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Toward a semiempirical density functional theory of chemical binding*

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The new ideas of *bond electronegativity* and *bond hardness* are introduced, and a semiempirical density functional approach to the theory of molecular electronic structure and chemical binding is outlined. There result effective electronegativity equalization procedures that permit calculation of binding energies as well as partial charges. By a modelling of the bond electronegativity and bond hardness, a density functional interpretation of earlier bond charge models is established. Some numerical results are given for diatomic molecules.

Key words: Electronic structure — Bond electronegativity — Bond hardness

1. Introduction

In recent years, density functional theory [1] has been shown to be a versatile tool in many branches of physics and chemistry [2]. In electronic structure theory, it has not only produced useful schemes for computation but it has also provided a framework for introducing new concepts [1]. Among others, one has the concepts of chemical potential [3] (the electronegativity of chemistry), chemical hardness [4] (both global [5] and local [6]) and softness [7], Fukui function [8], and local temperature of the electron cloud [9]. Some of these quantities had been introduced earlier, and were already known to be very useful in chemistry, but they now have received a stronger basis. With the help of two new conceptions, *bond electronegativity* and *bond hardness*, the present paper further explores the applicability of the density functional formalism for understanding of the chemical bond itself.

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

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Density functional theory (DFT) is exact and it is a theory of electron density. It therefore should contain the theory of chemical bonds without resorting to orbitals. That is the subject of the present work.

Charge density reorganization and transfer play an important role in molecule formation. Concepts and methods have been developed in chemistry where the net electron densities localized within certain regions (instead of the whole electron density as a point function) are of prime concern. Examples are the atomic charges within molecules [10], in general shared unequally between atoms in a molecule. Although these charges find definition within conventional orbital theories, for example, through Mulliken population analysis, they can also be predicted through simple procedures like electronegativity equalization [11]. Electronegativity equalization was initially proposed without the rigor of theory, but it has recently found rigorous justification [3, 12, 13].

Atomic charges correlate well with many properties [12], but simplified point charge models sometimes fail to predict good energies [10, 14]. The main reason is that charge transfer between atoms is set proportional to their electronegativity difference; hence for homonuclear molecules, no net charge transfer is predicted. Models based on atomic electronegativities alone fail to take proper account of covalent binding, although empirical incorporation of covalent terms can lead to reasonable results for energies [15, 16]. Charge accumulation in the bond region plays a very important role in chemical binding [17], however, and so may be expected to explicitly appear in the formulation.

To describe molecule formation within a density theory, we propose to invoke the concept of bond electronegativity, by assigning an electronegativity value to the bond region (normally higher than the isolated atom values) [18]. This is rigorous since the chemical potential is defined at each point in space [3, 19]. For any region an electronegativity can be assigned; at equilibrium it must be the same for all regions. A higher electronegativity at the bond center when two atoms are brought to the equilibrium distance *without charge transfer* [20] can account for charge transfer to the bond region, even for homonuclear molecules. This new bond charge - bond electronegativity model thus involves three point charges in a diatomic molecule - two on the atomic sites and another at the bond center. Binding energy is predicted as the energy involved in this charge transfer plus the electrostatic interaction among all charges.

A bond charge model for a chemical bond was earlier introduced involving two localized charge centers at the two atomic sites and a bond charge[21-23]. The bond charge was considered to be delocalized along the bond and the resultant kinetic energy (evaluated from a one-dimensional box model) together with the interaction energy of the three charges (calculated using the mean location of the bond charge at the bond center) yielded the binding energy. The concern was mainly for the potential energy curve and the constants W_1 and W_2 in the total energy expression $W(R) = W_0 + W_1/R + W_2/R^2$ were related to the charge, force constant and the equilibrium distance. The term W_0 was subsequently correlated with the bond charge [24] and an electronegativity concept was introduced into this analysis [25–28]. In the present study, we shall attach density functional interpretation to the constants W_0, W_1, W_2, by modelling the *bond electronegativity* and *bond hardness*, thereby obtaining a generalized bond charge model based on DFT. We shall also find a close analogy to the classical semiempirical theories of electronic structure [29–30].

2. Bond-charge bond-electronegativity model for chemical binding

The energy of a many-electron system characterized by an external potential $v(\boldsymbol{r})$ is a unique functional [1] of its electron density $\rho(\boldsymbol{r})$. During the formation of a molecule from the isolated atoms, the electron densities of the atoms undergo distortion (mainly in the valence region leaving the core unaltered); also, the electron cloud is subjected to a modified external potential. The potential $v(\boldsymbol{r})$, given by $-Z/r$ for an isolated atom of nuclear charge Z, is now modified due to the additional field arising from the nuclei and the charge cloud of the neighboring species. Considering the diatomic case for simplicity, the process of molecule formation can thus be viewed as a two-step process: first placing the unperturbed atoms at a distance equal to the equilibrium distance R_e and then allowing the charge reorganization to occur with the interaction switched on simultaneously. The bonding energy for the molecule AB therefore can be written as an expansion in $\Delta\rho(\boldsymbol{r})$ and $\Delta v(\boldsymbol{r})$,

$$\begin{aligned}\Delta E &= E_{\text{mol}} - (E_{\text{A}}^0 + E_{\text{B}}^0)\\ &= \int \frac{\delta E}{\delta\rho(\boldsymbol{r})}\Delta\rho(\boldsymbol{r})\,d\mathbf{r} + \int \frac{\delta E}{\delta v(\boldsymbol{r})}\Delta v(\mathbf{r})\,d\boldsymbol{r}\\ &\quad + \text{second order terms} + Z_{\text{A}}Z_{\text{B}}/R. \end{aligned} \tag{1}$$

