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Atomic energy in the 'Atoms in Molecules' theory and its use for solving chemical problems

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Abstract. The theoretical and practical aspects of the use of atomic energy in R Bader's theory 'Atoms in Molecules' for solving problems of physical and structural chemistry are considered. The bibliography includes 148 references.

I. Introduction

In the majority of conventional experimental and calculation methods for the investigation of molecules, whole molecules are considered, as a number of key molecular characteristics (energy, charge and dipole moment in particular) can be precisely determined only for the entire molecule, and not for its parts. At the same time some important chemical concepts (*e.g.* chemical bond, atom, functional group, electronegativity, charge, polarization, chemical reaction *etc.*) are local characteristics.[1] So, the schemes allowing partitioning the molecular properties into the inputs of fragments always attracted the interest of chemists. This is how the concepts of atomic charges, bonding dipoles, later Natural Bonding Orbitals approach (NBO) and some others have emerged. The methods for the separation of molecules into fragments in real space are standing apart, while the theoretical bases of these methods can be quite different. The methods of the Voronoi – Dirichlet[2] polyhedra and the Hirshfeld[3] surfaces have attained a certain extent of recognition, but they are significantly exceeded by prevalence and application by R Bader's theory 'Atoms in Molecules' (AIM).[4] In contrast to other methods, this theory offers a universal partitioning scheme of the electron density function $\rho(\mathbf{r})$ into fragments, for which the principle of the Schwinger stationary action is fulfilled, hence any properties, characteristic of a molecule as a whole, can be physically correctly estimated also for these fragments.[4]

The AIM theory is based on the topological analysis of the electron density distribution function $\rho(\mathbf{r})$, while the 'origin' of the function $\rho(\mathbf{r})$ does not matter: it can be obtained both from the quantum chemical calculations and on the basis of the high-resolution X-ray diffraction data.[5,6] Although the function $\rho(\mathbf{r})$ obtained experimentally is approximate by definition, its precision was shown to be sufficient for the evaluation of the potential energy density function[7,8] and even for the estimation of the crystal packing energy.[9–12] The latter fact is of particular interest as it allows a direct comparison of the AIM calculations with the experimental results.

The topic of the present review is, first of all, the analysis of examples of separation of molecular characteristics into the contributions of separate fragments by means of Bader's theory. Among molecular properties, energy attracts the greatest interest of chemists as it is changes in the energy that define the direction of the majority of chemical reactions. That is why the main part of this review is dedicated to the analysis of the literature data on the separation of the molecular energy into the inputs of separate atoms in order to show the prospects of the application of atomic energies in structural chemistry. The review contains necessary theoretical basics and some additional details are given when necessary. A separate section is dedicated to the practical aspects of calculations within the framework of the AIM theory.

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II. Atomic energy terms of the 'Atoms in Molecules' theory

1. Fundamental of the 'Atoms in Molecules' theory

According to the Hohenberg – Kohn theorem,[13] the energy of the ground state (E_{gs}) of a multielectron system is the

functional of the electron density distribution, which defines all properties of a system

$$E_{gs} = F[\rho(\mathbf{r})].$$

The main achievement of Bader's 'Atoms in Molecules' theory is the extension of the quantum mechanics principle of the Schwinger stationary action onto open subsystems. By means of analysis of the electron density gradient field, it was shown that such generalization is possible only in the case where the boundary condition is fulfilled, *i.e.* the presence of a surface $S(\Omega,\mathbf{r})$ defining the subsystem border for which the electron density gradient perpendicular to this surface in every point is equal to zero:[4, 14–16]

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0,$$
$$\forall \mathbf{r} \in S(\Omega, \mathbf{r}),$$

where $\mathbf{n}(\mathbf{r})$ is a unit normal vector to the surface S in every point defined by the radius-vector $\mathbf{r}$; Ω is a spatial domain corresponding to an atom. Since the boundary condition is defined in terms of the electron density the quantum subsystem is defined in real space. For every observed value one can obtain the expected value as well as the equation for the subsystem movement based on the principle of the stationary action for a given subsystem. The integration of a function $A_i(\mathbf{r})$ over the volume defined by the surface $S(\Omega,\mathbf{r})$ gives its total value

$$\langle A_i \rangle = \int_{\Omega} A_i(\mathbf{r}) d\tau \quad (1)$$

($d\tau$ is aspatial domain).

