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A Description of the Chemical Bond in Terms of Local Properties of Electron Density and Energy

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Chemical bonding is described in terms of the properties of the one-electron density $\varrho(\mathbf{r})$ and the local energy density $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$. Analysis of a variety of different bonds suggests that covalent bonding requires the existence of a saddle point $\mathbf{r}_p$ of $\varrho(\mathbf{r})$ in the internuclear region (necessary condition) and a predominance of the local potential energy $V(\mathbf{r})$ at $\mathbf{r}_p : |V_p| > G_p$ and, hence, $H_p < 0$. A covalent bond can be characterized by the position of $\mathbf{r}_p$, the value and the anisotropy of ϱ_p. These properties of $\varrho(\mathbf{r})$ can be used to define polarity, order and π-character of the bond. Information about concentration and depletion of electronic charge at $\mathbf{r}_p$ is provided by the Laplacian of ϱ_p, $\nabla^2 \varrho_p$. Investigation of $\nabla^2 \varrho(\mathbf{r})$ does not suffice to detect weak covalent bonds, an observation which is always valid if accumulation of electronic charge in the internuclear region is taken as the sole indicator for bonding. Interactions between closed shell systems as experienced in ionic, hydrogen bonded or van der Waals systems lead to a positive value of H_p. In this case, shared electron density causes destabilization rather than stabilization of the molecule.

INTRODUCTION

Certainly, the most fruitful concept in chemistry has been the concept of the chemical bond. Evidence for its immense impact on chemical research and chemical thinking is found in numerous publications, review articles and textbooks solely devoted to the description of chemical bonds.[1-9] Although the success of the concept of the chemical bond in descriptive chemistry is indisputable, a detailed quantum mechanical treatment of bonding has turned out to be a difficult enterprise. This is only partially due to the lack of accurate wave functions for polyatomic molecules. The major difficulties simply result from the fact that atoms in molecules and the chemical bonds linking them together are *non-observables*[10]. Thus, as a theoretician one is often confronted with the following disturbing observation: The more intuitive and empirical atom and bond properties are used within a given chemical concept, the more successfully does the latter contribute to the solution of practical problems, whereas a serious attempt at a rigorous quantum mechanical definition of atoms and bonds often leads to a break-down of the whole conceptual approach.

Theoretical attempts to understand the physical nature of the chemical bond can roughly be divided into two categories.[11] The first includes those which consider the energy lowering upon formation of a molecule from atoms. Utilizing the virial theorem, the molecular energy is partitioned in a physically meaningful way and the bond formation is described in terms of the changes of the various energy contributions.[12,13] The second category comprises those attempts, which approach chemical bonding from the electrostatic viewpoint. Within this approach the electric forces exerted on the nuclei by the electrons of a molecule are analyzed with the aid of the Hellmann-Feynman theorem.[11,14]

Since both the molecular energy[15] and the forces in a molecule are connected with the electron density, it is reasonable to focus a discussion of the chemical bond on the properties of the density distribution. The behavior and distribution of electrons around the nucleus constitute the fundamental character of an atom. This should also apply to the atoms in a molecule and to the ties linking them together. Therefore, a detailed analysis of the molecular electron density distribution should yield a valid description of the chemical bond. This has been amply verified and has led to rather sophisticated descriptions of chemical bonding.[1-9] Noteworthy, in this respect, is the work of Bader on the analysis of the one-electron density distribution $\varrho(\mathbf{r})$.[16]

The aim of this work is to suggest a model of the chemical bond, which takes advantage of the interrelation between electron density distribution, molecular energy, and chemical bonding. The three basic assets of any model of the chemical bond should be its physical significance, its generality, and its applicability to practical problems. We believe that these assets can only be achieved if a model of the chemical bond is developed on a solid quantum mechanical basis. However, this should not exclude its clarity. A model of bonding has to be used by chemists and, therefore, should contain well-known features of more empirical bonding concepts, *e. g.* the notion of covalency, ionicity, order, type and polarity of bond. Furthermore, any new model of the chemical bond should not be inconsistent with what has been learned from energetic and electrostatic descriptions of bonding. We attempt to fulfill these requirements by combining an analysis of local properties of the electron density distribution $\varrho(\mathbf{r})$ with a similar analysis of local energy properties. Bader's topological analysis of $\varrho(\mathbf{r})$[16] turns out to be particularly useful for this purpose as was shown recently.[17,18]

In the first section we briefly review the possibility of defining atoms in molecules by partitioning of the molecular space. In Section II we derive a necessary and a sufficient condition for bonding upon which our model of the chemical bond is based. Sections III and IV are devoted to a description of covalent and ionic bonding. We close by offering an idea on how our model of the chemical bond can best be used.

I. DEFINITION OF AN ATOM IN A MOLECULE

Before discussing the chemical bond it is essential to clarify the term *atom in a molecule.* An isolated atom is physically observable. It is the union of a nucleus with positive charge Z and of Z negatively charged electrons. As soon as an atom is part of a molecule this definition no longer applies.

An atom in a molecule does not possess a specific number of electrons. There is no unique way to divide the electrons of a molecule between the various atoms. Therefore, an atom in a molecule is neither experimentally nor quantum mechanically observable.[10] As a consequence, the chemical bond is also not observable. There is no way to *measure* a bond or any bond property. A chemical bond can only be defined within a suitable model, a prerequisite of which is the definition of an *atom in a molecule.*

A bound atom is an example of an open quantum system, which exchanges charge and momentum with its environment. There exists no state function of a bound atom. Hence, the normal approach to describe a bonded atom should be based on the density matrix formalism for open systems[19]. One could, however, employ the molecular state function Ψ for the description of the atom in the molecule, provided an atomic subspace Ω_A could be defined.

A theory of molecular subspaces has been derived by Bader and coworkers[20,21] which is based on the finding that the principle of stationary action can be generalized to a particular class of subsystems which are determined with the aid of the *zero-flux* surfaces $S(\mathbf{r})$ defined by Eq. (1) (see also Figure 1):

$$\nabla \varrho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \qquad \forall\ \mathbf{r} \in S(\mathbf{r}) \tag{1}$$

where $\varrho(\mathbf{r})$ is the one-electron density distribution and $\mathbf{n}$ is the unit vector normal to the surface S. For all surface points the flux of $\nabla \varrho(\mathbf{r})$ vanishes. Utilizing (1) the total molecular space can be partitioned into subspaces Ω.

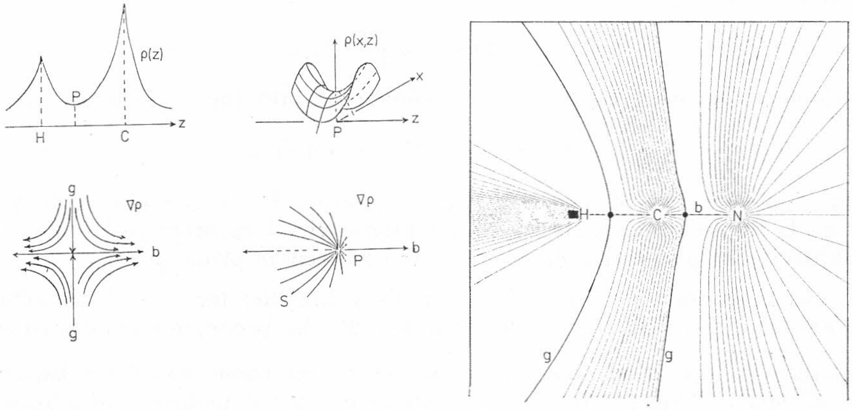


Figure 1. Zero-flux surface S and bond saddle point P. (a) schematic representation of $\varrho(\mathbf{r})$ and $\nabla \varrho(\mathbf{r})$ in one and two dimensions for the CH bond of HCN. **b** denotes the path of maximum electron density; **g** is the trace of S in the x, z plane. The directions of the trajectories $\nabla \varrho(\mathbf{r})$ are indicated. (b) Calculated gradient vector field $\nabla \varrho(\mathbf{r})$ of HCN. Zero-flux surfaces are indicated in the same way as in (a).