This is a completely local formula involving local change in density and local change in external potential [31]. Changes are relative to the unperturbed atoms, placed, as indicated above, a distance $R = R_e$ apart.

We now develop a semilocal or regional approach by dividing the molecule into three regions—the two atomic regions Ω_{A} and Ω_{B} and the bond region Ω_{AB}. The energy, density, and potential changes can then be written as

$$\begin{aligned}\Delta E &= \Delta E_{\text{A}} + \Delta E_{\text{B}} + \Delta E_{\text{AB}},\\ \Delta\rho(\boldsymbol{r}) &= \Delta\rho_{\text{A}}(\boldsymbol{r})_{r\in\Omega_{\text{A}}} + \Delta\rho_{\text{B}}(\boldsymbol{r})_{r\in\Omega_{\text{B}}} + \Delta\rho_{\text{AB}}(\boldsymbol{r})_{r\in\Omega_{\text{AB}}},\\ \Delta v(\boldsymbol{r}) &= \Delta v_{\text{A}}(\boldsymbol{r})_{r\in\Omega_{\text{A}}} + \Delta v_{\text{B}}(\boldsymbol{r})_{r\in\Omega_{\text{B}}} + \Delta v_{\text{AB}}(\boldsymbol{r})_{r\in\Omega_{\text{AB}}}. \end{aligned} \tag{2}$$

Such a spatial decomposition is not unique; nevertheless, it is useful. Equation (1) thus becomes

$$\begin{aligned}\Delta E &= \int_{\Omega_{\text{A}}} \frac{\delta E}{\delta\rho_{\text{A}}(\boldsymbol{r})}\Delta\rho_{\text{A}}(\boldsymbol{r})\,d\boldsymbol{r} + \int_{\Omega_{\text{B}}} \frac{\delta E}{\delta\rho_{\text{B}}(\boldsymbol{r})}\Delta\rho_{\text{B}}(\boldsymbol{r})\,d\boldsymbol{r} + \int_{\Omega_{\text{AB}}} \frac{\delta E}{\delta\rho_{\text{AB}}(\mathbf{r})}\delta\rho_{\text{AB}}(\boldsymbol{r})\,d\boldsymbol{r}\\ &\quad + \int_{\Omega_{\text{A}}} \frac{\delta E}{\delta v_{\text{A}}(\boldsymbol{r})}\Delta v_{\text{A}}(\boldsymbol{r})\,d\boldsymbol{r} + \int_{\Omega\text{B}} \frac{\delta E}{\delta v_{\text{B}}(\boldsymbol{r})}\Delta v_{\text{B}}(\boldsymbol{r})\,d\boldsymbol{r}\\ &\quad + \int_{\Omega_{\text{AB}}} \frac{\delta E}{\delta v_{\text{AB}}(\boldsymbol{r})}\Delta v_{\text{AB}}(\boldsymbol{r})\,d\boldsymbol{r} + \cdots + \frac{Z_{\text{A}}Z_{\text{B}}}{R}, \end{aligned} \tag{3}$$

where $\Delta v_X(\boldsymbol{r})|_{\boldsymbol{r}\in\Omega_X}$ is the potential change in Ω_X arising from the charges (nuclei as well as electron cloud) occupying the neighbouring regions ($\boldsymbol{r}\notin\Omega_X$). The integrations extend over the volumes indicated. The functional derivative $\delta E/\delta\rho$ is the chemical potential μ which is a constant under equilibrium conditions [3], where one expects $\delta E/\delta\rho_A=\mu_A$, $\delta E/\delta\rho_B=\mu_B$, etc. In the present situation, however, in which two atoms are brought to equilibrium distance, not an equilibrium situation before charge redistribution, one can include a weak $\boldsymbol{r}$-dependence of $\delta E/\delta\rho$ by writing, in each region A, B, AB,

$$\frac{\delta E}{\delta\rho_X}\equiv\mu_X(\boldsymbol{r})=\mu_X(\boldsymbol{R}_X^0)+(\boldsymbol{r}-\boldsymbol{R}_X^0)\nabla\mu_X|_{\boldsymbol{R}=\boldsymbol{R}_X^0} \tag{4}$$

where $\boldsymbol{R}_X^0$ is centered in the region Ω_X. Using (4) and the formulas $\delta E/\delta v(\boldsymbol{r})=\rho(\boldsymbol{r})$, $\int\Delta\rho(\boldsymbol{r})\,d\boldsymbol{r}=\Delta N$, etc., one then obtains from (3),