Taking into account that the principle of the stationary action is fulfilled for both the subsystem and the system as a whole, any average for an observed multielectron system A can be represented as a sum of subsystem inputs $\langle A_i \rangle$.

Bader suggested that the open subsystems of a multinuclear multielectron system correspond to the definition of an atom in a molecule or a crystal[4] as on the basis of a big number of theoretical investigations it was established that a molecule or a crystal can be represented as a total of fragments, each containing only one nulceus[4] (for the problem of the existence of non-nuclear attractors in alkali metals, beryllium and silicon crystals see Refs 17–22). The values of the expected for a subsystem directly define the atomic characteristics in a molecule. The atomic charge, for example, is equal to

$$q = Z - \int_{\Omega} \rho(\mathbf{r}) d\tau, \quad (2)$$

where Z is the charge of the atomic nucleus.

For the description of the ground state of a multielectron system, it is sufficient to use the one-particle Lagrangian density connected with the function $\rho(\mathbf{r})$ of the ground state by the following relationship:

$$L(\mathbf{r}) = -\frac{1}{4}\nabla^2\rho(\mathbf{r}).$$

The integral of the Lagrangian density over the entire multielectron system (*i.e.*, the molecule) and the atom Ω is equal to zero.

$$\int_{\Omega} L(\mathbf{r}) d\tau = \oint \nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) d\mathbf{r} = 0.$$

Due to these properties of the Lagrangian, the quantum mechanical descriptions of an atom and a molecule in the AIM terms coincide in general.[4, 14–16]

It was shown that the virial of the force density leads to the expression

$$-L(\mathbf{r}) = 2g(\mathbf{r}) + v(\mathbf{r}), \quad (3)$$

where $g(\mathbf{r})$ and $v(\mathbf{r})$ are local densities of kinetic and potential energies, respectively.[16] The local potential energy $v(\mathbf{r})$ defines the mean effective field affecting an electron in a multielectron system.

As one can see from Eqn (3), the Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$ is directly connected with the local kinetic and potential energy densities in every point of a system:

$$L(\mathbf{r}) = -\frac{1}{4}\nabla^2\rho(\mathbf{r}) = 2g(\mathbf{r}) + v(\mathbf{r}). \quad (4)$$

Analyzing the sign of the Laplacian (sum of the second derivatives) of a scalar function, one can define the regions of its concentration [$\nabla^2\rho(\mathbf{r}) < 0$] and depletion [$\nabla^2\rho(\mathbf{r}) > 0$]. Thus, on the basis of expression (4) one has a possibility to separate spatial domains in which the stabilizing contribution of the potential energy dominates leading to the accumulation of the electron density.[23, 24]

The electron density $h_e(\mathbf{r})$ (its integration over the atom Ω and subsequent summation for all atoms in a system gives the total energy of the latter) is defined as follows:

$$h_e(\mathbf{r}) = v(\mathbf{r}) + g(\mathbf{r}) = -K(\mathbf{r}), \quad (5)$$

where $K(\mathbf{r})$ is another definition of the kinetic energy based on the first order density matrix $\rho(\mathbf{r},\mathbf{r}')$.[25, 26] The parameter $K(\mathbf{r})$, and hence $h_e(\mathbf{r})$, can attain both positive and negative values[25, 26] in contrast to the positively defined kinetic energy density. Two forms of the kinetic energy $K(\mathbf{r})$ and $g(\mathbf{r})$ are related through the expression[26]

