whenever $\epsilon_{\text{HOMO}}^{\alpha}$ and $\epsilon_{\text{HOMO}}^{\beta}$ correspond to different principal quantum numbers, we have assumed both I_α and I_β to be given by negative of $\epsilon_{\text{HOMO}}^{\alpha}$, the orbital energy corresponding to the less strongly bound up-spin electron, since only the valence shell is known to play an important role in chemical binding. For the hydrogen atom also, we have used the same prescription to obtain the parameter I_β.

To obtain the EA for the down spin, we have performed the density functional calculation corresponding to (N_α, $N_\beta + {}^1/_2$) electrons with an occupation $n_{i\beta} = 0.5$ in the otherwise lowest unoccupied (LUMO) empty orbital for down-spin electrons and assumed A_β to be given by (within the Slater transition state concept) this orbital energy, i.e., $A_\beta = -\epsilon_{\text{LUMO}}^{\beta}$. For the up-spin EA, this approach could not however be employed within the present prescription, and we have evaluated A_α through the proportionality approximation, i.e.,

$$A_{\alpha} = (\epsilon_{\text{LUMO}}^{\alpha}/\epsilon_{\text{LUMO}}^{\beta})A_{\beta} \quad (26)$$

While we have employed this scheme for the alkali metal and halogen atoms, for the alkaline earth metals, the EA values are small and have been assumed to be zero here. For the hydrogen atom, it is difficult to obtain $\epsilon_{\text{LUMO}}^{\alpha}$, even on using SIC and therefore its up-spin EA has been obtained by assuming the ratio of the up-spin and down-spin EA values of this atom to be the same as that of the nearest alkali atom, i.e., Li atom. The calculated results on I_α, I_β, A_α, and A_β for hydrogen as well as a number of alkali metal, alkaline earth, and halogen atoms are presented in Table 1, from which the quantities χ_α, χ_β, η_α, and η_β are obtained using the finite difference approximation. The quantity $\eta_{\alpha\beta}^{A}$ is obtained as ($I_\alpha - A_\beta$) which correspond to the expected value $|\Delta N_\alpha^A| = |\Delta N_\beta^A| = 0.5$ in the first step of spin transfer in a homonuclear diatomic molecule.

While the atomic parameters are obtained from a rigorous density functional calculation as discussed above, for the interatomic or bond related quantities, we have introduced models. Using the analogy of electrostatic potential,[21] we assume the bond chemical potential[4,5] μ_{AB} to be proportional to the sum of the atomic chemical potentials and write

$$\mu_{AB} = k_{1}(\mu_{A} + \mu_{B}) \quad (27)$$

Motivated by the approximate proportionality of hardness with inverse[22] of size and also with electronegativity, we propose, for the bond hardness η_{AB}, the model

$$\eta_{AB} = k_{2}(\chi_{\text{bond}})^{1/2}/R_{AB} \quad (28)$$

where the parameter k_2 has been chosen as the bond order (i.e., unity for the homonuclear alkali metal, hydrogen, and halogen diatomics and 2.0 for the homonuclear alkaline earth molecules). The proportionality parameter k_1 in eq 27 is assumed to be

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(21) This is based on the observation that the chemical potential is approximately equal to the electrostatic potential at the covalent radius and the electrostatic potential is additive, see: Politzer, P.; Parr, R. G.; Murphy, D. R. *Phys. Rev.* **1985**, *B31*, 6809.

(22) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1993**, *97*, 4951.