It has been shown that all properties of Ω are quantum mechanically defined in the same way as for the total molecular system.[20,21] This is an important finding, which can be made plausible by describing the system under consideration with the aid of the hypervirial theorem. Thus, the molecular expectation value of a hermitian operator $\hat{F}$ where F is a function of momentum and space only, can be evaluated with Eq. (2)[22]

$$< \Psi \,|\, \hat{H}\hat{F} - \hat{F}\hat{H} \,|\, \Psi > = 0 \tag{2}$$

assuming that Ψ is a molecular state function according to $\hat{H}\,\Psi = E\,\Psi$. In order to evaluate the same expectation values for subspaces Ω Eq. (3) has to be fulfilled[23]:

$$< \Psi \,|\, \hat{H}\hat{F} - \hat{F}\hat{H} \,|\, \Psi >_{\Omega} = 0 \tag{3}$$

If one considers only operators $\hat{F}$, which do not involve differentiation with respect to parameters contained in $\hat{H}$, Eq. (3) can be rewritten according to

$$< \Psi \,|\, \hat{H}\hat{F} \,|\, \Psi >_{\Omega} - < \hat{H}\,\Psi \,|\, \hat{F}\,\Psi >_{\Omega} = 0 \tag{4}$$

Inserting the molecular Hamiltonian

$$\hat{H} = -1/2\,\nabla^2 + \hat{V} \tag{5}$$

Eq. (4) simplifies to

$$< \Psi \,|\, \nabla^2 \hat{F} \,|\, \Psi >_{\Omega} - < \nabla^2 \Psi \,|\, \hat{F}\,\Psi >_{\Omega} = 0 \tag{6}$$

due to the cancellation of potential energy terms. With the aid of the Gaussian integral theorem (7)

$$\int_{\Omega_A} \nabla^2 \hat{F}\, d\,\omega = \oint_{S} \nabla\, \hat{F}\, d\,\sigma \tag{7}$$

the volume integral of Eq. (6) can be converted into the surface integral (8)

$$\oint_{S} (\Psi^* \,\nabla\, \hat{F}\,\Psi - \nabla\,\Psi^* \,\hat{F}\,\Psi) \cdot \mathrm{d}\,\sigma = 0 \tag{8}$$

with $d\sigma = \mathbf{n} \cdot dS$. Eq. (8) is a sufficient condition for a regional hypervirial theorem. It implies the existence of a regional virial theorem (see below) and the additivity of properties F_{Ω} yielding the molecular property F.

It has been shown[21c] that condition (8) is fulfilled for zero-flux surfaces. Thus, knowing the stationary state function Ψ, the properties associated with the operators $\hat{F}$ specified above are obtained in the same way for subspace Ω as for all space. This finding can be extended via the principle of stationary action for any operator $\hat{F}$.[21e]

Although subspaces Ω are quantum mechanically well-defined, there is no *a priori* indication that they can be associated with an atomic region. Justification for setting $\Omega = \Omega_A$ is, however, provided by the topological features of $\varrho(\mathbf{r})$[16,21] and the evidence obtained from the analysis of computed molecular densities $\varrho(\mathbf{r})$ and their associated gradient vector field $\nabla\varrho(\mathbf{r})$.[17,18,24] The following observations have been made:

(*i*) There are as many subspaces in a molecule as there are atoms in a molecule.

(*ii*) Each subspace contains just one atomic nucleus.

Hence, it is reasonable to denote subspaces Ω determined by Eq. (1) as atomic regions Ω_A, and to use them for a quantum mechanical definition of an atom in a molecule.[25]

II. DEFINITION OF THE CHEMICAL BOND

Once an atom in a molecule has been defined, it is possible to distinguish between bonded and nonbonded atoms. In the first case, two atoms A and B are separated by a common zero-flux surface S (A, B). In the second case, the two atomic subspaces are separated by at least one other subspace belonging to a third atom. We conclude that a necessary condition for the existence of a chemical bond between atoms A and B is the existence of a common zero-flux surface S (A, B). This condition is certainly not sufficient as becomes immediately clear when considering the van der Waals complex He_2 or two atoms A and B separated by such a distance that bonding is no longer possible. In these cases, the atomic regions of A and B are still separated by a common surface S (A, B). The same applies if A and B belong to two different molecules described by the wave function of the corresponding supermolecule (for examples, see Figure 2).

In order to distinguish between bonding and nonbonding situations, a second condition has to complement the first one. The second condition should be sufficient to detect a bond AB.

It has been shown that the gain in energy, ΔE, resulting from bond formation is due to a complex interplay of kinetic (T) and potential energy (V), contributions to ΔE.[6,7] When going from the separated atoms to the bonded ones, T increases while V decreases, the net effect being negative and leading to the stability of the molecule. For small molecules like H_2^+ or H_2 the change in the total average kinetic energy upon bond formation has been split into contributions parallel and perpendicular to the bond axis.[7c,13] During bond formation the latter increases, while the former decreases substantially keeping the overal increase of T to a minimum. Charge is concentrated perpendicular to the bond axis which leads to a lowering of V and stabilization of the molecule upon bond formation. Thus, the dominance of V in the internuclear region could be used as a condition for bonding. Unfortunately, a detailed analysis of parallel and perpendicular contributions becomes troublesome in the case of polyatomic molecules. This is in particular true, if bonding in delocalized systems is considered.[8b]

Alternatively, one could consider an accumulation of electronic charge in the internuclear region as being indicative of bonding. For example, such an accumulation could be detected by investigating difference or deformation electron density distributions. As a matter of fact this approach, in particular its pictorial representation in the form of difference density maps, has become quite popular among chemists.[9] Nevertheless, it suffers from serious drawbacks. First of all, it is by no means clear which parts of the molecule belong to the bonding region. *There is no unique way to define a bonding region.* Such a definition, however, would be essential if the difference density would be both positive and negative in the internuclear region. Secondly, the determination of difference densities implies the definition of a reference state. Again, this cannot be done in a general and unique manner. This becomes

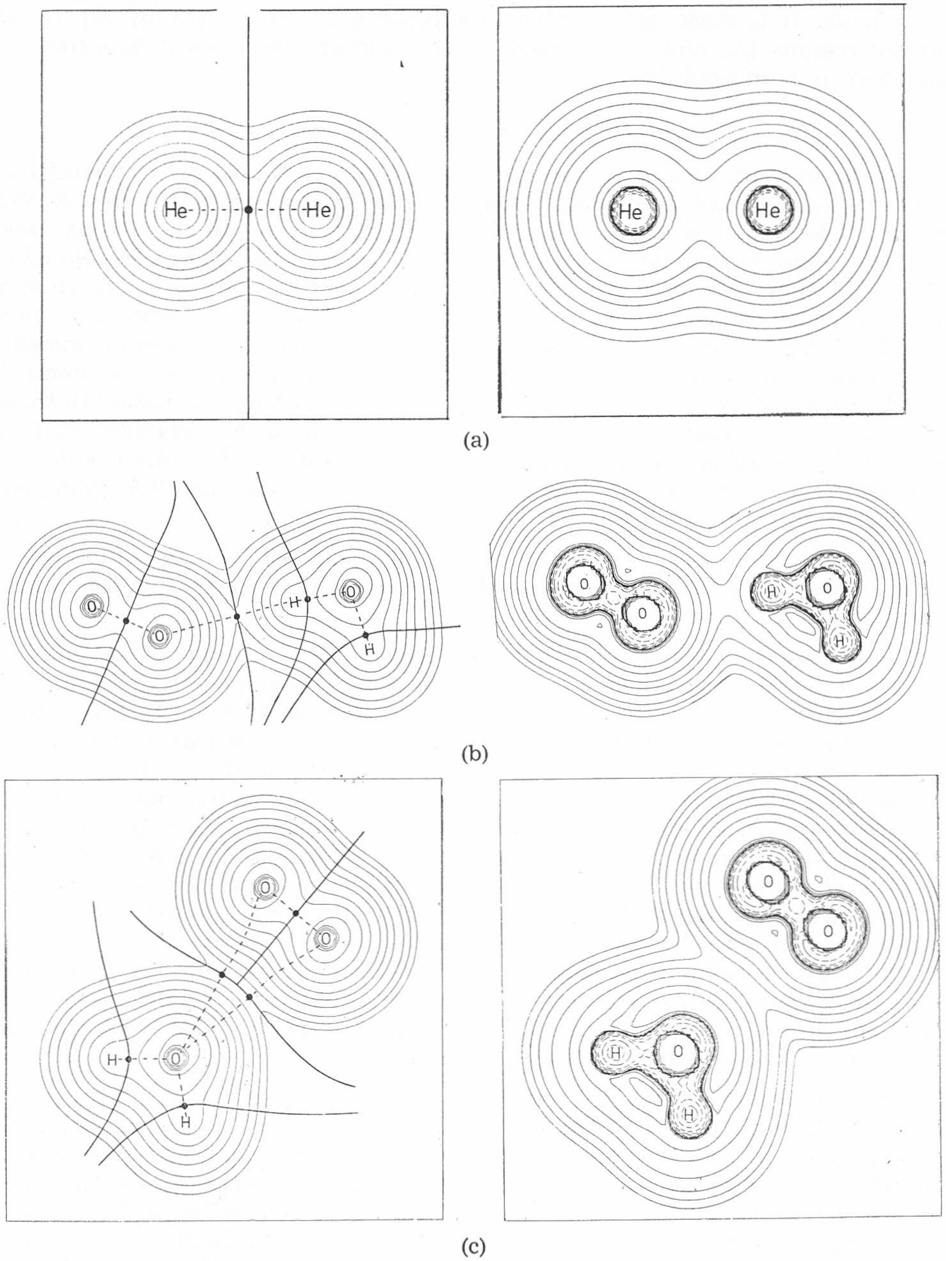


Figure 2. Conturline diagrams of $\varrho(\mathbf{r})$ and $\nabla^2\varrho(\mathbf{r})$ for (a) the van der Waals complex He_2, (b) the H bonded complex O_2—H_2O, and (c) the non-H bonded complex O_2—H_2O. The zero-flux surfaces are indicated in the $\varrho(\mathbf{r})$ diagrams by heavy lines, the internuclear saddle points P by dots and the paths of maximum electron density by dashed lines. In the $\nabla^2\varrho(\mathbf{r})$ plots, dashed lines indicate regions of charge concentration. (O_2—H_2O from D. Cremer and L. Curtiss, unpublished results; HF/STO-3G and HF/6-31G* calculations)[41].

obvious when trying to analyse bonding in ions with partial or full delocalization of charge, *e. g.* cyclopolyenyl cations.