$$K(\mathbf{r}) = g(\mathbf{r}) - \frac{1}{4}\nabla^2\rho(\mathbf{r}).$$

The special role of the electron density function $\rho(\mathbf{r})$ and its derivatives in the formation of molecular structure lead Bader to the idea of using topological analysis of this function.[4] It was shown by Bader that the structure of a multielectron system with the nuclear configuration $\{R\}$ is fully and uniquely defined by the set and type of critical points (CP) of the electron density $\{\mathbf{r}_c\}$ in which the gradient of $\rho(\mathbf{r})$ becomes equal to zero [$\nabla\rho(\mathbf{r}) = 0$]. The type of CP is defined by the signatures of the eigenvalues of the matrix of second derivatives of $\rho(\mathbf{r})$ [the Hessian $A(\mathbf{r}_c)$], calculated in CP:

$$A(\mathbf{r}_c) = \begin{pmatrix} \frac{\partial^2}{\partial x^2} & \frac{\partial^2}{\partial x \partial y} & \frac{\partial^2}{\partial x \partial z} \\ \frac{\partial^2}{\partial y \partial x} & \frac{\partial^2}{\partial y^2} & \frac{\partial^2}{\partial y \partial z} \\ \frac{\partial^2}{\partial z \partial x} & \frac{\partial^2}{\partial z \partial y} & \frac{\partial^2}{\partial z^2} \end{pmatrix} \rho(\mathbf{r}).$$

The eigenvalues λ_i of the matrix $A(\mathbf{r}_c)$ [the principal curvature components of $\rho(\mathbf{r})$ in CP] define the type of CP, designated as (ω,λ), where ω is the rank of the matrix (the number of nonzero eigenvalues), and λ is the signature (algebraic sum of signatures of the eigenvalues). In the region of the energetically stable configurations of nuclei (where forces acting on the atoms are equal to zero) critical points $\rho(\mathbf{r})$ in a molecule have the rank of three; CP with $\omega < 3$ is degenerate and unstable. In this case, any slight variation of the electron density, which causes the shift of atoms, leads either to the disappearance of CP or its bifurcation into stable critical points with $\omega = 3$.

When all eigenvalues of the matrix $A(\mathbf{r}_c)$ are negative the critical point corresponds to local maximum of $\rho(\mathbf{r})$, and when all of them are positive, to local minimum. When two eigenvalues are negative (positive), the $\rho(\mathbf{r})$ value in CP corresponds to the maximum (minimum) in the plane defined by two positive (negative) eigenvalues and the minimum (maximum) along the axis perpendicular to this plane. Thus, CP of $(3,-3)$ type corresponds to the position of a nucleus, CP of $(3,+3)$ type, to the formation of cage (polyhedral) structure, while saddle CP of $(3,-1)$ type plays a special role in the structure, being an indicator of chemical bonding.[4] In general case, the number and the type of CP realized in a multielectron system are defined by the Poincaré – Hopf relationship

$$n-b+r-c=1,$$

where n is the number of nuclei, b is the number of bond paths, r is the number of rings, c is the number of polyhedra. The set (n, b, r, c) is characteristic of a given molecule.

A detailed characteristic of the $\rho(\mathbf{r})$ distribution is the vector field $\nabla\rho(\mathbf{r})$, its gradient lines are described by the integral equations

$$\mathbf{r}(s) = \mathbf{r}_0 + \int_0^s \nabla\rho[\mathbf{r}(t)]\mathrm{d}t,$$

where $\mathbf{r}_0$ is the initial coordinate.

All gradient lines of this field beginning in the infinity end in CP $(3,-3)$, therefore such points (*i.e.*, atomic nuclei) are regarded as attractors of the vector field. All gradient trajectories ending on a nucleus in CP $(3,-3)$ define the spatial region of a chemical system called the basin of this nucleus. The unity of the nucleus and electron density within the boundaries of its basin defines both free and bound atom.