$$\begin{aligned}\Delta E=\mu_A\Delta N_A+\mu_B\Delta N_B+\mu_{AB}\Delta N_{AB}+\nabla\mu_A\cdot\int_{\Omega_A}(\boldsymbol{r}-\boldsymbol{R}_A^0)\Delta\rho_A\,d\boldsymbol{r}\\+\nabla\mu_B\cdot\int_{\Omega_B}(\boldsymbol{r}-\boldsymbol{R}_B^0)\Delta\rho_B\,d\boldsymbol{r}+\nabla\mu_{AB}\cdot\int_{\Omega_{AB}}(\boldsymbol{r}-\boldsymbol{R}_{AB})\Delta\rho_{AB}\,d\boldsymbol{r}\\+\int_{\Omega_A}\rho_A\Delta v_A\,d\boldsymbol{r}+\int_{\Omega_B}\rho_B\Delta v_B\,d\boldsymbol{r}+\int_{\Omega_{AB}}\rho_{AB}\Delta v_{AB}\,d\boldsymbol{r}+\cdots\frac{Z_AZ_B}{R}.\end{aligned} \tag{5}$$

Here we have introduced the quantity $\mu_{AB}=\delta E/\delta\rho_{AB}=\partial E/\partial N_{AB}$, the *bond chemical potential.* Introducing the atomic charges q_A, q_B and the bond charge $q_{AB}(q=-\Delta N)$ and also the dipole moments $\boldsymbol{d}_A$, $\mathbf{d}_A$ and $\boldsymbol{d}_{AB}$ ($\boldsymbol{d}_X=-\int_{\Omega_X}(\boldsymbol{r}-\boldsymbol{R}_X^0)\Delta\rho\,d\boldsymbol{r}$), (5) becomes

$$\begin{aligned}\Delta E&=-\mu_Aq_A-\mu_Bq_B-\mu_{AB}q_{AB}\\&\quad+\frac{q_Aq_B}{R}+\frac{q_Aq_{AB}}{R_A}+\frac{q_Bq_{AB}}{R_B}\\&\quad+\nabla\mu_A\cdot\boldsymbol{d}_A+\nabla\mu_B\cdot\boldsymbol{d}_B+\nabla\mu_{AB}\cdot\boldsymbol{d}_{AB}\\&\quad+\cdots\text{other terms involving dipole interactions,}\end{aligned} \tag{6}$$

where the electrostatic terms have been approximated assuming electrostatic interaction between point charges and dipoles. R_A and R_B are distances of the bond charge from atoms A and B. The terms involving the dipoles are very important for dealing with polyatomic molecules, e.g. for studying the bent geometry of a triatomic molecule, for which the presence of lone pairs plays a vital role. The dipole terms can take into account this effect and thus lead to correct predictions of molecular shapes [32]. We neglect these terms for the time being.

Equation (6) includes only first-order terms, however, higher order corrections can easily be incorporated, e.g. by considering terms second-order with respect to $\Delta N(q)$. Thus,

$$\begin{aligned}\Delta E = & -\mu_A q_A - \mu_B q_B - \mu_{AB} q_{AB} \\ & + \eta_A q_A^2 + \eta_B q_B^2 + \eta_{AB} q_{AB}^2 \\ & + \frac{q_A q_B}{R} + \frac{q_A q_{AB}}{R_A} + \frac{q_B q_{AB}}{R_B} + \cdots .\end{aligned} \tag{7}$$

Here η_A and η_B are the atomic hardnesses defined as $\eta = \frac{1}{2}(\partial\mu/\partial N)$. The *bond hardness* η_{AB} is defined as

$$\eta_{AB} = -\frac{1}{2}\frac{\partial\mu_{AB}}{\partial q_{AB}}. \tag{8}$$

Equation (7) shows that the energy change consists of the charge transfer contribution plus the electrostatic interaction between the resulting charges.

Using the conservation of charge

$$q_A + q_B + q_{AB} = 0, \tag{9}$$

(7) can be simplified to

$$\begin{aligned}\Delta E = & (\mu_{AB} - \mu_A) q_A + (\mu_{AB} - \mu_B) q_B \\ & + \left(\eta_A + \eta_{AB} - \frac{1}{R_A}\right) q_A^2 + \left(\eta_B + \eta_{AB} - \frac{1}{R_B}\right) q_B^2 \\ & + \left(2\eta_{AB} + \frac{1}{R} - \frac{1}{R_A} - \frac{1}{R_B}\right) q_A q_B .\end{aligned} \tag{10}$$

This energy expression can also be viewed as the energy associated with the creation of two charges q_A and q_B at two centers (one near A and another near B) at an effective distance apart $R_{\text{eff}} = [2\eta_{AB} + 1/R - 1/R_A - 1/R_B]^{-1}$, the effective centers being characterized by effective chemical potentials $(\mu_A - \mu_{AB})$ and $(\mu_B - \mu_{AB})$ and effective hardnesses $(\eta_A + \eta_{AB} - 1/R_A)$ and $(\eta_B + \eta_{AB} - 1/R_B)$ respectively.

