

Chemical Bonds without Bonding Electron Density— Does the Difference Electron-Density Analysis Suffice for a Description of the Chemical Bond?***

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Carefully executed X-ray diffraction experiments on peroxides^[1,2] have indicated that the difference electron-density distribution $\Delta\rho(r)$ in the region of the OO bond is negative. The $\Delta\rho(r)$ -distributions in certain CC, CN, CO, and CF bonds in various organic molecules are also surprisingly small^[2,3]. Since $\Delta\rho(r)$ provides at least a qualitative measure for the accumulation of electron density in the bonding region^[4], bonding models in which the existence of a covalent bond is dependent upon a finite bonding electron density $\Delta\rho(r)$ appear somewhat dubious^[2]. We report here a novel approach to the description of the chemical bond, which confirms that the formation of covalent bonds does not necessarily bring about an increase in electron density in the bonding region.

The analysis of difference or deformation electron-densities $\Delta\rho(r) = \rho(r) - \rho'(r)$, although experimentally quite useful, is problematic since it requires the definition of an appropriate reference density $\rho'(r)$ ^[4,5]. Therefore, we have analyzed the electron-density distribution $\rho(r)$ directly from its assigned Laplace field $\nabla^2\rho(r)$. It is an important property of the Laplace field to indicate concentrations of its associated scalar field without requiring a reference field^[6]. The "Laplace concentration" reflects the behavior of the principle curvatures λ_i ($i = 1, 2, 3$) of $\rho(r)$ in the three directions of space (λ_i : eigenvalue of the matrix of second derivatives of $\rho(r)$). The curvature λ_1 along the bond is always positive since $\rho(r)$ has a minimum there. The curvatures λ_2 and λ_3 perpendicular to the bond axis are negative, corresponding to an increase in $\rho(r)$ towards the bond axis. If the charge concentration perpendicular to the bond axis is predominant ($|\lambda_2| + |\lambda_3| > |\lambda_1|$), a negative value for $\nabla^2\rho(r)$ results, synonymous with a concentration of $\rho(r)$ in the bonding region.

The Laplace fields $\nabla^2\rho(r)$ determined by HF/6-31G* calculations for some selected bonds are shown in Figure 1 in the form of contour line diagrams. The broken lines occur in regions with charge concentrations ($\nabla^2\rho(r) < 0$) which, on the basis of simple chemical concepts, can be assigned to bonding and lone-pair electrons^[7]. The concentration of $\rho(r)$ in the bonding region decreases along the series CC, CN, CO, CF and CC, OO, FF, respectively (see Fig. 1 and Table 1), which qualitatively goes hand in hand with a decrease in covalent bond strength^[8].

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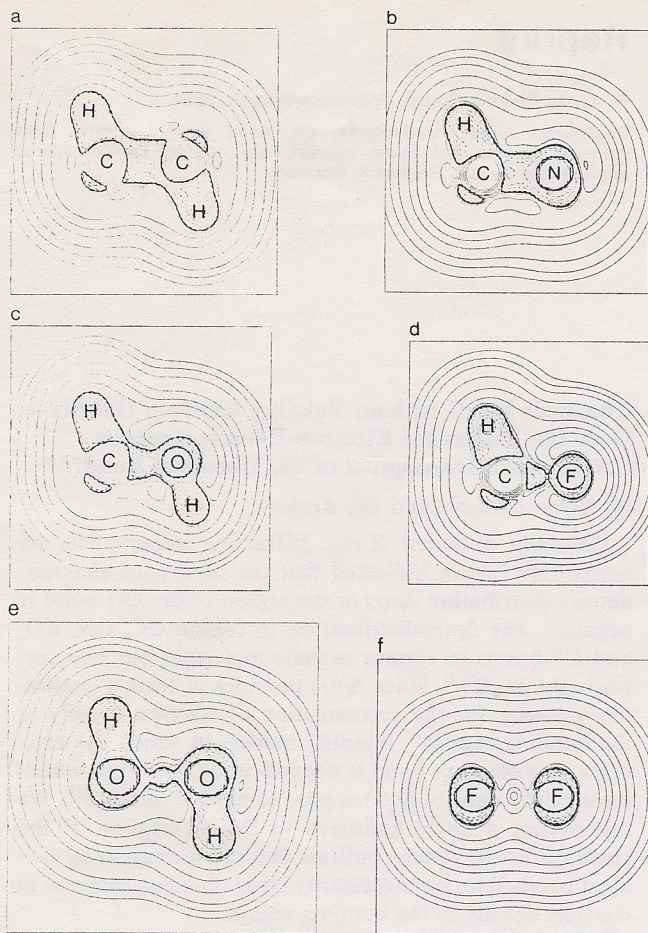