The intersection of zero flux surfaces of $S(\Omega,\mathbf{r})$ gradient between pairs of neighbouring atoms corresponds to the existence of CP $(3,-1)$, which is prerequisite and a sufficient condition for the existence of a chemical bond (regardless of its type and strength). Among all gradient trajectories one should especially emphasize those that start in CP $(3,-1)$ and end in CP $(3,-3)$. These gradient trajectories define a line along which $\rho(\mathbf{r})$ attains maximum values in respect of any nearest lateral point. The presence of such gradient trajectories suggests the accumulation of $\rho(\mathbf{r})$ in the interatomic space and is a necessary and sufficient condition of the existence of a chemical bond. That is why saddle CP $(3,-1)$ and gradient lines passing through this point and CP $(3,-3)$ were called bond critical point and bond path, respectively.[4]

Analysis of eigenvalues (λ_i) of the Hessian matrix allows a detailed description of the character of atomic interactions. The trace of eigenvalues is equal to the Laplacian of the electron density in a given CP:

$$\nabla^2\rho(\mathbf{r}) = \lambda_1 + \lambda_2 + \lambda_3.$$

In CP $(3,-1)$, the negative eigenvalues λ_1 and λ_2 correspond to eigenvectors perpendicular to bond line, while positive eigenvalue λ_3, to the vector, oriented along the bond line. Thus, λ_1 and λ_2 values are the measure of contraction of electron density in the direction of CP $(3,-1)$ along the bond line, while λ_3, on the contrary, is the measure of the electron density shift from CP $(3,-1)$ towards atomic nuclei. If a bond has a cylindrical symmetry, then in CP $(3,-1)$ $\lambda_1 = \lambda_2$, but with a noticeable contribution of a π-component the equality of negative eigenvalues is violated. The ratio of eigenvalues λ_1 and λ_2 allows estimating the extent of deviation of electron density in CP $(3,-1)$ from cylindrical symmetry. For the quantitative estimation of a π-component contribution for a bond it was suggested[27] to use a parameter called ellipticity (ε):

$$\varepsilon = \frac{\lambda_1}{\lambda_2} - 1.$$

The ratio of eigenvalues λ_1/λ_3 allows description of the character of interaction between atoms.[23] When $|\lambda_1/\lambda_3| > 1$ $[\nabla^2\rho(\mathbf{r}) < 0]$, for this interatomic interaction the compression of the electron density along the bond line towards CP $(3,-1)$ dominates, which leads to the sharing of electron density by both atoms. Such a character of interaction is typical of covalent bonds and in the AIM terms is called shared interaction.[23,24] For these interactions, high values of $|\nabla^2\rho(\mathbf{r})|$ and $\rho(\mathbf{r})$ in CP $(3,-1)$ are typical. On the contrary, when $|\lambda_1/\lambda_3| < 1$ $[\nabla^2\rho(\mathbf{r}) > 0]$, for this interatomic interaction the outflow of the electron density from CP $(3,-1)$ in the direction of the nuclei dominates, and $\rho(\mathbf{r})$ is more concentrated in the atomic basins. Such an interaction is called closed-shell interaction and is typical of ionic, highly polar covalent and hydrogen bonds as well as of the van-der-Waals and specific intermolecular interactions. For closed-shell interactions the values of $|\nabla^2\rho(\mathbf{r})|$ and $\rho(\mathbf{r})$ in CP $(3,-1)$ are significantly smaller than for the covalent bonds.

However, positive value of the Laplacian of the electron density does not always imply that the interaction is of the closed-shell type. In reality, in CP $(3,-1)$ for a number of homopolar bonds,[28] covalent polar bonds,[29,30] metal π-complexes,[31,32] coordination bonds[33,34] and strong hydrogen bonds,[35–37] despite the positive value of $\nabla^2\rho(\mathbf{r})$ in CP $(3,-1)$, the electron density in the bond CP has a rather high value. That is why Cremer and Kraka have suggested[24] using the value of the local electron density $h_e(\mathbf{r})$ as a quantitative criterion for the covalent bond. Numerous investigations have shown that covalent bonds are characterized by the negative values of $h_e(\mathbf{r})$ (see Refs 6, 24, 38 and papers cited therein). So, a necessary criterion for the covalent bond (shared interaction) is the negative value of the local electron density $[h_e(\mathbf{r}) < 0]$. It should be noticed that even with the positive values of $\nabla^2\rho(\mathbf{r})$ in CP $(3,-1)$ [see Eqns (3)–(5)] a bond is of the covalent type, once the following relationship is satisfied

$$\frac{1}{4}\nabla^2\rho(\mathbf{r}) < |v(\mathbf{r})|.$$

Such interactions in the AIM theory terms are called intermediate interactions.[23,24] Apparently, such a name for the interatomic interactions is connected with the fact that topology of $\rho(\mathbf{r})$ in CP $(3,-1)$ 'visually' coincides with that for the closed-shell interactions, while the relationship of the contributions of kinetic and potential energy densities, on the contrary, corresponds to covalent bonds.