By minimizing (10) with respect to q_A and q_B, we obtain

$$\begin{aligned}(\mu_{AB} - \mu_A) + 2\left(\eta_A + \eta_{AB} - \frac{1}{R_A}\right) q_A + \left[2\eta_{AB} + \frac{1}{R} - \frac{1}{R_A} - \frac{1}{R_B}\right] q_B = 0, \\ (\mu_{AB} - \mu_B) + 2\left(\eta_B + \eta_{AB} - \frac{1}{R_B}\right) q_B + \left[2\eta_{AB} + \frac{1}{R} - \frac{1}{R_A} - \frac{1}{R_B}\right] q_A = 0,\end{aligned} \tag{11}$$

which can be solved for q_A and q_B and hence q_{AB} and the energy.

Equations (11) can also be obtained through the equalization of effective chemical potential at the two atoms and the bond center, that is by equating the three expressions

$$\mu_{\mathrm{A}}^{\mathrm{eff}}=\mu_{\mathrm{A}}-2\eta_{\mathrm{A}}q_{\mathrm{A}}-\frac{q_{\mathrm{B}}}{R}-\frac{q_{\mathrm{AB}}}{R_{\mathrm{A}}},$$

$$\mu_{\mathrm{B}}^{\mathrm{eff}}=\mu_{\mathrm{B}}-2\eta_{\mathrm{B}}q_{\mathrm{B}}-\frac{q_{\mathrm{A}}}{R}-\frac{q_{\mathrm{AB}}}{R_{\mathrm{B}}},$$

$$\mu_{\mathrm{Bond}}^{\mathrm{eff}}=\mu_{\mathrm{AB}}-2\eta_{\mathrm{AB}}q_{\mathrm{AB}}-\frac{q_{\mathrm{A}}}{R_{\mathrm{A}}}-\frac{q_{\mathrm{B}}}{R_{\mathrm{B}}}. \tag{12}$$

The resulting expression for charge takes a very simple form for homonuclear diatomic molecules,

$$q_{\mathrm{A}}=q_{\mathrm{B}}=-\tfrac{1}{2}q_{\mathrm{AB}}=\frac{-(\mu_{\mathrm{bond}}-\mu_{\mathrm{atom}})}{2[\eta_{\mathrm{atom}}+2\eta_{\mathrm{bond}}-\frac{7}{2}\cdot 1/R]}. \tag{13}$$

Thus, if the atomic and bond electronegativities and hardnesses are known, one has a consistent scheme for the calculation of charges and energies for the particular value of R. For heteronuclear diatomic molecules, although the atomic and bond charges q_{A}, q_{B} and q_{AB} ($\equiv -q_{\mathrm{A}}-q_{\mathrm{B}}$) can be calculated, the results will depend on the choice of R_{A} and R_{B} ($R_{\mathrm{A}}+R_{\mathrm{B}}=R_{\mathrm{e}}$) in the bond. Note that to correlate with the atomic charges calculated by other methods, the bond charge has to be suitably divided between the two atoms.

The molecule is here modelled as a collection of charges. This suggests a dielectric model, in which one assumes a dielectric constant for the interaction between the charges. Thus, the (q/R) type of terms in the above equations may be multiplied by a factor k, the dielectric constant for the dielectric medium corresponding to a molecule.

3. Semiempirical density functional theory

The connection of the present method with the semiempirical theories of molecular electronic structure can be exposed by starting with the energy expression in the Hückel method [29],

$$E=\sum_{r}\alpha_r q_r+\sum_{r<s}2p_{rs}\beta_{rs}. \tag{14}$$

for a diatomic molecule, comparing with only the three terms of (7). One establishes an equivalence by identifying the atomic coulomb integral α_r with the electronegativity $\chi_r(\equiv-\mu_r)$, the bond order p_{rs} with the bond charge $-q_{rs}$, and the resonance integral β_{rs} with the bond chemical potential (actually $q_{rs}\approx -2p_{rs}\cdot S_{rs}$ and $\chi_{rs}(=-\mu_{rs})=-\beta_{rs}S_{rs}^{-1}$). A comparison with the Wolfsberg-Helmholtz expression for β, $\beta=K\cdot\frac{1}{2}S(\alpha_r+\alpha_s)$, implies $\chi_{rs}=K\cdot\frac{1}{2}(\chi_r+\chi_s)$. The fact that the proportionality constant K is empirically greater than unity clearly indicates that the bond electronegativity before bond formation is higher than the average of the atomic electronegativities—consistent with a subsequent charge accumulation in the bond region. The observation that the electrostatic potential at the covalent radius is a measure of the chemical potential [33] also argues that the bond chemical potential (before bond formation) should be roughly the sum of atomic chemical potentials.