Fig. 1. Contour line diagram of the Laplace field $\nabla^2\rho(r)$ (HF/6-31G* calculations) for a) C_2H_6 (staggered), b) CH_3NH_2 (staggered, HCN *trans*), c) CH_3OH (staggered, HCOH *trans*), d) CH_3F , e) H_2O_2 (trans), and f) F_2 . Broken lines indicate regions with charge concentrations. Atoms lying outside the reference plane are not shown.

In contrast to the results of the analysis of $\Delta\rho(r)$ ^[11], the Laplace field of $\rho(r)$ indicates that charge is concentrated in the region of the OO bond. Apparently, the quantity $\nabla^2\rho(r)$ is a more sensitive measure for the description of charge accumulation than $\Delta\rho(r)$. The experimental observation that bonding electron density can be absent for specific covalent bonds is, however, confirmed in the case of the FF bond^[9]. Clearly, a characterization of the covalent bond by $\nabla^2\rho(r)$ is insufficient. The chemical bond can only be satisfactorily described if in addition to electrostatic also energetic aspects are considered^[10].

Bond formation is associated with a gain in molecular energy, and this gain is a result of a complex interplay of changes in potential and kinetic energy^[11]. One possibility to analyze these changes in the bonding region is provided by the relation $2G(r) + V(r) = \frac{1}{2}\nabla^2\rho(r)$, derived by Bader, which connects the kinetic energy density $G(r)$ and the potential energy density $V(r)$ with the Laplace field of $\rho(r)$ ^[12]. Pointwise analysis of $G(r)$ and $V(r)$ indicates that for covalent bonds the local energy density $H(r) = G(r) + V(r)$ at sites of maximum concentration of $\rho(r)$ is always negative (stabilizing)^[12b, 13]. This also applies to the F-F bond: Although electron density flows out of the internuclear region upon bond formation, the residual density is sufficient to contribute towards bond stabilization via an increase in $|V(r)|$ (Table 1).

Table 1. Characterization of covalent bonds by electron density and energy density [a].

Molecule	Bond	$\rho(r_c)$ [e·Å ⁻³]	$\nabla^2\rho(r_c)$ [e·Å ⁻⁵]	$G(r_c)$	$V(r_c)$ [Hartree·Å ⁻³]	$H(r_c)$
C_2H_6	C-C	1.880	-24.844	1.032	-3.803	-2.771
CH_3NH_2	C-N	1.866	-22.713	0.935	-3.466	-2.531
CH_3OH	C-O	1.858	-18.366	0.983	-3.267	-2.284
CH_3F	C-F	1.769	-10.517	1.199	-3.134	-1.935
H_2O_2	O-O	1.837	-4.753	1.190	-2.713	-1.523
F_2	F-F	2.335	2.908	2.247	-4.292	-2.045

[a] HG/6-31G* calculations with optimized geometries. The point r_c corresponds to the maximum density in the bonding region.

The condition $H(r) < 0$ in the bonding region holds for all covalent bonds studied to date (ca. 100)^[13]; not, however, for ionic bonds, H bonds, or van der Waals bonds. Thus, specifically those bonds which exhibit either zero or a very small bonding electron density should be investigated with the aid of the local energy density $H(r)$. For this purpose, analysis of the local property $H(r_c)$ is adequate for a qualitative description of bonding, whereas for a quantitative treatment the behavior of $H(r)$ in the whole bonding region must be considered^[13].