2. Calculation of atomic energies based on wave functions

Using a virial theorem for atoms, it was established [39] that for the corresponding mean values of atomic energies the following relationship is satisfied:

$$E(\Omega) = -T(\Omega) = \frac{1}{2}V(\Omega), \tag{6}$$

where $T(\Omega) = G(\Omega) = K(\Omega)$ is the kinetic energy of an atom, V is the potential energy of an atom, while $E(\Omega)$ corresponds to the input of a pseudoatom into the total energy of a system. Hereinafter we shall use the notation $X(\Omega)$ considering a value X calculated for a molecular fragment confined by the zero-flux surface of the gradient of the electron density.

Thus, it is sufficient to calculate only the kinetic energy $T(\Omega)$ for the calculation of the energy of an atom, which facilitates the calculation and sometimes interpretation of the atomic energy. At the same time the additivity persists for the atomic energies, *i.e.*, their sum is equal to the total energy of a molecule.

Considerations on the virial theorem for atoms given above referred to an ideal wave function Ψ for the molecule in which the sum of forces on each atom is equal to zero. However, in practice using *ab initio* methods, one can obtain only approximate wave function Ψ_{approx} for a molecule consisting of more than one atom; as a rule, for such a wave function even the virial theorem for the molecule is satisfied only with a certain accuracy. The violation of the virial theorem for the atoms (the deviation of the relationship between the kinetic and potential energies from the ideal values $V/T = -2$) leads to the loss in additivity of atomic energies:

$$\sum_{\Omega=1}^{n_{\text{at}}} [-T(\Omega)] = -T \neq E.$$

There are two main ways for solving of this problem. First, one can achieve the satisfaction of the virial theorem for atoms for Ψ_{approx} by scaling the coordinates of the wave function by the coefficient ζ:[40,41]

$$\zeta = -\frac{1}{2}\frac{V}{T} = -\frac{1}{2}\left(\frac{E}{T} - 1\right).$$

The physical meaning of the coefficient ζ can be more easily understood by representing it as

$$\zeta = 1 + \varepsilon,$$

where ε is a small correction additive, which characterizes the deviation from the virial theorem for a given wave function Ψ_{approx}:

$$\zeta = \frac{1}{2} - \frac{1}{2}\frac{E}{T} = 1 - \frac{1}{2}\frac{E}{T} - \frac{1}{2} = 1 + \varepsilon,$$

$$\varepsilon = -\frac{1}{2}\frac{E}{T} - \frac{1}{2} = -\frac{1}{2}\frac{V}{T} - 1.$$

However, the scaling transformation of the wave function coordinates unavoidably leads to the deviation of the molecular geometry from the equilibrium one, hence, forces appear on atoms and the molecular energy becomes nonstationary.[42] Moreover, some molecular and the 'Bader' atomic properties loose agreement upon such transformation with the energies calculated for the scaling of the wave function. Therefore, rough scaling of the wave function does not improve the situation in principle. Strictly speaking, the scaling of coordinates should be performed during the self-consistent field optimization, which will result in the correct equilibrium geometry and stable energy value and concomitant satisfaction of the virial theorem for the molecules. However the satisfaction of the virial theorem for molecules is prerequisite but not sufficient for the fulfillment of the atomic virial theorem, therefore no ideal result can be achieved. So, instead of the complicated and non-standard procedure described above, as a rule, it is the kinetic energy that is scaled to obtain the full energy of an atom:

$$E(\Omega) = \frac{E}{T}T(\Omega) = (1-\gamma)T(\Omega), \tag{7}$$

$$\gamma = -\frac{V}{T} = 2\zeta = 2 + 2\varepsilon.$$

Equation (7) can be applied in the cases where the coefficient ε is relatively small. The artifacts emerging upon the scaling of atomic energy according to Eqn (7), are discussed in Section III in more detail.