This discussion already suggests that a model of the chemical bond should consider both the energetic and the electrostatic aspect in order to derive necessary and sufficient conditions for bonding. On the other hand, it should circumvent a partitioning of molecular space into bonding and nonbonding areas. Also, the definition of reference energies or densities may limit the applicability of a model of the chemical bond. In view of these considerations, we will proceed in the following way. First, a kinetic and a potential energy density are defined and their local contributions are compared. Then, energy densities are related to properties of the charge distribution. Finally, a simple condition is derived to distinguish a bonding from a nonbonding situation.

II.1. *Local Energy Densities*

If $f(\mathbf{p}, \mathbf{q})$ is the distribution function of momentum and space coordinates, the classical definition of a local kinetic energy density $T(\mathbf{q})$ is given by[26]

$$T(\mathbf{q}) = \int f(\mathbf{p}, \mathbf{q})\, p^2/2m \, \mathrm{d}\mathbf{p} \tag{9}$$

Integration of $T(\mathbf{q})$ over the space Ω_A leads to the total kinetic energy $T(\Omega_A)$:

$$T(\Omega_A) = \int_{\Omega_A} T(\mathbf{q}) \, \mathrm{d}\mathbf{q} \tag{10}$$

By applying the rules of correspondence between classical variables and quantum mechanical operators, a local kinetic energy density in quantum mechanics can be obtained. Cohen[26] has summarized the set of all possible quantum distributions $g(\hat{p}, \hat{q})$ which can lead to a specific local kinetic energy. He showed that all possible definitions of a kinetic energy density when integrated over an Ω_A determined by (1), yield the same average value for the kinetic energy, *i. e.* the kinetic energy is uniquely defined in this case. We consider here just one of the possible kinetic energy densities, namely

$$G(\mathbf{r}) = 1/2\, \nabla \nabla' \Gamma^1(\mathbf{r}, \mathbf{r}')\big|_{\mathbf{r}=\mathbf{r}'} \tag{11}$$

where Γ^1 is the one-electron density matrix.[7c]

$G(\mathbf{r})$ can be deduced directly from the classical expression for T and has the advantage of being always positive definite. Furthermore, $G(\mathbf{r})$ can be related to the local potential energy density $V(\mathbf{r})$ with the aid of Eq. (12)[27]:

$$2\,G(r) + V(\mathbf{r}) = 1/4\, \nabla^2 \varrho(\mathbf{r}) \tag{12}$$

$V(\mathbf{r})$ is a prescription of the *average field* experienced by a single electron in a many particle system with:

$$V(\mathbf{r}) = N \int \mathrm{d}\tau' \,[\Psi^* (-\mathbf{r}\, \nabla \hat{V})\, \Psi] \tag{13}$$

where $\mathrm{d}\tau'$ denotes the spin coordinates of all N electrons and the cartesian coordinates of all N electrons but one.

Integration of Eq. (12) over the region Ω_A leads to

$$2\,G(\Omega_A) + V(\Omega_A) = \frac{1}{4} \int_{\Omega} \nabla^2 \varrho(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{14}$$

Utilizing Eq. (7) one gets the regional virial theorem[27]:

$$2\,G\,(\Omega_A) + V\,(\Omega_A) = \frac{1}{4}\oint_S \nabla\,\varrho\,(\mathbf{r})\,\mathbf{n}\cdot \mathrm{d}S = 0 \qquad (15)$$

where the term on the right hand side of Eq. (15) vanishes because of (1).

The local virial theorem offers two possibilities of describing the effects of chemical bonding:

1. One can analyse the Laplacian of $\varrho\,(\mathbf{r})$ in the bonding region. In general, the Laplacian of any scalar field is negative, where the scalar field concentrates. This becomes obvious, when considering the definition of the second derivative of ϱ in the one-dimensional case[28]:

$$\begin{aligned} &\lim_{\Delta x\to 0}\{\varrho\,(x) - 1/2\,[\varrho\,(x-\Delta x) + \varrho\,(x+\Delta x)]\} = \\ &-1/2\lim_{\Delta x\to 0}\{[\varrho\,(x+\Delta x) - \varrho\,(x)] - [\varrho\,(x) - \varrho\,(x-\Delta x)]\} = \qquad (16)\\ &-1/2\,(\mathrm{d}^2\varrho/\mathrm{d}x^2)\cdot \mathrm{d}x^2 \end{aligned}$$

If the second derivative and, hence, the curvature of ϱ is negative at x, then ϱ at x is larger than the average value of ϱ at all neighbouring points. Accordingly, the analysis of $\nabla^2\,\varrho\,(\mathbf{r})$ will give evidence of charge concentration and/or depletion in the bonding region without defining a reference density. This approach could be favorably used within an electrostatic model of the chemical bond.

2. Alternatively, the local energy densities $G\,(\mathbf{r})$ and $V\,(\mathbf{r})$ could be compared in the bonding region:

$$H\,(\mathbf{r}) = G\,(\mathbf{r}) + V\,(\mathbf{r}) \qquad (17)$$

where $H\,(\mathbf{r})$ integrated over the total molecular space yields the molecular electronic energy $E = T + V$, with $T = \int G\,(\mathbf{r})\cdot \mathrm{d}\mathbf{r}$ and $V = \int \mathrm{V}\,(\mathbf{r})\cdot \mathrm{d}\mathbf{r}$. Since $V\,(\mathbf{r})$ is always negative and $G\,(\mathbf{r})$ always positive, the sign of the energy density $H\,(\mathbf{r})$ reveals whether $V\,(\mathbf{r})$ or $G\,(\mathbf{r})$ dominate in the bonding region. A clear dominance of $V\,(\mathbf{r})$ indicates that accumulation of electronic charge in the internuclear region is stabilizing. If the local kinetic energy outweighs $V\,(\mathbf{r})$, internuclear charge concentration is destabilizing, typical for a nonbonded situation.

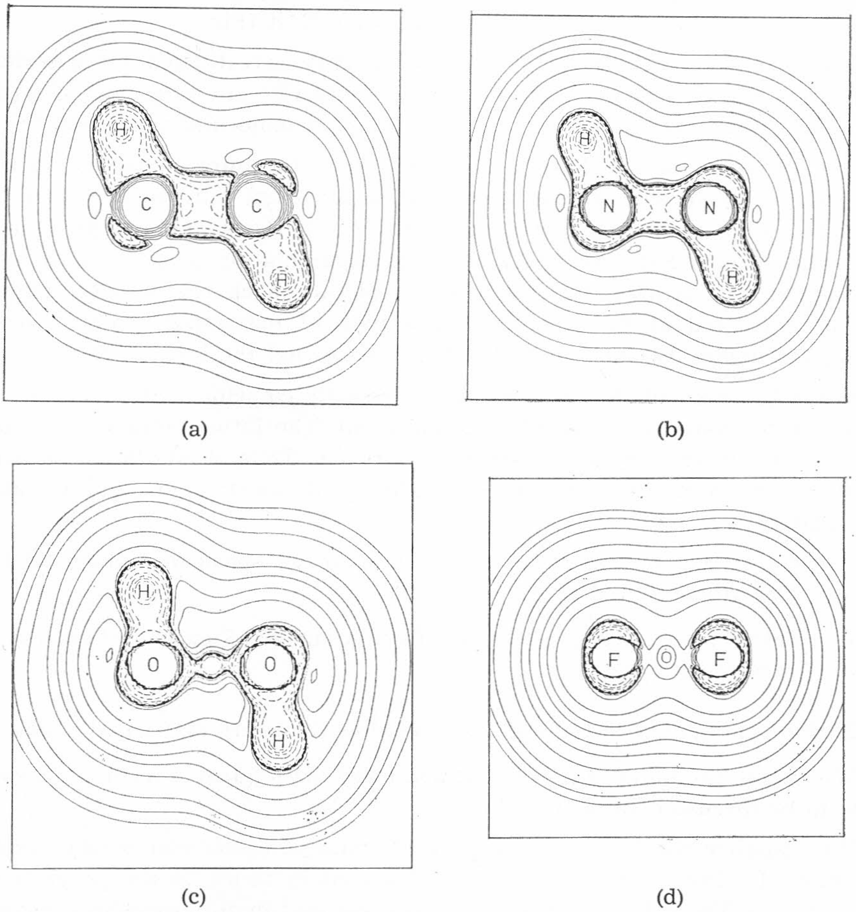
This tentative interpretation of $H\,(\mathbf{r})$ becomes somewhat clearer when Eq. (17) is rewriten with the aid of Eq. (12)[29]:

$$H\,(\mathbf{r}) = 1/2\,(V\,(\mathbf{r}) + 1/4\,\nabla^2\,\varrho\,(\mathbf{r})) \qquad (18)$$

