A New Electronegativity-based Approach to Chemical Binding

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A new theory of chemical binding modelled through the accumulation of electron density at the bond centre using the concepts of bond electronegativity and bond hardness is reported and shown to provide accurate prediction of bond energies for a number of diatomic and simple polyatomic (AB_n) molecules.

Electronegativity is one of the key parameters[1] employed for understanding chemical binding and reactivity in molecular systems. Being a measure of the electron-attracting or -donating power of a species (*e.g.* an atom), it has been employed mostly to the study of interatomic charge transfer and the associated ionic binding energy in molecule formation. It is only recently that the scope of this otherwise versatile concept has been further widened[2,3] through the formulation of covalent binding within an electronegativity-based framework. It has been possible to predict[2] quite accurately the bond energies of homonuclear diatomic molecules from the atomic electronegativity and related parameters. In this work, we extend this approach to the case of heteronuclear diatomic and simple polyatomic (AB_n) molecules, where both the ionic and covalent terms contribute to binding.

In recent years, the concept of electronegativity has been rejuvenated through density functional theory,[4] according to which the energy of an N-electron system characterised by an external potential $V(r)$, is a unique functional of its electron density $\rho(r)$ and the energy functional $E[\rho]$ assumes a minimum value for the true density satisfying the Euler equation $(\delta E/\delta\rho) = \mu$. The electronegativity (χ) defined as the negative energy derivative $-(\partial E/\partial N)$ is now identified[4,5] as the negative of the chemical potential μ of the electron cloud, permitting a rigorous quantum mechanical evaluation and also providing justification for the electronegativity equalisation procedures proposed intuitively. The hardness parameter (η) defined[6] through the second derivative $(1/2)(\partial^2E/\partial N^2)$ can also be calculated using electron density through the concept of local hardness.[7]

The formation of a molecule from the constituent atoms is associated with a reorganisation of the electron densities of the atoms and the resulting energy change in the process is a measure of the binding energy. The chemical binding in a simple polyatomic molecule AB_n is viewed here as a two-step process. In the first step, owing to electronegativity difference of the atoms, there is a net interatomic charge transfer leading to an equalised chemical potential of the partially charged atoms. When each of these B atoms are placed at a distance R from the central atom A, a lowering of chemical potential of the bond regions is observed, which drives the second step of charge transfer to each bond region from the adjacent atomic regions. To describe the charge transfer to the bond region, we have introduced[2,3,8] the concepts of 'bond electronegativity' and 'bond hardness', which is rigorous since chemical potential is defined at all points and also for regions or subspaces. The first step contributes to ionic binding, while the second provides a measure of covalent contribution. Clearly for homonuclear diatomics, the second step itself provides the total binding energy.

The binding energy of a molecule can be calculated through a simple perturbation expansion of the energy-density functional, owing to the density reorganisation in these two processes. Partititioning the molecular space into several subspaces (regions) denoting atomic and bond regions, and representing the density only by the zeroth moment, *i.e.* its integral over that subspace denoting the number of electrons in that region, one obtains the expression for the energy change on charge reorganisation due to molecule formation, given by eqn. (1), where the summation extends over all sites and $R_{\alpha\beta}$ represents the mean distance between α-th and β-th sites. The effective chemical potential of the α-th site is given by eqn. (2), where ε represents the effective relative permittivity,[9] which can differ from unity as a measure of overlap or shielding correction.

We now consider the first step of charge transfer corresponding to ionic binding in an AB_n molecule by considering only the atomic regions in eqns. (1) and (2). Equating the effective chemical potentials [eqn. (2)] of all the atoms subject to the charge conservation $\sum_\alpha \Delta N_\alpha = 0$, and substituting the resulting ΔN_α in eqn. (1), the ionic contribution to A–B bond energy is obtained as eqn. (3), where R is the A–B bond length. The interaction between sites not directly bonded are ignored here for simplicity.

$$\Delta E = \sum_\alpha \mu_\alpha \Delta N_\alpha + \sum_\alpha \eta_\alpha (\Delta N_\alpha)^2 + (1/2)\sum_\alpha \sum_\beta \Delta N_\alpha \Delta N_\beta / \varepsilon R_{\alpha\beta} \quad (1)$$

$$\mu_\alpha^{\text{eff}} = \mu_\alpha + 2\eta_\alpha \Delta N_\alpha + \sum_\beta \Delta N_\beta / \varepsilon R_{\alpha\beta} \quad (2)$$

$$D_{AB}^{\text{ion}} = (1/4n)(\mu_A - \mu_B)^2/(\eta_A + \eta_B/n - 1/\varepsilon R) \quad (3)$$