Table 1. Calculated Values[a] of Spin-Dependent Ionization Potentials and Electron Affinities for Atoms

atom	I_α	A_α	I_β	A_β
H	13.6050	0.3710	13.6050	0.4895
Li	5.3422	0.3284	5.3422	0.4333
Na	5.1433	0.2173	5.1433	0.4562
K	4.2874	0.2305	4.2874	0.4383
Rb	4.0709	0.2221	4.0709	0.4395
Cs	3.6933	0.2299	3.6933	0.4213
Be	8.8965	0.0000	8.8965	0.0000
Mg	7.4645	0.0000	7.4645	0.0000
Ca	5.9134	0.0000	5.9134	0.0000
Sr	5.4670	0.0000	5.4670	0.0000
F	20.4564	0.0078	18.6591	3.0613
Cl	13.8904	0.1254	13.0777	3.6002
Br	12.5049	0.1868	11.8553	3.4765
I	11.0290	0.2137	10.5196	3.3427

[a] Present calculation using Kohn–Sham density functional theory with self-interaction correction within the local density approximation (see text for details). All results are in electron volts.

Table 2. Bond Dissociation Energies (D_{AA}) and Bond lengths (R_{AA}) of Selected Homonuclear Diatomic Molecules

molecule (A_2)	A–A bond energy in kcal/mol exptl[a]	calcd[b]	bond length[c] (Å)
H_2	103.2	90.3	0.742
Li_2	25.0	20.1	2.672
Na_2	17.3	18.7	3.078
K_2	11.8	14.5	3.923
Rb_2	10.8	12.4	4.950
Cs_2	10.4	11.2	5.309
Be_2	51.0	45.0	2.500
Mg_2	31.0	31.3	3.435
Ca_2	25.0	24.8	3.947
Sr_2	20.0	22.2	4.200
F_2	37.0	37.0	1.418
Cl_2	57.3	57.3	1.988
Br_2	45.4	50.9	2.284
I_2	35.6	45.0	2.666

[a] Experimental bond dissociation energies are from ref 24. [b] Bond dissociation energies calculated using eq 25 and the atomic parameters of Table 1. [c] Bond lengths (R_{AA}) used in calculation are from ref 24, except Rb_2, Cs_2, Mg_2, Ca_2, and Sr_2 molecules for which R_{AA} values are taken from ref 25.

Table 3. Bond Dissociation Energies, Bond Charges, and Bond Lengths of Selected Simple Heteronuclear Molecules

molecule (AB_n)	A–B bond energy D_{AB} (kcal/mol) exptl[a]	calcd[b]	$(\% D^{I}_{AB})$[c]	bond charge[d] $\Delta N_{A,B}$	bond length[e] R_{AB} (in Å)
HF	135.0	126.4	43.7	0.933	0.918
HCl	102.3	102.7	12.5	1.226	1.274
HBr	86.6	94.1	9.9	1.260	1.408
HI	70.4	87.2	9.1	1.311	1.608
LiH	58.0	49.6	85.4	0.532	1.595
NaH	47.0	49.5	70.1	0.771	1.887
KH	43.0	48.2	76.8	0.757	2.244
RbH	39.0	47.5	76.0	0.786	2.367
CsH	42.0	47.0	82.3	0.718	2.494
LiF	137.0	135.5	96.8	0.403	1.547
LiCl	111.0	108.9	89.7	0.670	2.020
LiBr	100.0	95.9	85.2	0.759	2.170
LiI	83.0	82.3	78.2	0.870	2.392
NaF	114.0	117.1	94.1	0.523	1.840
NaCl	97.5	93.4	83.9	0.801	2.361
NaBr	86.7	83.8	80.5	0.849	2.502
NaI	72.7	73.7	75.2	0.917	2.710
KF	117.0	121.3	96.4	0.474	2.130
KCl	101.0	97.6	89.9	0.723	2.667
KBr	90.5	88.3	87.6	0.770	2.821
KI	78.0	78.6	83.9	0.840	3.048
RbF	117.0	116.7	96.3	0.490	2.266
RbCl	106.0	97.0	91.7	0.680	2.787
RbBr	92.0	87.8	89.8	0.721	2.945
RbI	79.0	78.1	86.8	0.785	3.177
CsF	120.0	122.1	97.5	0.435	2.345
CsCl	104.5	101.3	94.1	0.622	2.906
CsBr	99.5	92.2	92.6	0.667	3.072
CsI	80.0	82.6	90.1	0.737	3.315
BeF_2	151.0	155.2	57.8	0.902	1.400
$BeCl_2$	110.0	103.3	32.9	1.055	1.750
$BeBr_2$	89.0	87.2	27.9	1.062	1.910
BeI_2	69.0	73.8	23.1	1.077	2.100
MgF_2	123.0	126.5	66.4	0.819	1.770
$MgCl_2$	97.0	92.1	43.5	1.012	2.180
$MgBr_2$	81.0	79.8	38.7	1.025	2.340
MgI_2	63.0	68.4	33.4	1.045	2.540
CaF_2	132.0	134.6	75.8	0.797	2.100
$CaCl_2$	103.0	102.4	55.5	1.022	2.510
$CaBr_2$	96.0	90.3	50.8	1.044	2.670
CaI_2	78.0	78.5	45.1	1.076	2.880
SrF_2	132.0	137.2	79.9	0.757	2.200
$SrCl_2$	112.0	103.1	60.1	1.000	2.670
$SrBr_2$	97.0	91.8	55.8	1.023	2.820
SrI_2	80.0	80.3	50.2	1.057	3.030