The second term measures the depletion of charge from the interatomic region. This depletion does not necessarily imply a loss of chemical bonding.[30] As long as $V\,(\mathbf{r})$ dominates Eq. (18), a negative $H\,(\mathbf{r})$ and stabilization of the molecule results. Thus, if bonding is solely described by determining the degree of charge concentration in the internuclear region, not all chemical bonds of a molecule may be detected. This seems to be the case when electron-rich atoms like O and F are linked together. For example, Savariault and

Lehmann[31a] have obtained a negative deformation density in the OO bond region of H_2O_2 by combining X-ray and neutron diffraction measurements. The same observations have been made in the case of organic peroxides.[31b] Theoretical difference densities of H_2O_2 and F_2 are all negative in the region between the heavy atoms. Surprisingly low bond deformation densities are detected for CN, CO and CF bonds of various organic molecules.[31c,31d] Dunitz has attributed the lack of charge accumulation in the bonds of electron rich atoms (as measured by the deformation density) to the exclusion principle, which prohibits excessive charge accumulation in a constrained area.[31b]

Contrary tc the results of difference density analysis, evaluation of $\nabla^2 \varrho(\mathbf{r})$ of H_2O_2 (Figure 3) indicates charge concentration in the OO bond. Concentration of $\varrho(\mathbf{r})$ is clearly smaller as in the case of a NN or CC single bond (Figure 3), but still sufficient to visualize the heavy atom bond in a pictorial representation of $\nabla^2 \varrho(\mathbf{r})$. This is not true in the case of the F_2 molecule. The Laplacian of $\varrho(\mathbf{r})$ (Figure 3) is positive in the whole interatomic region despite the co-



(a) (b) (c) (d)

Figure 3. $\nabla^2 \varrho(\mathbf{r})$ plots of (a) C_2H_6 (staggered), (b) N_2H_4 (trans), (c) H_2O_2 (trans), and (d) F_2. Dashed lines indicate regions of charge concentrations. Atoms above and below the reference plane are not indicated. (HF/6-31G* calculations).

valent bond between the F atoms. Similar observations can be made for some other weak bonds between electron-rich atoms.

These results suggest that the condition $\nabla^2 \varrho(\mathbf{r}) < 0$ and, probably, any other measure of charge concentration is not sufficient to detect all chemical bonds. Clearly, the situation, where $2G(\mathbf{r}) > |V(\mathbf{r})| > G(\mathbf{r})$, is not covered, if bonding is investigated with the Laplacian of $\varrho(\mathbf{r})$ via Eq. (12). Therefore, it seems to be more appropriate to choose $H(\mathbf{r})$ as an indicator for bonding interactions.

So far, no decision has been made how to define the bonding region. In view of the partitioning of molecular space by zero-flux surfaces $S(\mathbf{r})$, it is reasonable to constrain the analysis of $\varrho(\mathbf{r})$ and $H(\mathbf{r})$ to these interatomic surfaces. One can further facilitate the analysis by considering just one point of $S(\mathbf{r})$, namely the point $\mathbf{r}_p$ which is the sing of all gradient trajectories forming $S(\mathbf{r})$ (Figure 1). The point $\mathbf{r}_p$ corresponds to a saddle point of $\varrho(\mathbf{r})$, *i. e.* $\varrho_p \equiv \varrho(\mathbf{r}_p)$ is a minimum of $\varrho(\mathbf{r})$ in the direction along the internuclear axis. but a maximum in all directions perpendicular to it (Figure 1).

The properties of $\varrho(\mathbf{r})$ have been thoroughly investigated for a series of compounds and it has been shown that a pointwise investigation of $\varrho(\mathbf{r})$ at its saddle points leads to useful information about molecular properties.[16,24]

The existence of a saddle point $\mathbf{r}_p$ of $\varrho(\mathbf{r})$ in the interatomic region is inseparably coupled with the existence of a zero-flux surface $S(\mathbf{r})$ and *vice versa*. The point $\mathbf{r}_p$ may be considered as the result of a strong charge contraction in the surface $S(\mathbf{r})$ towards $\mathbf{r}_p$. Charge accumulation perpendicular to the internuclear axis is partially offset by a depletion of charge density along the axis. $\mathbf{r}_p$ is located at the minimum of a path of maximum electron density linking the nuclei. Because of this it has been called the *bond path*.[16,24]

It has to be noted that $\mathbf{r}_p$ does not necessarily coincide with the position $\mathbf{r}_c$ of maximum charge concentration in the bond. The latter point is defined by $\nabla(\nabla^2 \varrho(\mathbf{r})) = 0$ while $\mathbf{r}_p$ is defined by $\nabla \varrho(\mathbf{r}) = 0$. Thus, if additional information about the properties of $\varrho(\mathbf{r})$ is needed, both locations $\mathbf{r}_p$ and $\mathbf{r}_c$ can be investigated.

In view of the considerations outlined above we speak of a chemical bond between two atoms A and B if

1. a saddle point $\mathbf{r}_p$ and, hence, a zero-flux surface S exists between A and B (necessary condition)

and

2. the local energy density $H(\mathbf{r}_p)$ is smaller than zero (sufficient condition).

We denote the bond as a covalent bond and distinguish it from noncovalent bonds to be discussed in Section IV.

We visualize the bond by the path of maximum electron density linking the nuclei. In Table I some bonds are analysed in terms of the properties of $\varrho(\mathbf{r})$ and $H(\mathbf{r})$. The values of $H(\mathbf{r}_p) \equiv H_p$ suggest that in all molecules considered bonds are covalent. This applies also to CN, CO, CF, NN, OO and FF bonds, most of which possess a positive $\nabla^2 \varrho(\mathbf{r}_p) \equiv \nabla^2 \varrho_p$.

TABLE I

Characterisation of Covalent Bonds with the Aid of Local Properties of Electron and Energy Density[a]

Molecule	Bond[b]	R / Å	$\Delta \mathbf{r}_p$[c] / %	$\varrho(\mathbf{r}_p)$ / e Å^{-3}	$\nabla^2 \varrho(\mathbf{r}_p)$ / e Å^{-5}	$G(\mathbf{r}_p)$	$V(\mathbf{r}_p)$ / hartree Å^{-3}	$H(\mathbf{r}_p)$
H_2	H—H	0.730	0	1.692	—27.243	0.000	—1.910	—1.910
LiH	Li—H	1.636	10.4 (Li)	0.230	3.448	0.236	—0.249	—0.013
BeH_2	Be—H	1.369	15.2 (Be)	0.604	4.138	0.606	—0.890	—0.284
BH_3	B—H	1.180	13.1 (B)	1.251	—7.742	0.837	—2.221	—1.324
CH_4	C—H	1.084	26.0 (H)	1.846	—22.977	0.284	—2.349	—2.065
CH_3CH_3	C—C	1.527	0	1.707	—15.953	0.344	—1.802	—1.458
NH_3	N—H	1.002	49.3 (H)	2.312	—41.737	0.350	—3.621	—3.271
N_2H_4	N—N	1.414	0	2.195	—17.350	1.033	—3.405	—2.372
H_2O	O—H	0.947	61.0 (H)	2.475	—50.155	0.445	—4.399	—3.954
H_2O_2	O—O	1.393	0	2.249	—9.509	1.528	—3.721	—2.193
H_2OO	O—O	1.487	0	1.418	12.354	1.761	—2.665	—0.904
HF	H—F	0.911	67.9 (H)	2.420	—68.987	0.499	-5.830	—5.331
F_2	F—F	1.345	0	2.335	2.908	2.247	—4.292	—2.045
CH_3NH_2	C—N	1.453	26.7 (C)	1.866	—22.762	0.978	—3.549	—2.571
CH_3OH	C—O	1.399	36.4 (C)	1.775	—3.493	2.416	—5.081	—2.665
CH_3F	C—F	1.364	36.8 (C)	1.606	12.914	3.030	—5.155	—2.125
NH_2OH	N—O	1.404	10.9 (N)	2.155	—13.522	1.194	—3.360	—2.166
NH_3O	N—O	1.377	6.5 (O)	2.262	—6.449	1.761	—3.968	—2.207
HOF	O—F	1.375	7.1 (O)	2.190	—1.047	1.829	—3.732	—1.903
CH_2CH_2	C=C	1.317	0	2.467	—29.495	1.003	—4.295	—3.292
CH_2NH	C=N	1.250	34.2 (C)	2.737	—9.515	4.170	—9.002	—4.832
CH_2O	C=O	1.184	34.9	2.906	20.227	6.235	—11.060	—4.825
N_2H_2	N=N	1.215	0	3.199	—30.818	2.072	—6.296	—4.224
O_2 ($^3\Sigma g$)	O=O	1.168	0	3.979	—26.304	3.543	—8.935	—5.392
HNO	N=O	1.174	27.1 (N)	3.574	—38.539	4.810	—12.318	—7.508
C_2H_2	C≡C	1.185	0	2.820	—30.881	2.234	—6.499	—4.265
HCN	C≡N	1.132	32.3 (C)	3.313	22.105	7.402	—13.253	—5.851
N_2	N≡N	1.078	0	4.801	—66.490	4.132	—12.905	—8.773
CO	C≡O	1.114	34.0 (C)	3.371	41.533	8.402	—13.928	—5.526