For the second step of charge transfer, we now consider the bond sites in addition to the atomic ones and follow the same steps with eqns. (1) and (2) starting with the equalised chemical potentials $\mu_A{}^* = \mu_B{}^* = \mu^*$ for the partially charged A and B atoms. The resulting expression representing the covalent contribution to the bond energy is given by eqn. (4).

$$D_{AB}^{\text{cov}} = n(\mu^* - \mu_{\text{bond}})^2 (n\eta_A + \eta_B - 1/\varepsilon R) /[(2n\eta_A - 1/\varepsilon R)(2\eta_B - 1/\varepsilon R) + (2\eta_{\text{bond}} - 3/\varepsilon R)(2n\eta_A + 2\eta_B - 2/\varepsilon R)] \quad (4)$$

We now model the bond chemical potential μ_{bond} as the sum of the adjacent atomic site μ^* values (true for electrostatic potential) and the bond hardnedss η_{bond} obtained through the softness average[10] of A and B atoms. For a homonuclear diatomic molecule, this simplification of eqn. (4) leads to the result shown as eqn. (5).

$$D_{AA} = (\mu_A)^2/(6\eta_A - 7/\varepsilon R) \quad (5)$$

We now aim at expressing the heteronuclear covalent energy D_{AB}^{cov} in terms of the homonuclear bond energies D_{AA} and D_{BB}. While this cannot be done precisely, introducing an approximation $\eta_A \approx \eta_B/n$, and also in the limit of a large value of R, we obtain eqn. (6), which for a diatomic molecule simplifies to eqn. (7).

$$D_{AB}^{\text{cov}} = (3/2n)[(n+1)/(n+5)][(1/2)(D_{AA} + D_{BB}) + (nD_{AA}D_{BB})^{\frac{1}{2}}] \quad (6)$$

$$D_{AB}^{\text{cov}} = (1/2)[(1/2)(D_{AA} + D_{BB}) + (D_{AA}D_{BB})^{\frac{1}{2}}] \quad (7)$$

Eqns. (3) and (6) provide a new scheme for the calculation of the total A–B bond energy in an AB_n molecule from the atomic electronegativity and hardness parameters and the data for the A–A and B–B bond energies. This extends our earlier work[3] in which the effect of electrostatic interaction was not taken into account.

Using the values of atomic electronegativity, hardness, and A–A bond energies and bond lengths from the literature[3] and assuming a value of 1.5 for ε, the A–B bond energies in a number of AB_n molecules (with n = 1, 2, 3, 4) are calculated and the resulting bond energies are compared with the experimental values in Fig. 1. The agreement of the results is very good. The percentage error is only 2.8% for 28 diatomic and triatomic molecules (*i.e.* n = 1 and 2) and is 3.6% for a total of 39 molecules, including cases with n = 3 and 4.

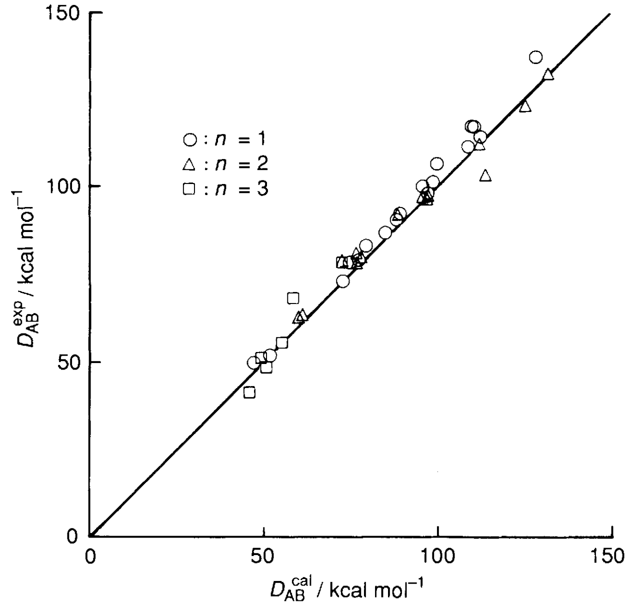

Fig. 1 Plot of the experimental A–B bond energies against the calculated bond energies for selected AB_n molecules. 1 cal = 4.184 J.

The novel features of this work can now be summarised. Eqn. (6) [or (7)] provides a new equation to obtain the covalent energy in a heteronuclear polyatomic (or diatomic) molecule, in contrast to the geometric mean used earlier empirically (see *e.g.* Ref. 11). Also eqns. (3) and (6) together represent a scheme for quite accurate prediction of the total bond energy. The present model of chemical binding has a close connection with the semiempirical quantum chemical procedures[8] and is being generalised further to the study of chemical reactivity.

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