The equivalence of the energy expression of (7) with Hückel theory is in fact complete only for a homonuclear diatomic molecule. The Hückel method of energy minimization with respect to the coefficients is equivalent to a minimization with respect to charges [34] (also equivalent to effective electronegativity equalization [13]). However, the evaluation of charges requires E to have a nonlinear dependence on q. In Hückel theory, the relation $q_{AB} = \sqrt{q_A q_B} \cdot S_{AB}$ provides the nonlinearity; we have not assumed this. For the polyatomic case, furthermore, equivalence is lacking due to the summation over molecular orbitals. Thus in general the present approach provides a simple semiempirical density functional theory, much like but not identical with the Hückel method.

Here, the nonlinear dependence of E on q enters (7) through higher order terms. Modifications of the Hückel method by modifying the α-parameter to take into account the charge-dependence - the so called ω-technique [35], i.e.

$$\alpha_r = \alpha_r^0 - \omega\beta \cdot q_r - \omega'\beta \sum_{r \neq s} q_s, \tag{15}$$

is equivalent to adding higher order terms involving hardness ($\eta_r \approx \omega\beta$) and potential $R^{-1} \approx \omega'\beta$ etc.). The modified β-version of Lennard-Jones, Longuet-Higgins and Salem [29] is analogous to considering the bond hardness terms.

The inclusion of hardness corrections may be seen to be equivalent to including the electron repulsion terms in PPP theories [30]. The energy expressions in PPP theory are:

$$\begin{aligned} E &= \tfrac{1}{2} \sum_{i,j} p_{ij}(H_{ij} + F_{ij}), \\ F_{ii} &= H_{ii}^{\text{core}} + \tfrac{1}{2} p_{ii}(ii \mid ii) + \sum_{j \neq i} p_{jj}(ii \mid jj), \\ F_{ij} &= H_{ij}^{\text{core}} - \tfrac{1}{2} p_{ij}(ii \mid jj). \end{aligned} \tag{16}$$

A comparison of (16) with (7) shows a close connection between the two, with the identifications $\mu_i \approx H_{ii}^{\text{core}}$; $\mu_{ij} = H_{ij}^{\text{core}}$; $\eta_i = (ii \mid ii)$; $\eta_{ij} = (ii \mid jj)$. The definition of the atomic hardness as the effective interatomic repulsion integral is known from the Pariser approximation (I-A) [30] and the Parr-Pearson definition of hardness [4]. The bond hardness represents the interatomic electron repulsion integral. The presence of electron repulsion is reflected in increased hardness.

This connection can be elaborated using the recent definition of local hardness [6]. Thus using

$$\eta(\boldsymbol{r}) = \frac{1}{2N} \int \frac{\delta^2 F}{\delta\rho(\boldsymbol{r})\,\delta\rho(\boldsymbol{r}')} \rho(\boldsymbol{r}')\, d\boldsymbol{r}', \tag{17}$$

where the universal functional $F(\rho)$ $(=E[\rho]-\int v(\boldsymbol{r})\rho(\boldsymbol{r})\,d\boldsymbol{r})$ is the kinetic energy plus the electron repulsion, it can be shown that in the valence-only picture, the kinetic energy part of the functional F does not contribute-hence only the electron repulsion contribution (classical electrostatic and exchange correlation) determines the hardness. This argument can be applied to both atomic and bond hardnesses. The global hardness can be obtained from the local hardness using the relation $\eta=\int \eta(\boldsymbol{r})f(\boldsymbol{r})\,d\boldsymbol{r}$, where $f(\boldsymbol{r})(=\delta\rho(\boldsymbol{r})/\delta N)$ is the Fukui function [8].

4. Modelling of the bond electronegativity and bond hardness

The bond electronegativity and the bond hardness can, in principle, be calculated from the expressions

$$\mu_{\text{bond}}=\frac{-1}{q_{\text{bond}}}\int \frac{\delta E}{\delta\rho}\rho(\boldsymbol{r})\,d\boldsymbol{r}$$

$$\eta_{\text{bond}}=\int \eta_{\text{bond}}(\boldsymbol{r})f_{\text{bond}}(\boldsymbol{r})\,d\boldsymbol{r},\qquad \eta_{\text{bond}}(\boldsymbol{r})=-\frac{1}{2q_{\text{bond}}}\int \frac{\delta^2 F}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')}\rho(\boldsymbol{r}')\,d\boldsymbol{r}' \tag{18}$$

where the integrations are to be performed over the bond region only.

As already has been mentioned, the bond electronegativity (chemical potential) at the equilibrium distance is approximately given by the sum of the atomic electronegativities (chemical potentials). However, modification of the chemical potential in the bond region would also be contributed to by the compression of the atoms. Our plan here is to model the bond electronegativity and the bond hardness so as to reproduce or predict the other quantities.