[a] HF/6-31G* calculations at optimized geometries. HF/6-31G* geometries have been taken from D. DeFrees, B. A. Levi, S. K. Pollack, W. J. Hehre, J. S. Binkley, and J. A. Pople, *J. Amer. Chem. Soc.* **101** (1979) 4085. Geometries of peroxides are taken from D. Cremer, *General and Theoretical Aspects of the Peroxide Group* in: S. Patai (Ed.), *Chemistry of Functional Groups, Peroxides*, John Wiley, New York, 1983, p. 1.

[b] The single or multiple bond character is indicated according to the value of ϱ_p.

[c] For the definition of the shift parameter $\Delta \mathbf{r}_p$ see text. $\Delta \mathbf{r}_p$ is given relative to the atom given in parantheses.

III. CHARACTERIZATION OF THE COVALENT BOND

A quantum mechanically based definition of the chemical bond should facilitate the description of bond properties. With the aid of the definition developed in Section II it should be possible to characterize a covalent bond utilizing properties of both ϱ_p and H_p.

III.1. *The Value of ϱ at the Bond Saddle Point — The Bond Order*

Integration of $\varrho(\mathbf{r})$ over the zero-flux surface leads to the electron density

$$N(A, B) = \oint_S \varrho(\mathbf{r}) \cdot n(\mathbf{r}) \cdot dS \tag{19}$$

Since the electron density in the interatomic surface is propportional to the forces exerted on the bonding electrons by the nuclei, $N(A, B)$ should provide a measure of bond strength. This has been verified for CC bonds of hydrocarbon molecules.[24b]

The evaluation of $N(A, B)$ from calculated $\varrho(\mathbf{r})$ distributions has to be done numerically and, therefore, it is very time consuming. On the other hand, the charge at $\mathbf{r}_p$ should be proportional to the charge in the surface as long as one considers interactions between the same atoms A and B. This is confirmed by the data given in Table II. They show that a large value of ϱ_p is typical for a large $N(A, B)$ and a large bond energy (strength). In order to make the analysis as easy as possible we constrain ourselves in the following to a discussion of classes of bonds, each of which is specified by the atoms A, B. If one considers, *e. g.*, just CC bonds, calculated ϱ_p values provide a measure for typical bond properties. For example, electron densities at the saddle point $\mathbf{r}_p$ correlate with bond lengths R as shown in Figure 4.[33] Similar linear relationships result for NN, OO, CN or CO bonds. In each case, the slope of the line $\varrho_p = \varrho_p(R)$ depends on the method used to determine $\varrho(\mathbf{r})$, *i. e.* in the case of LCAO—SCF calculations on the basis set employed. Its dependence on the nature of atoms A and B is surprisingly small, which suggests that lines $\varrho_p(R)$ may be transformed into each other by a suitable shift parameter $s(A, B)$.[34]

TABLE II

Camparison of Electronic Charges at the Bond Saddle Point and in the Zero-Flux Surface[a]

Molecule	Bond AB	ϱ_p / $e \cdot Å^{-3}$	$N(A, B)$ / $e \cdot Å^{-1}$
CH_3CH_3	C—C	1.707	2.241
CH_2CH_2	C=C	2.467	3.145
CH_3NH_2	C—N	1.866	2.331
CH_2NH	C=N	2.737	3.225
HCN	C≡N	3.313	3.863
CH_3OH	C—O	1.775	2.283
CH_2O	C=O	2.906	3.134
CO	C≡O	3.371	3.129

[a] HF/6-31G* calculations at optimized HF/6-31G* geometries.

Since the ϱ_p values yield a classification of bonds AB similar to that obtained by comparing AB bond lengths, it is appealing to use ϱ_p for the definition of a bond order $n(A, B)$. This can be done by assigning $H_nA—BM_m$, $H_{n-1}A = BH_{m-1}$ and $H_{n-2}A \equiv BH_{m-2}$ Lewis bond orders of 1, 2, and 3. In all cases studied so far (A, B = C, N, O) a satisfactory fit between $n(A, B)$ and $\varrho_p(A, B)$ is obtained by the exponential relationship (20)[17]:

$$n(A, B) = \exp\{a \cdot [\varrho_p(A, B) - b]\} \tag{20}$$

For reasons of simplicity, $n(A, B) = 1$ is fixed by setting $b = \varrho_p(H_nA—BH_m)$. This does not cause any significant change of the slope a. An illustrative example for the use of Eq. (20) is given in Figure 5. Parameters a, b are given in Table III for some selected bonds AB.

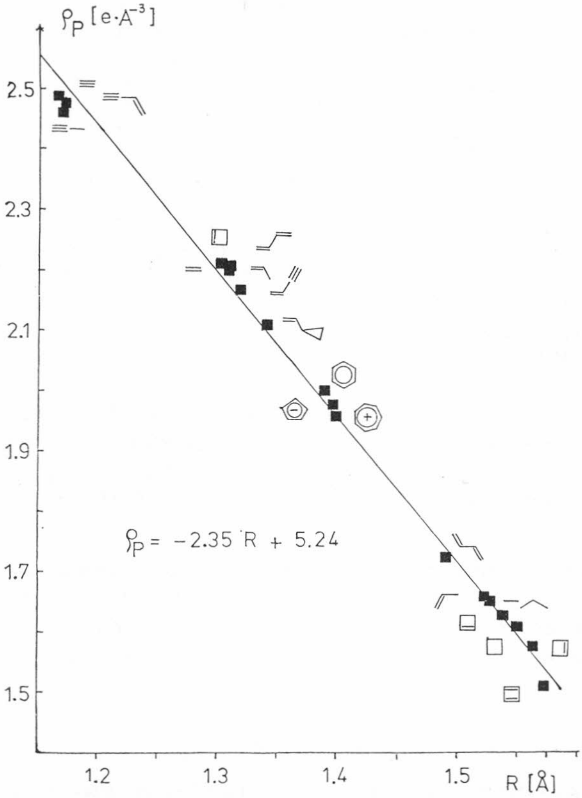


Figure 4. Relationship between the electron density at the saddle point $\mathbf{r}_p$ and the bond length R. (HF/STO-3G calculations from Ref. 17).

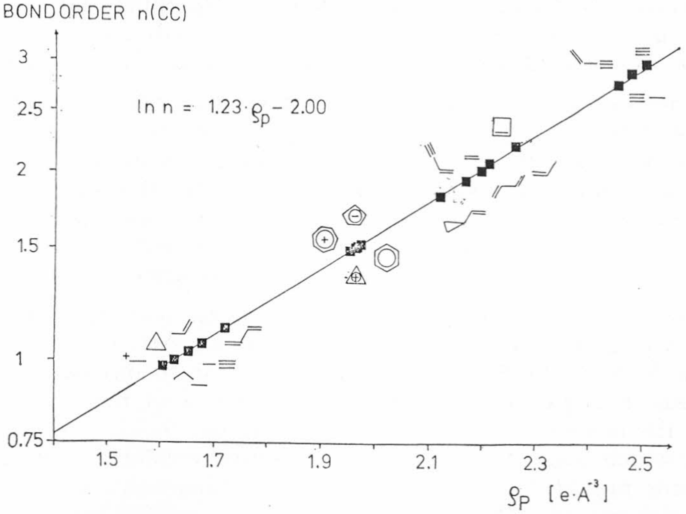


Figure 5. Definition of a bond order n for CC bonds. (HF/STO-3G calculations from Ref. 17).