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[1] J. M. Savariault, M. S. Lehmann, *J. Am. Chem. Soc.* 102 (1980) 1298.

[2] J. D. Dunitz, P. Seiler, *J. Am. Chem. Soc.* 105 (1983) 7056.

[3] a) P. Chakrabarti, P. Seiler, J. D. Dunitz, *J. Am. Chem. Soc.* 103 (1981) 7378; b) J. D. Dunitz, W. B. Schweizer, P. Seiler, *Helv. Chim. Acta* 66 (1983) 123.

[4] a) P. Coppens, E. D. Stevens, *Adv. Quantum Chem.* 10 (1977) 1; b) P. Coppens, *Angew. Chem.* 89 (1977) 33; *Angew. Chem. Int. Ed. Engl.* 16 (1977) 32; c) J. D. Dunitz: *X-ray Analysis and the Structure of Organic Molecules*, Cornell University Press, Ithaca, NY 1979.

[5] Difficulties arise, inter alia, in the investigation of ions with delocalized charge, e.g. cations or anions of cyclopolynes.

[6] The significance of the Laplace field can be understood from the definition of the second derivative. In the one-dimensional case

$$\lim_{\Delta x \rightarrow 0} [\rho(x) - \frac{1}{2}[\rho(x - \Delta x) + \rho(x + \Delta x)]] = -\frac{1}{2} \lim_{\Delta x \rightarrow 0} [\rho(x + \Delta x) - \rho(x)] - [\rho(x) - \rho(x - \Delta x)] = -\frac{1}{2}(\rho/dx^2) \cdot dx^2$$

is valid.

If the second derivative, and hence the curvature of ρ , is negative, $\rho(x)$ is larger than the average value of ρ at all neighboring points; P. M. Morse, H. Feshbach: *Methods of Theoretical Physics, Bd. 1*, McGraw-Hill, New York 1953, p. 6.

[7] R. F. W. Bader, *J. Am. Chem. Soc.*, in press.

[8] A significant correlation between electron density properties and thermochemically derived bond energies is obtained if the total electron density in the bonding region is considered. See e.g. R. F. W. Bader, T. Tang, Y. Tal, F. W. Bieler-König, *J. Am. Chem. Soc.* 104 (1982) 946.

[9] Investigations by M. Breitenstein, H. Dannöhe, H. Meyer, A. Schweig, W. Zittlan in P. Coppens, M. B. Hall: *Electron Distributions and the Chemical Bond*, Plenum Press, New York 1982, p. 255 indicate that in correlation-corrected calculations, the electron density $\rho(r)$ in the bonding region is smaller than that obtained by HF calculations. Since this results in more positive curvature both in and perpendicular to the bond direction, an improvement in the calculation will lead to an even larger $\nabla^2\rho(r)$ value.

[10] According to the Hohenberg-Kohn theorem (P. Hohenberg, W. Kohn, *Phys. Rev.* 136 (1964) B864) an as yet unknown connection exists between energy and electron density.

[11] K. Ruedenberg, *Rev. Mod. Phys.* 34 (1962) 326.

[12] a) R. F. W. Bader, *J. Chem. Phys.* 73 (1980) 2871; b) $G(r)$ and $V(r)$ are defined by the first-order density matrix $\Gamma^1(r, r')$:

$$G(r) = \frac{1}{2} \nabla \nabla' \Gamma^1(r, r')|_{r=r'}; V(r) = \text{trace } \vec{\sigma}(r), \\ \vec{\sigma}(r) = \frac{1}{2} [(\nabla \nabla' + \nabla' \nabla) - (\nabla \nabla' + \nabla' \nabla)] \Gamma^1(r, r')|_{r=r'}$$

When integrated over the total molecular space, $G(r)$ and $V(r)$ yield the kinetic and potential energies of the molecule, respectively. Correspondingly, $E = \int H(r) dr$ applies for the electronic molecular energy.

[13] D. Cremer, E. Kraka, *Croat. Chem. Acta*, in press.