For simple homonuclear diatomic molecules, equations can be rewritten for the dissociation energy D_e, the bond charge $Q\equiv q_{\text{AB}}$ (a negative number) and the electronegativity of the molecule, χ^{mol} as follows:

$$D_e=-(\chi_0-\chi)Q-\tfrac{1}{2}\left(\eta+2\eta_0-\frac{7}{2}\cdot k\cdot\frac{1}{R}\right)Q^2=-\frac{Q}{2}(\chi_0-\chi), \tag{19}$$

$$Q=\frac{-(\chi_0-\chi)}{(\eta+2\eta_0-\tfrac{7}{2}\cdot k\cdot 1/R)}, \tag{20}$$

$$\chi_{\text{mol}}=\chi_{\text{atom}}-Q\left[\eta-\tfrac{3}{2}\cdot k\cdot\frac{1}{R}\right], \tag{21}$$

where χ_0 and η_0 are the bond electronegativity and hardness. Equations (19)-(21) are in atomic units. If χ and η are to be expressed in electron volts, the terms involving the dielectric constant k must be multiplied by 27.212.

Table 1 presents numerical results for the values of bond electronegativity and hardness that consistently conform to the known values of D_e, χ_{mol} and the bond charges of Parr and Borkman [21] for some simple diatomic molecules. The bond hardnesses are lower than the atomic ones while the bond electronegativities are

Table 1. Bond electronegativity - bond hardness parameters for simple diatomic molecules

Molecule	χ_{mol} [a] (ev)	χ_{atom} [a] (ev)	η_{atom} [a] (ev)	R_e [b] (au)	$-Q$ [b] (au)	D_e [b] (kcal/mol)	k^{-1}	χ_0 (ev)	η_0 (ev)	C_1 (ev)	C_2 (ev)	C_2' (ev)
F_2	9.39	10.41	7.01	2.712	1.80	37.0	1.99	12.19	5.830	13.11	15.81	31.41
Cl_2	6.94	8.31	4.698	3.757	2.52	57.9	2.07	10.30	4.162	28.13	15.64	32.41
Br_2	6.58	7.602	4.238	4.316	2.68	45.9	2.05	9.087	3.547	27.67	15.31	31.35
I_2	5.91	6.758	3.697	5.04	2.83	35.9	2.03	7.858	3.009	27.95	15.16	30.73
C_2	8.07	6.262	4.994	2.347	2.40	147.0	4.10	11.57	3.557	29.26	8.35	34.24
O_2	6.25	7.538	6.076	2.283	2.26	120.2	2.69	12.15	5.736	24.04	13.10	35.23
P_2	5.125	5.615	4.869	3.577	3.05	117.1	2.27	8.945	3.979	42.61	14.23	32.29
S_2	5.53	6.217	4.140	3.570	2.87	84.0	2.61	8.756	3.482	32.35	12.43	32.45

[a] Values from [39]
[b] Values from [21]

higher than the atomic values ($\chi < \chi_0 < 2\chi$). The values of the dielectric constant (k) indicate that it depends on the nature of the bond; for multiple bonds, the screening is stronger. All these values correspond to the equilibrium distances. The formalism should, however, be equally applicable at other internuclear distances, provided the R-dependences of χ_0 and η_0 are suitably modelled. We now turn to that.

In the PPP theory [30], the quantity (I-A), the atomic hardness, is a measure of the intra-atomic electron repulsion integral. Analogously, the bond hardness here can be thought of as a measure of the interatomic electron repulsion, and consequently, as in the PPP theory, this term can be modelled by R^{-1} dependence. Such a reciprocal correlation of atomic hardness with the covalent radius has been earlier proposed [27]. More complicated dependence (for example, log η varying as log R^{-1}) has, however, been shown to lead to better correlation [36].

For modelling the bond electronegativity, one can proceed in several ways. Since the bond center has constant density ($\nabla\rho = 0$), the kinetic energy can be modelled after the Thomas-Fermi (perhaps in one dimension) or particle-in-a-box model [37]. Bond chemical potential then can be evaluated rigorously. However, it has been argued that the resonance integral (which corresponds to bond electronegativity in this model) involves mainly a kinetic contribution [38]. In the bond charge model of Parr and Borkman [21], the kinetic energy was modelled as an R^{-2} dependent term. Therefore, as an initial attempt, we take the bond electronegativity to have a similar dependence. Rationalization of this R^{-2} modelling follows also from Politzer's work showing that (Q/R^2) at the equilibrium distance approximately represents the bond order (p_{rs}) [28]. Comparing (14) with the first three terms of (7), it is clear that the $p_{rs}\,\beta_{rs}$ term represents $(Q/R^2)(\mu_{\text{bond}}R^2)$. Hence, since $\rho_{rs} \sim Q/R^2$, the resonance integral $\beta_{rs} \sim \mu_{\text{bond}} \cdot R^2$; that is, $\mu_{\text{bond}} \sim \beta_{rs}/R^2$, which suggests a R^{-2} dependence of the bond electronegativity. We therefore assume

$$\chi_0 = \chi + \frac{C_1}{R^2} \tag{22}$$

and

$$\eta_0 = \frac{C_2}{R}. \tag{23}$$

The dissociation energy (19) can now be written as

$$\begin{aligned} D_e &= -(\chi_0 - \chi)Q - \tfrac{1}{2}\left(\eta + 2\eta_0 - \frac{7}{2}k \cdot \frac{1}{R}\right)Q^2 \\ &= -\tfrac{1}{2}\eta Q^2 - (c_2 - \tfrac{7}{4}k)\frac{Q^2}{R} - \frac{C_1 Q}{R^2}. \end{aligned} \tag{24}$$