TABLE III

Constants for the Bond Order Relation Given in Eq. (20)[a]

Bond	a	$b/e \cdot A^{-3}$
CC	0.94	1.52
CN	0.78	1.87
CO	0.65	1.77
OO	0.40	2.25

[a] All calculations have been carried out at the HF/6-31G* level of theory employing optimized geometries. In order to assign appropriate Lewis bond orders, the following reference molecules have been considered:

CC: C_2H_6, C_2H_4, C_2H_2 [17]; CN: CH_3NH_2, CH_2NH;
CO: CH_3OH, CH_2O; OO: H_2O_2, O_2

Observation of Figure 5 reveals that CC bond orders cluster in four areas, namely close to $n = 1$, 1.5, 2 and 3 according to the four major bond types experienced in carbon chemistry. It is interesting to note that Hückel aromatic compounds like $C_3H_3^+$, $C_5H_5^-$, C_6H_6 or $C_7H_7^+$ possess a n(C,C) of about 1.5.

Other covalent bonds A, B can be typified in a similar manner. This adds further support to the assumption that analysis of $\varrho_p(A, B)$ suffices to get useful information about the strength of a bond AB. However, if different atom combinations A, B are to be compared, a more detailed analysis of $\varrho(\mathbf{r})$ is necessary.

III.2. *The Position of* $\mathbf{r}_p$ — *Polarity of the Bond*

An electronegative atom A accumulates more electronic charge in the vicinity of its nucleus than an electropositive atom B. Accordingly, the bond saddle point $\mathbf{r}_p$ is shifted towards B. The shift of $\mathbf{r}_p$ provides a rough measure for the expansion of Ω_A and the compression of Ω_B. Since the atomic charges Q_A and Q_B are obtained by integrating $\varrho(\mathbf{r})$ over subspaces Ω_A and Ω_B, the position of $\mathbf{r}_p$ also indicates which atom is more negatively (positively) charged.

If one denotes with Δ the deviation of $\mathbf{r}_p$ from the mid-point AB, then the value of $\Delta(\mathbf{r}_p) \equiv \Delta_p$ provides a quantitative measure for the polar character of the bond AB. In Table I, Δ_p values are given in per cent, normalized with the maximum shift, which is $R/2$. Obviously, the shift parameter Δ_p increases with increasing difference between the electronegativities of atoms A and B. The value of Δ_p depends also to some extent on the nature of the bond (single or multiple) and on the type of atoms attached to A and B.

An interesting observation can be made when plotting electronegativity differences $\Delta\chi$ against calculated positions of $\mathbf{r}_p$ for AH_n molecules (Figure 6). When going from Li to F the AH saddle point shifts progressively towards the H nucleus. For H_2O, $\mathbf{r}_p$ is located within 0.186 Å of the H nucleus. In the case of the HF molecule, extrapolation of $\mathbf{r}_p$ values yields a $\mathbf{r}_p$, H distance of just 0.03 Å, which suggests that $\mathbf{r}_p$ might eventually coincide with the position of the nucleus provided $\Delta\chi$ is large enough. Actual calculation of $\mathbf{r}_p$ for HF leads to a distance of 0.189 Å similar to that found for H_2O. It seems as if for the OH bond a *compressibility limit* is already reached beyond which the

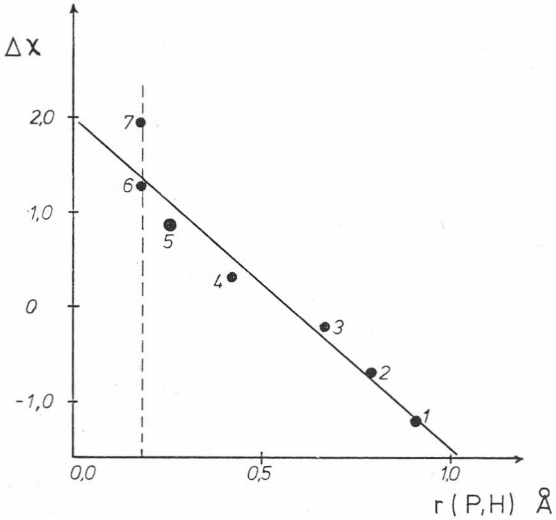


Figure 6. Correlation of electronegativity differences $\Delta\chi = \chi(A) - \chi(H)$ with distances $r(P, H)$ for AH_n molecules (LiH (**1**), BeH_2 (**2**), BH_3 (**3**), CH_4 (**4**), NH_3 (**5**), H_2O (**6**), HF (**7**)). $r(P, H)$ measures the distance of the bond saddle point P from the H nucleus. The dashed line indicates the »compressibility limit«. (HF/6-31G** calculations).

hydrogen subspace can no further be compressed even when bordering on a subspace of a more electronegative atom.[35] The same observation can be made for AH molecules which indicates that the compressibility limit does not depend on the number of H atoms attached to the heavy atom.

The observation of a compressibility limit of Ω_H is important in two ways. First, it suggests that the description of very polar bonds should be carried out in a qualitative rather than a quantitative way if just Δ_p is considered. Secondly, it supports the assumption that there is always just one nucleus centered in a subspace Ω determined with Eq. (1). For example, one could think of a situation where an electron-poor atom like H is bonded to an electron-rich atom without being separated from the latter by a zero-flux surface, *i. e.* the electron density of H is completely enveloped by the electron-rich atom. It seems that this situation is avoided due to the existence of a compressibility limit of the electron-poor atom.

III.3. *Anisotropy of* ϱ_p — *The* π- *Character of a Covalent Bond*

The concentration of negative charge at $\mathbf{r}_p$ is determined by the three principal curvatures of ϱ_p.[28] Analytically, these are given as the eigenvalues of the Hessian matrix of $\varrho(\mathbf{r})$, the trace of which is equal to $\nabla^2 \varrho(\mathbf{r})$. At $\mathbf{r}_p$ the two eigenvalues λ_1 and λ_2 ($\lambda_1 < \lambda_2$) are negative while the third, λ_3 is positive. The corresponding eigenvectors $\mathbf{v}_i$ point into directions perpendicular ($\mathbf{v}_1, \mathbf{v}_2$) and paralell to the bond axis ($\mathbf{v}_3$). If $|\lambda_1| + |\lambda_2| > \lambda_3$, negative charge concentrates at $\mathbf{r}_p$; otherwise it is depleted.

For a single bond like the CC bond in ethane, electronic charge is isotropically distributed around the bond axis as is revealed by a contour line diagram of $\varrho(\mathbf{r})$ depicted in a plane perpendicular to the CC bond axis and containing $\mathbf{r}_p$ (Figure 7). The curvature of ϱ_p in directions $\mathbf{v}_1$ and $\mathbf{v}_2$ is identical according to degenerate eigenvalues $\lambda_1 = \lambda_2$.

For a double bond like the CC bond in ethylene, charge is no longer isotropically distributed around the bond axis. The contour lines are elliptic, where the degree of ellipticity can be measured by the ratio of the negative eigenvalues λ_1 and λ_2. In a previous paper[17] a bond ellipticity ε has been defined:

$$\varepsilon = \lambda_1/\lambda_2 - 1 \qquad (21)$$

measuring the anisotropy of the electron distribution at $\mathbf{r}_p$. The eigenvector $\mathbf{v}_2$ is perpendicular to the direction of the molecular plane, which means that the lower curvature λ_2, *i. e.* the larger extension of electron density into molecular space, is found in the direction of the π-orbitals.

Although the distinction between σ- and π-electrons is no longer relevant when discussing the observable $\varrho(\mathbf{r})$, it is nevertheless appealing to relate features of ϱ_p to features of the σ/π-model. A large ε is indicative af a large anisotropy of $\varrho(\mathbf{r})$ and, hence, of a strong deviation from σ-type bond character. For unstrained polyenes and cyclopolyenes containing no hetero atoms, the anisotropy of $\varrho(\mathbf{r})$ is predominantly due to the π-character of the bond in consideration. Accordingly, the value of ε can be used to assess the π-character of a bond.[17] If the calculated ε value of a CC bond is normalized with ε (ethylene) (Figure 7), the π-character can be given in per cent.

On the other hand, anisotropies of $\varrho(\mathbf{r})$ may be due to other reasons than π-character of the bond. For example, the presence of an electron lone pair

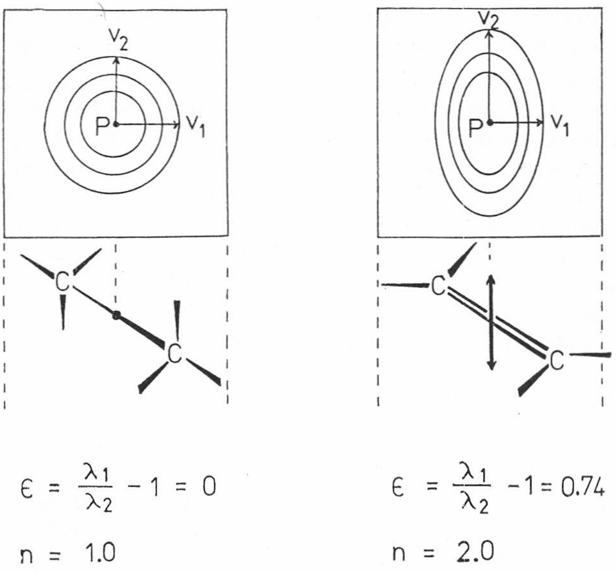


Figure 7. Qualitative illustration of the density distribution $\varrho(\mathbf{r})$ around CC single and CC double bond at the saddle point P. The directions of steep and soft curvature of ϱ_p are given by the eigenvectors $\mathbf{v}_1$ and $\mathbf{v}_2$. The later is taken as the »direction« of the bond ellipticity as indicated by the double-head arrow. (Values for C_2H_6 and C_2H_4 from HF/STO-3G calculations).