[a] Experimental bond dissociation energies are from ref 24. [b] Bond dissociation energies calculated using eq 24 and the atomic parameters of Table 1. [c] Relative spin transfer (step I) contribution (in percentage) $\%D^{I}_{AB} = 100[\Delta E^{I}/(\Delta E^{I} + \Delta E^{II})]$ calculated from eqs 14 and 23. [d] Bond charges (ΔN_{AB}) calculated using eq 21. [e] Bond lengths (R_{AB}) used in calculation are from ref 24.

different for different molecules and is determined[23] for a homonuclear molecule A_2 by demanding the bond charge predicted by eq 22 to be equal to unity (i.e., $-2\Delta N_A = 1.0$). For a heteronuclear bond, the parameter k_1 as well as k_2 are obtained as the arithmetic averages of the values of the same for the corresponding homonuclear molecules, i.e.

$$k_1^{AB} = (k_1^{AA} + k_1^{BB})/2 \tag{29}$$

with a similar relation for k_2.

For modeling the atom–atom and atom–bond hardnesses we use expressions similar to those of semiempirical molecular electronic structure theories and thus employ[18] for $\eta_{A,B}$ the simple Mataga–Nishimoto type relation

$$\eta_{A,B} = (a_{AB} + R_{AB})^{-1} \tag{30}$$

while for the atom–bond hardness $\eta_{A,AB}$, we use[18] the Ohno type expression

$$\eta_{A,AB} = (a_{A,AB}^{\;2} + R_{A,AB}^{\;2})^{-1/2} \tag{31}$$

where $a_{AB} = 2/(\eta_A + \eta_B)$ and $a_{A,AB} = 2/(\eta_A + \eta_{AB})$. Assuming the bond site to be located at the bond midpoint for simplicity, one has $R_{A,AB} = R_{AB}/2$.

We have calculated the homonuclear bond energies of hydrogen and a number of alkali, alkaline earth, and halogen molecules using the calculated atomic parameters of Table 1 along with the models discussed above. The results are compared with the experimental values in Table 2, and the overall agreement is found to be quite good.

For heteronuclear molecules the additional parameters $\{\eta^{A,B}_{\sigma\sigma'}\}$ are also to be modeled. For simplicity, we have modeled these quantities by the Ohno type expression, viz.

$$\eta^{A,B}_{\sigma\sigma'} = (\tilde{a}_{AB}^{\;2} + R_{AB}^{\;2})^{-1/2} \tag{32}$$

where $\tilde{a}_{AB}$ has been obtained by approximating a_{AB}. Since a_{AB}

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(23) For the fluorine molecule however, we obtain k_1 by using the Experimental bond energy in eq 25, since the bond charge for F_2 is known to be small (much less than 0.5) even from ab initio calculation. See, for example: Fraga, S.; Ransil, B. J. *J. Chem. Phys.* **1961**, *34*, 727.