At $R = R_e$, D_e denotes the equilibrium dissociation energy; for other neighboring values of R, (24) shows a close connection with the Parr–Borkman bond-charge-model energy expression, namely [21],

$$E = W_0 + W_1/R + W_2/R^2. \tag{25}$$

Table 1 presents the numerical values of C_1 and C_2 obtained from the equilibrium properties, for a few molecules. Also given are the values of $C_2'(\equiv C_2/k)$ defined by

$$\eta_0 = k \cdot \frac{C_2'}{R}. \tag{26}$$

It is interesting that for several diatomic molecules, the value of C_2' is very nearly a constant. The average value of C_2' is 32.51 ± 1.42 eV. Near constancy is also observed in the values of C_1 for a given class of atoms.

Politzer has proposed [24] that the constant term W_0 in the Parr–Borkman model energy expression (26) is related to Q^2 by

$$W_0 = B \cdot Q^2. \tag{27}$$

Politzer found a linear correlation of B with the ionization potentials of the atoms. Correlation of B with $1/R_e$ was also fairly good. Comparison with (24) shows that the constant B can be interpreted as $\eta/2$; this rationalizes the correlations observed by Politzer. Pasternak attempted to interpret this term as an expansion of the type $aQ + bQ^2$ from consideration of charge transfer when the atoms are separated to infinity [25]. Our (19) will lead to this result with $a = \mu$ and $b = \frac{1}{2}\eta$ if the constant term in the modelling of χ_0 by (22) is properly chosen. One may also mention a different aproach to W_0 by Ohwada [40] which is based on an effective nuclear charge model.

The modelling of bond electronegativity and hardness by (22) and (23) is only illustrative. However, the near constancy of the parameters C_1 and C_2 indicates that such modelling is meaningful at least for studying the properties at equilibrium for homonuclear molecules. The prediction of the full potential energy curve, although of much interest, has not been attempted here and could be achieved only through better modelling of the R-dependence of these quantities, especially the bond electronegativity term. Of importance is the study of the chemical potential of the molecule as a function of internuclear distance, on which work has started only recently [41].

5. Concluding remarks

The concepts of electronegativity and hardness for the bond region introduced here provide a means for investigating covalent binding through the electronegativity picture. This gives a generalized electronegativity equalization scheme and a method for the calclation of partial charges as well as energies for molecules. Although the present calculations have been restricted to simple diatomics, the formalism and the concepts are general enough also to describe complex cases. The approach is a semilocal or regional approach to DFT and as here formulated constitutes a semiempirical density functional theory.

Such a density functional model can be thought of as a dielectric model which considers the atoms and molecules as a dielectric medium [42]. Other dielectric models for diatomics have also been proposed earlier [43] in the spirit of Phillips [44]. The recent work of Pearson considers a two-way flow to take into account the delocalization of electron density corresponding to covalent bonding [5]. Electrostatics is deeply connected to chemical binding. For polar bonds, an electrostatic model has been proposed by Benson [45].

The present model provides a scheme for calculating the chemical potential of a molecule from that of its constituent atoms. Although such methods already existed for heteronuclear diatomics which consider atomic electronegativities alone, they fail to predict chemical potential changes for homonuclear diatomics. The concept of bond electronegativity thus broadens the scope of electronegativity-based theories.

The connection with the Parr–Borkman bond charge model is only illustrative. A more accurate comparison could be developed by more correct modelling of the R-dependence of χ_0 and η_0; this also would permit predicting correct potential energy curves as well as chemical potential curves.

It may be noted that the bond electronegativity is, in a sense, a "pair electronegativity" [46]—because it is an electron pair (partially of course) which is accumulated in the bond region whereas the electrons that come from the atoms usually are single electrons (again partially).

The fact that χ_0 and η_0 are analogue of the parameters of Hückel theory and the modified β-theories of Lennard-Jones, Longuet-Higgins and Salam [29] suggest that the reactivity indices introduced by Coulson and Longuet-Higgins [47], *viz.*, the self and mutual polarizabilities originally defined through the parameters of Hückel theory, can be redefined in terms of density functional concepts. Indeed, the semilocal generalization of the hardness kernel as well as the softness leads directly to the concepts of self and mutual softnesses.

More work on these several ideas should prove profitable.