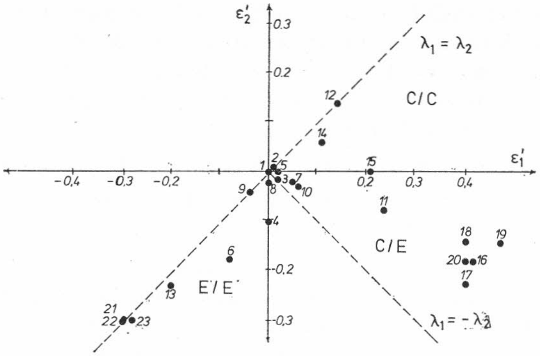


Figure 8. Comparison of effective ellipticities ε_1' and ε_2' of some CC bonds: CH_3—CH_2CH_3 (**1**), CH_3—$CH(CH_3)_2$ (**2**), CH_3—$CHCH_2$ (**3**), cyclopropane (**4**), cyclobutane (**5**), CH_2—$CHCH$ (**6**), $CHCH$—CH_2CH_2 (**7**), $CHCH_2$—CH_2CH (**8**), CH_3—CCH (**9**), CH_2CH—$CHCH_2$ (**10**), benzene (**11**), $CH_3CH_2^+$ (**12**), CH_3—$CHCH_3^+$ (**13**), cyclopropenyl cation (**14**), tropylium cation (**15**), $CH_2{=}CH_2$ (**16**), $CH_3CH{=}CH_2$ (**17**), $CH_2CH{=}CH$ (**18**), $CH_2CH{=}CHCH_2$ (**19**), $CH_2{=}CHCHCH_2$ (**20**), $HC{\equiv}CH$ (**21**), $CH_3C{\equiv}CH$ (**22**), $CH_2CHC{\equiv}{\equiv}CH$ (**23**). The line $\lambda_1 = \lambda_2$ corresponds to an isotropical charge distribution. C: contraction, E: expansion of charge relative to the CC bond of ethane. (HF/STO-3G calculations).

in the vicinity of a σ-bond can lead to a distortion of the bond density. Furthermore, one has to be cautious when analysing bond ellipticities for $n > 2$. If n approaches 3, λ_1 and λ_2 become similar. For the triple bond, again a concentric distribution of $\varrho(\mathbf{r})$ around the bond axis is achieved ($\varepsilon = 0$). It is, however, common in chemical practice to think of a triple bond as a union of a σ and two orthogonal π bonds. We take this into consideration by defining the two effective ellipticities ε_i'

$$\varepsilon_i' = \lambda_i/\lambda_{(A-B)} - 1 \qquad i = 1,\ 2 \tag{22}$$

where λ(A—B) is the curvature of ϱ_p of the corresponding AB single bond. Thus, a negative value of the effective ellipticity ε_i' indicates an expansion of electron density in the direction $\mathbf{v}_i$ measured relative to the curvature of ϱ_p(A—B); correspondigly a positive ε_i' results if the electron density is contracted at $\mathbf{r}_p$ relative to the AB single bond.

In Figure 8 some effective ellipticities of CC bonds of hydrocarbons are compared in an ε_1', ε_2'-diagram. Since $|\lambda_1| > |\lambda_2|$, all points ($\varepsilon_1'$, ε_2') are either on or below the line $\lambda_1 = \lambda_2$. The points lying on this line belong to CC bonds, which possess a uniform charge distribution around the internuclear axis ($\varepsilon = 0$), while those off the line have a finite anisotropy at $\mathbf{r}_p$. Three areas can be distinguished in the ε_1', ε_2'-diagram:

1. The contraction-contraction area: CC bonds falling in this area are characterized by steeper curvatures λ_1, λ_2 than found for the CC bond of ethane. Electron density is contracted in the zero-flux surface towards $\mathbf{r}_p$. This can be the result of a positive charge at one of the C atoms.

2. The contraction-expansion area: It seems to be typical that an expansion of electron density into the π-direction of a double or aromatic bond is accompanied by a contraction of electron density (increase of curvature) in the perpendicular direction. At least, this is suggested by the curvatures λ_i of polyenes and cyclopolyenes.
3. The expansion-expansion area: In this area all triple bonds can be found. Electronic charge expands uniformly into space, reflected by a softening of curvatures λ_i, *i. e.* λ_1, $\lambda_2 \rightarrow 0$.

The spread of effective ellipticities reveals that calculated anisotropies can be due to various reasons, not just because of π-bond character. Therefore, it is advisable to discuss ε values only in conjunction with ε' values and other properties of $\varrho(\mathbf{r})$. A valid description of π-bond character on the basis of calculated ε values is, however, admissible in all those cases where the σ/π-model of the MO theory applies.

III.4. *Deviation of the Location of* $\mathbf{r}_p$ *from the Internuclear Axis — Bent Bonds*

The path of maximum electron density between two atoms, the bond path, does not necessarily coincide with the internuclear axis. It may be bent as in the case of the cyclopropane molecule[36] (Figure 9). The parameter d (AB), which is the perpendicular distance of $\mathbf{r}_p$ from the axis AB, can be used to assess the bent bond character of a particular atomic linkage. For strained ring compounds, *e. g.*, the bond paths are outwardly curved from the perimeter of the ring, yielding d (AB) values up to 0.2 Å. The lengths of the bond path can exceed that of the distance R_e by a factor 1.00—1.02.[24b]

In a model of the chemical bond, which is based on the existence of zero-flux surface and path of maximum electron density, the notion of bond length may be constrained to the length of the bond path R_b rather than the distance R_e. Similarly, one may distinguish between the internuclear angle α defined by the positions of the nuclei and the interpath angle γ defined in Figure 9. For strained organic molecules containing the cyclopropane unit interpath angles between 80°—85° are found, which are considerably smaller than the interorbital angle of 104° derived from the hybrid orbitals of cyclopropane.[37]

It has to be noted that calculated values of γ are also slightly smaller than the corresponding α values in the case of acyclic molecules, *e. g.*, NH_3 or H_2O.

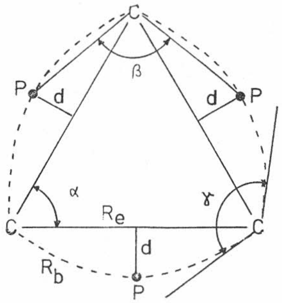


Figure 9. Definition of parameters R_b, R_e, d, α, β and γ in case of curved paths of maximum electron density (dashed lines) found for strained molecules like cyclopropane.

There, the displacement of $\mathbf{r}_p$ may be viewed as opposing an increase of the bond angles α. In this way, curvature of a bond path can provide information which nuclear motion of a molecule are facilitated or retarded by the properties of $\varrho(\mathbf{r})$.

IV. CHARACTERIZATION OF NON-COVALENT BONDS

It is common in chemistry to contrast the covalent bond with the ionic bond. The distinction between covalent and ionic bonds is, of course, strongly model dependent. It is further complicated by the fact that the notion of ionic character mixes features of both the energetic and the electrostatic approach to bonding. From the energy viewpoint, ionic bond character is the result of ionic structures contributing to a VB wave function of the molecule.[38] Thus, a covalent bond may be stabilized by ionic character found in VB calculations. From the electrostatic viewpoint, ionic character is connected with a transfer of electronic charge from one atom to the other imparting a partial positive charge to the first atom and a partial negative charge to the second one. Thus, a determination of atomic charges with Eq. (23) should aid a description of ionic bond character,

$$Q_A = Z_A - \int_{\Omega_A} \varrho(\mathbf{r})\, d\mathbf{r} \tag{23}$$

Atomic charges obtained with Eq. (23) pose two problems. First, they suggest strong charge transfer in cases where common chemical understanding expects covalent bonds (see, *e. g.*, Table IV). Secondly, any discussion of ionic character in terms of atomic charges is confronted with the task of specifying which charge transfer is significant and which is not. Clearly, this problem cannot be solved in a unique manner.

TABLE IV

Atomic Charges of AH_n Molecules[a]

Molecule	Q (A)	Q (H)
LiH	+0.915	—0.915
BeH_2	+1.740	—0.870
BH_3	+2.136	—0.712
CH_4	+0.228	—0.057
NH_3	—1.131	+0.377
OH_2	—1.238	+0.619
FH	—0.751	+0.751

[a] (HF/6-31G** calculations) Q is evaluated from Eq. (23).