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(25) *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, FL, 1989.

is inversely proportional to ($\eta_A + \eta_B$) and again η is inversely proportional[22] to R_{AB}, we assume $\bar{a}_{AB}$ equal to R_{AB} in general and as $(R_{AA}R_{BB})^{1/2}$ for alkali fluorides and alkali hydrides where the sizes of the more electronegative atoms are small. While the Ohno type expression (32) is used for molecules involving all monovalent atoms, for others such as alkaline earth halides, an arithmetic average of the Mataga–Nishimato (eq 30 with $\bar{a}_{AB}$ in place of a_{AB}) and Ohno type (eq 32)) expressions is found to be more appropriate.

Using the calculated values of the atomic parameters and the modeling discussed above, the bond energies of a number of diatomic alkali halide, hydrogen halide, and alkali hydride molecules and also polyatomic halides of the alkaline earth atoms have also been calculated with the help of the present prescriptions, and the results are compared with experimental bond energies in Table 3. The average percentage error for the total of 54 homonuclear and simple heteronuclear polyatomic molecules studied here (excluding alkali metal hydrides) is 5.7, while the same for the 40 heteronuclear molecules is only 4.0. In view of the small size of hydrogen which contains only one electron, the electronegativity based prescriptions are expected to be less accurate for molecules containing hydrogen. The present results even for these molecules are still quite reasonable and if one excludes the molecules containing hydrogen, the percentage errors indicated above improves considerably becoming only 5.3 and 3.4, respectively. Considering the fact that in certain cases the experimental error is high and we have not used any adjustable parameter, the prediction by the present scheme can be considered to be very good.

Since the net bond energy is obtained here as a sum of two contributions given by eqs 14 and 23, corresponding to steps I and II of electron density reorganization, it is of interest to compare the relative magnitudes of these two components. We have therefore included in Table 3, the percentage contribution of step I to the total calculated bond energy for each molecule. Also tabulated are the values of the bond charge (ΔN_{AB}) involved in step II. Although both the steps operate simultaneously, in the present partitioning, step I which corresponds to spin transfer includes the conventional ionic contribution to bond energy along with partial covalent part. The covalent contribution to bond energy is however mostly contributed by the charge transfer to bond region considered in step II. It is thus interesting to observe the systematic trend of the variation of relative contribution of step I as well as the bond charge as one passes from highly ionic to less polar molecules. Thus, the spin-transfer (step I) contribution diminishes, while the bond charge increases as one moves from fluoride to iodides. In general, less ionic molecules are associated with less relative contribution from spin transfer and higher values for the bond charge. For homonuclear diatomics, the ionic contribution vanishes and consequently the contribution of step I is found to be much lower as expected.

5. Concluding Remarks

In the present work, we have described chemical binding through a generalized electronegativity equalization procedure. The spin-dependent electronegativity and hardness parameters for atoms have been calculated through spin-polarized Kohn–Sham density functional theory with self-interaction correction within the local density approximation.

The spin transfer governed by the spin-dependent electronegativity and hardness parameters includes the interatomic charge transfer leading to ionic binding in heteronuclear molecules along with part of the covalent binding. The electron density accumulation in the bond region is linked only with covalent binding and has been studied through the concepts of bond electronegativity and bond hardness.

The intermolecular and bond parameters have been modeled here using mostly standard expressions used in semiempirical molecular electronic structure theories, and as such no adjustable parameter has been employed. Although at present standard bond distances are used to obtain the energy, we hope to succeed in providing better R-dependent models for these quantities in the future and thus obtain estimates of bond lengths directly. Prediction of molecular geometry through the electronegativity equalization based approaches is one of our major goals.

Apart from the very good accuracy of the predicted results for simple polyatomic (AB_n) molecules, the present approach also provides information about the integrated spin-density at each atom, which might be of importance in problems involving magnetic field. While we have been concerned here only with binding, further work involving spin-polarized generalization of the Fukui function[26] and other reactivity indices[27] would be of considerable interest.

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