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References and notes

1. Parr RG (1983) Ann Rev Phys Chem 34:631
2. Dreizler RM, da Providencia J (1975) Density functional methods in physics. Plenum Press, New York
3. Parr RG, Donnelly RA, Levy M, Palke WE (1978) J Chem Phys 68:3801
4. Parr RG, Pearson RG (1983) J Am Chem Soc 105:7512
5. Pearson RG (1985) J Am Chem Soc 107:6801
6. Berkowitz M, Ghosh SK, Parr RG (1985) J Am Chem Soc 107:6811
7. Yang W, Parr RG (1985) Proc Natl Acad Sci 82:6723
8. Parr RG, Yang W (1984) J Am Chem Soc 106:4049; Yang W, Parr RG, Pucci R (1984) J Chem Phys 81:2862

9. Ghosh SK, Berkowitz M, Parr RG (1984) Proc Natl Acad Sci USA 81:8028; Ghosh SK, Berkowitz M (1985) J Chem Phys. 83:2976; practical computational advantages of these formalisms for calculation of Compton profiles and exchange energies can be found in: (a) Parr RG, Rupnik K, Ghosh SK (1986) Phys Rev Lett 56:1555; (b) Ghosh SK, Parr RG (1986) Phys Rev A 34:785
10. Hall GG (1985) Adv Atom Molec Phys 20:41
11. Sanderson RT (1951) Science 114:670
12. Mortier WJ, Van Genechten K, Gasteiger J (1985) J Am Chem Soc 107:829
13. Mortier WJ (1987) In: Sen KD (ed) Electronegativity (Structure and bending, vol 66). Springer, Berlin Heidelberg, New York; Mortier WJ, Ghosh SK, Shankar S (1986) J Am Chem Soc 108:4315
14. For point charge models involving lone pairs as point charges see Kollman P (1978) J Am Chem Soc 100:2974
15. Sanderson RT (1976) Chemical bonds and bond energies (2nd edn). Academic Press, New York; Sanderson RT (1983) J Am Chem Soc 105:2259
16. Evans RS, Huheey JE (1970) J Inorg Nucl Chem 32:777
17. Rudenberg K (1962) Rev Mod Phys 34:326
18. The term bond electronegativity has been used earlier to denote electronegativity of orbitals forming the chemical bond: Hinze J, Whitehead MA, Jaffe HH (1963) J Am Chem Soc 85:148; see also Pritchard HO (1963) J Am Chem Soc 85:1876
19. Politzer P, Weinstein H (1979) J Chem Phys 71:4218
20. Parr RG, Bartolotti LJ (1982) J Am Chem Soc 104:3801
21. Parr RG, Borkman RF (1968) J Chem Phys 49:1055
22. Borkman RF, Simons G, Parr RG (1969) J Chem Phys 50:58
23. Simons G, Parr RG (1971) J Chem Phys 55:4197
24. Politzer P (1970) J Chem Phys 52:2157
25. Pasternak A (1977) J Chem Phys 26:101
26. Pasternak A (1980) J Chem Phys 73:593
27. Ray NK, Samuels L, Parr RG (1979) J Chem Phys 70:3680
28. Politzer P (1969) J Chem Phys 50:2780; Politzer P (1969) J Chem Phys 51:459
29. Coulson CA, O'Leary B, Mallion RB (1978) Hückel theory for organic chemists. Academic Press, London
30. Parr, RG (1963) Quantum theory of molecular electronic structure. Benjamin, New York
31. Nalewajski RF (1985) J Phys Chem 89:2831; see also: Nalewajski RF, Koninski M (1984) J Phys Chem 88:6234
32. Nakatsuji H, Koga T (1981) In: Deb BM (ed) The force concept in chemistry. Van Nostrand and Reinhold, New York; see also: Simons G (1972) J Chem Phys 56:4310
33. Politzer P, Parr RG, Murphy DR (1983) J Chem Phys 79:3859
34. Klopman G (1964) J Am Chem Soc 86:1463
35. Streitwieser A (1960) J Am Chem Soc 82:4123
36. Politzer P (1968) Trans Faraday Soc 64:2241
37. For a discussion of kinetic energy in Hückel method see: Pucci R, March NH (1981) J Chem Phys Phys 74:2936; see also: Henderson GA, Parr RG (1971) Theor Chim Acta 31:103
38. For example: Zerner MC, Parr RG (1978) J Chem Phys 69:3858
39. Yang W, Lee C, Ghosh SK (1985) J Chem Phys 89:5412
40. Ohwada K (1982) J Chem Phys 77:5040
41. Ohwada K (1984) J Chem Phys 80:1556
42. Zangwill A, Levine ZH (1985) Am J Phys 53:1177
43. Aslaksen EW (1972) Phys Rev A 6:1367
44. Phillips JC (1969) Covalent bonding in crystals, molecules and polymers. University of Chicago Press, Chicago
45. Benson SW (1978) Angew Chem Int Ed Eng 17:812; Benson SW, Luria M (1975) J Am Chem Soc 97:704, 3337; Luria M, Benson SW (1975) J Am Chem Soc 97:3342
46. The term "geminal electronegativity" has been earlier proposed by Ferreira R (1967) Adv Chem Phys 13:55 (see p 73). This concept is being further studied in this laboratory
47. Coulson CA, Longuet-Higgins HC (1947) Proc Roy Soc A 191:39; Chirgwin BH, Coulson CA (1950) Proc Roy Soc A 201:196; Longuet-Higgins HC, Wheland GW (1950) Ann Rev Phys Chem 1:133