

# Atomic and molecular properties from the density-functional definition of electronegativity

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Density-functional theory allows a systematic theoretical approach for quantifying electronegativity of atoms. Here I compare electronegativities of elements from some popular definitions with the corresponding values within the density-functional framework. I propose three new formulae for calculation of binding energy, electric dipole moment and molecular hardness, and have calculated values for several diatomic molecules using density-functional definition of electronegativity. The values in the first two cases are better than those obtained from any other known prescription. I also report improved atomic-hardness values for several neutral atoms, and propose constancy of the ratio of hardness and electronegativity values for atoms belonging to the same group in the periodic table.

OF the various qualitative ideas in chemistry, the concept of electronegativity has been very popular. Although there have been several attempts to obtain electronegativity scales only three of them have been successful in estimating different molecular properties in terms of those electronegativities. These scales have been worked out by Pauling's thermochemical method<sup>1,2</sup>, Mulliken's method<sup>3</sup> of averaging ionization potential and electron affinity, and Allred and Rochow's<sup>4</sup> scheme from classical Coulomb interactions. A spectroscopic scale has been proposed<sup>5</sup> recently, in which electronegativity is defined as the average one-electron energy of the valence-shell electrons for the isolated atoms in their ground states. This scale is claimed<sup>5</sup> to be 'the first quantitative quantum-mechanical realization of Pauling electronegativity scale'. However, most of the above methods are qualitative and empirical in nature. The first attempt at a systematic theoretical approach for calculating electronegativity was in density-functional theory (DFT), where electronegativity ( $\chi$ ) is defined as the negative of the chemical potential ( $\mu$ )<sup>6</sup> which is obtained from the Euler-Lagrange equation as<sup>7,8</sup>

$$\delta E[\rho]/\delta\rho = \mu = -\chi. \quad (1)$$

In equation (1)  $\rho$  is the electron density and the energy functional is given by

$$E[\rho] = T[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho], \quad (2)$$

where  $v(\mathbf{r})$  is the external potential, and  $T[\rho]$  and  $E_{xc}[\rho]$  are kinetic and exchange-correlation energy functionals respectively. Equation (1) would be a set of differential equations in the usual Kohn-Sham approach<sup>9</sup> and may be a single differential<sup>10</sup> or quadratic<sup>11</sup> equation depending on whether second- or first-gradient corrections to Thomas-Fermi functional are used for approximating  $T[\rho]$  in equation (2).

Electronegativity can be obtained in four different ways: (a) by obtaining  $\mu$  from a self-consistent solution of equation (1); (b) from the energies of the neutral atom and some of its cations and anions and numerically differentiating the  $E$  values with respect to the number of electrons for a constant external (nuclear) potential; (c) by calculating the ionization potential [ $I = (E_{\text{cation}} - E_{\text{neutral atom}})$ ] and the electron affinity [ $A = (E_{\text{neutral atom}} - E_{\text{anion}})$ ] and then applying Mulliken's definition<sup>3</sup>; and (d) by writing energy as a function of  $Z$  and  $N$  and analytically differentiating with respect to  $N$ , where  $Z$  and  $N$  are the numbers of protons and electrons respectively.

Considering the popularity of chemical concepts like electronegativity and hardness and their quantification within density-functional theory, what I would like to do in the present paper are the following: (i) to compare the  $\chi$  values obtained from different methods; (ii) to correlate molecular properties like bond-dissociation energies and dipole moments with density-functional  $\chi$ ; (iii) to analyse the assumed constancy of the proportionality between  $\eta$  and  $\chi$  for the elements belonging to the same group in the periodic table; and (iv) to obtain molecular hardness in terms of atomic electronegativities rather than atomic-hardness values.

## Method

The differences in electronegativities of the constituent atoms of a diatomic molecule provide estimates of different molecular properties, especially bond energy and dipole moment. There exist a number of relations correlating the bond-dissociation energy and the electronegativity difference. Some of them are the following:

(i) Pauling's geometric-mean relation<sup>1</sup>

$$D_{AB} = \bar{D}_{AB} + 30(\Delta\chi)^2, \quad (3)$$

where  $D_{AB}$  is the bond-dissociation energy of the