It can be argued that a lack or a decrease of shared electron density is indicative of ionic character.[39] In order to assess the amount of shared electron density, it is not sufficient to compare ϱ_p values as becomes obvious from the data of Table V. A reasonable alternative, however, is provided by the discussion of surface densities N(A, B) and the corresponding energy values H_p and H(A, B), respectively. If, *e. g.*, N(Li, F) is taken as the reference value for an ionic Li bond, then the computed N values will clearly describe the Li—Li bond as being covalent in spite of the relatively small ϱ_p value. On the other hand, the N(Li, C) value is of the same magnitude as N(Li, F) suggesting that the appertaining bonds possess both ionic character. The same conclusions can be reached when considering H_p or $H(A, B)$ values of Table V. For Li_2, a small but negative H_p value is calculated while $H_p(Li, C)$ and $H_p(Li, F)$ are both positive.

TABLE V

Analysis of Covalent and Ionic Li Bonds[a]

Molecule	Bond	$\frac{R}{Å}$	$\frac{\varrho_p}{e \cdot Å^{-3}}$	$\frac{N(A, B)}{e \cdot Å^{-1}}$	$\frac{\nabla^2 \varrho_p}{e \cdot Å^{-5}}$	$\frac{H_p}{hartree \cdot Å^{-3}}$	$\frac{H(A, B)}{hartree \cdot Å^{-1}}$
Li_2	Li—Li	2.807	0.083	0.743	−0.249	−0.018	−0.093
F_2	F—F	1.345	2.335	2.033	2.908	−2.045	−0.347
C_2H_6	C—C	1.527	1.707	2.241	−15.953	−1.458	−0.722
$LiCH_3$	Li—C	2.020	0.283	0.492	4.915	0.020	0.011
LiOH	Li—O	1.592	0.529	0.584	18.066	0.115	0.130
LiF	Li—F	1.566	0.508	0.507	19.505	0.162	0.153

[a] HF/6-31G* calculations at optimized geometries.

In view of these observations we extend our definition of the covalent bond by saying that $H_p > 0$ indicates a non-covalent closed shell interaction. In the particular case of LiF, the interaction can certainly be viewed as that effective in a contact-ion pair. Accordingly, the Li—C bond has also to be characterized as being ionic.

The physical relevance of our conclusion becomes evident if we recall that $H(\mathbf{r})$ is the sum of a local potential energy and a local kinetic energy contribution. The positive H_p indicates that the latter term dominates at $\mathbf{r}_p$, *i. e.* electron density at the saddle point is destabilizing rather than stabilizing. Although the shared electron density given by the value of $N(A, B)$ is substantial for both the LiF and LiC interaction, it does not lead to an energy gain which normally accompanies covalent bond formation. Since $H(\mathbf{r})$ is positive for all points of the zero-flux surface, values $H(LiC)$ and $H(LiF)$ are both larger than zero. The $H(LiC)$ value is somewhat smaller than $H(LiF)$ which can be interpreted in the sense of diminished ionic character in the case of the Li—C bond. Any mechanism which reduces N and correspondingly H, should lead to a stabilization of LiF or $LiCH_3$. For example, solvation of the contact-ion pair should be effective in this way.

The observation of $H_p > 0$ is not limited to ionic bonds. It is also found for H-bonded systems, van der Waals molecules and in the general case of repulsive interactions between two molecules or atoms. Thus, $H_p > 0$ indicates a closed-shell interaction between two atoms or ions. It is advisable to analyse interactions in these cases by comparing ϱ_p, $N(A, B)$, $\nabla^2 \varrho_p$, H_p and $H(A, B)$ values with those of appropriate reference systems.

V. CONCLUSIONS

The analysis of chemical bonding in terms of the properties of ϱ_p and H_p is computationally a straightforward procedure.[16,17] Implementation and computer time requirements are comparable to those of the Mulliken population analysis.[40]

Our definition of the covalent bond combines features of the electrostatic and energetic viewpoints of bonding. The discussion given in Section II clearly reveals that a description of bonding cannot be based on $\nabla^2 \varrho(\mathbf{r})$ alone. Concentration of electronic charge in the bond region is characteristic for most but not all covalent bonds.[30] In this respect, experimental observations of weak or negative bond deformation densities[31] are just an indication that the energetic aspect of bonding must not be missed. A depletion of charge from the bonding region, probably as a result of the Pauli principle, can lead to a relatively stable bond as long as the potential energy gain dominate bond formation.

In this context it has to be noted that deformation or difference densities may be poor measures of charge depletion. A more accurate account of charge concentration or depletion is provided by the Laplacian of $\varrho(\mathbf{r})$ as is shown in Figure 2 (see also Refs. 27 and 30)

Certainly, one can argue that analysis of $\varrho(\mathbf{r})$ and $H(\mathbf{r})$ at just one single point in the internuclear region is too much of a simplification. Changes in local energy in the immediate vicinity of the nuclei may be more important for bonding than changes close to $\mathbf{r}_p$. Since we are aware of this, we consider the approach presented above as the first stage of a more complete analysis of bonding. This should comprise:

1. Determination of $\mathbf{r}_p$; analysis of ϱ_p and H_p,
2. Determination of $\mathbf{r}_c$, the location of maximum charge concentration with the aid of $\nabla^2 \varrho(\mathbf{r})$.
3. Evaluation of the properties of the zero-flux surface; analysis of $N(A, B)$ and $H(A, B)$.
4. Analysis of $\varrho(\mathbf{r})$ and $H(\mathbf{r})$ in the total molecular space.

We have shown that one has to go beyond step **1** if covalent bonding is contrasted with ionic bonding. It is also clear that step **2** may be very informative with regard to the analysis of charge concentrations in electron lone pair regions. Also, one can expect an analysis of $\nabla^2 \varrho(\mathbf{r})$ to be particularly informative in those cases where *through-space*-interactions are operative in a molecule.[34]

Clearly, the model of the chemical bond provided by steps **1—4** presents an attractive and practically feasible but not final way for the description of the chemical bond. The later point becomes obvious when considering that both electrostatic *and* energetic features of a molecule should be determined by $\varrho(\mathbf{r})$ in a unique, yet unknown, manner according to Hohenberg and Kohn.[15]

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25. One has to note that there exists no unequivocal proof that observations (*i*) and (*ii*) always hold.
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29. Eq. (18) may be compared with the corresponding relationship between E and V obtained from the virial theorem, namely $E = \frac{1}{2} V$. On this basis, the first term of Eq. (18) can be considered as a classical, the second term as a non-classical contribution to the local potential energy, the later depending on the degree of charge concentration. Similarly, $E = -T$ and $H(\mathbf{r}) = -(G(\mathbf{r}) + \frac{1}{4} \nabla^2 \varrho(\mathbf{r}))$ may be compared[7c].
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32. At any point of the bond path $\varrho(\mathbf{r})$ is maximal with respect to a lateral displacement.
33. For strained molecules the length of the bond path R_b rather than the interatomic distance R_e should be considered. See Section III. 4.
34. D. Cremer, E. Kraka, unpublished results.
35. For example, if H is bonded to the very electronegative F^+ ion, the r_p, H distance is only slightly smaller than in HF (HF/6-31G* calculation at HF/6-31G* optimized geometry).
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40. One could argue that the analysis of $\varrho(\mathbf{r})$ is more costly than the Mulliken analysis since application of Eq. (1) requires that the hypervirial theorem is fulfilled, *i. e.* it is necessary that all calculations are carried out at equilibrium geometries. These, however, are routinely determined nowadays.
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SAŽETAK

Opis kemijske veze s pomoću lokalnih svojstava elektronske gustoće i energije

Dieter Cremer i Elfi Kraka

Kemijska veza može se opisati s pomoću jednoelektronske gustoće $\varrho(\mathbf{r})$ i lokalne gustoće energije. Analiza različitih kemijskih veza pokazuje da je za kovalentno vezanje neophodno postojanje točke $\mathbf{r}_s$ u prostoru između jezgri u kojoj $\varrho(r_s)$ ima svojstvo sedla. Nadalje, u toj točki lokalna potencijalna energija mora po apsolutnom iznosu biti veća od kinetičke energije. Proizlazi da su mnoga svojstva kemijskih veza, kao što su to na primjer red veze, polarnost ili π-karakter, određena položajem $\mathbf{r}_S$ i anizotropijom $\varrho(\mathbf{r}_S)$. Informacija o povećanju ili smanjenju elektronske gustoće može se dobiti s pomoću $\nabla^2 \varrho(\mathbf{r}_s)$. Može se pokazati da gustoća prekrivanja dovodi do destabilizacije pri interakciji sustavâ s popunjenim ljuskama. Ta se situacija pojavljuje u ionskim, i van der Waalsovim sustavima kao i kod vodikove veze.