3. Calculation of atomic energies from experimental data

The estimation of the energy $E(\Omega)$ from experimental data was earlier believed to be impossible as for the calculation of the kinetic and potential energy densities one needs the full wave function of a molecule, which is by definition unavailable from the experimental data. However, in 1997 it was shown [43] that the approximate description of the kinetic energy density as a function of $\rho(\mathbf{r})$ and its derivatives can be obtained using the so-called gradient expanding [44,45]

$$g(\mathbf{r}) = \frac{3}{10}(3\pi^2)^{2/3}\rho(\mathbf{r})^{5/3} + \frac{1}{72}\frac{[\nabla\rho(\mathbf{r})]^2}{\rho(\mathbf{r})} + \frac{1}{6}\nabla^2\rho(\mathbf{r}), \tag{8}$$

which taking into account the local virial theorem (4), allows deriving the expressions for the potential and electron energy densities:

$$v(\mathbf{r}) = -\frac{3}{5}(3\pi^2)^{2/3}\rho(\mathbf{r})^{5/3} - \frac{1}{36}\frac{[\nabla\rho(\mathbf{r})]^2}{\rho(\mathbf{r})} - \frac{1}{12}\nabla^2\rho(\mathbf{r}), \tag{9}$$

$$h_{\text{e}}(\mathbf{r}) = -\frac{3}{10}(3\pi^2)^{2/3}\rho(\mathbf{r})^{5/3} - \frac{1}{72}\frac{[\nabla\rho(\mathbf{r})]^2}{\rho(\mathbf{r})} + \frac{1}{12}\nabla^2\rho(\mathbf{r}). \tag{10}$$

The integration of $h_{\text{e}}(\mathbf{r})$ value defined in this way over the atomic basin gives the so-called experimental value of $E(\Omega)$.

In all papers considered in this review and dedicated to the investigation of the atomic energies, the experimental values were obtained using relationship (10).

III. The concept of transferability

It is evident that if two atomic basins or, in more general case, two molecular fragments enclosed by a zero-flux surface are characterized by the uniform electron density distribution, their properties are identical. This concept called transferability is a key in the AIM theory. However, a question arises how often in reality this situation happens and whether we can find its correspondence beyond the terms of Bader's theory.

The most convenient subject for the investigation of transferability of atomic group properties are n-alkanes for which the linear dependence of the calculated molecular energies on the number of methylene groups in the chain was found independently and is described by the equation

$$E(\text{n-}C_nH_{2n+2}) = 2E^0(CH_3) + nE^0(CH_2). \quad (11)$$

Equation (11) shows interesting properties: it is fulfilled for calculations by different methods and with different basis sets with the correlation coefficient 1.00000. In 1987, Bader showed [46] that for the unbranched alkanes the value $E^0(CH_2)$ obtained from the linear dependence of molecular energies is equal to the energy of a $|CH_2|$ fragment calculated by the integration of the electron energy density over this fragment (hereinafter, vertical lines designate zero-flux surface limiting molecular fragment). This correspondence showed that Bader's theory has a deep physical meaning and that the separation of a molecule into fragments within this theory is in good agreement with traditional chemical concepts. Judging from the identity of charges and energies of methylene in n-alkanes, one can suggest that these groups have so-called perfect transferability *i.e.*, that in n-alkane molecules not only the energies of these fragments are identical, but also charge density distributions and hence any properties of these fragments including those emerging under the influence of external fields. Later this supposition was confirmed for n-alkanes based of the analysis of experimental values of polarizability and magnetic susceptibility: the calculated properties of a $|CH_2|$ fragment satisfied the independently obtained additive scheme.[47] The concept of transferability up to now remains rather arguable; in a recent paper by Bader [1] it was shown that this phenomenon can be found not only from chemical considerations (the uniform behaviour of equal functional groups in different compounds in chemical reactions is its evident manifestation), but also through consideration of purely physical features of electrostatic interactions.

The cases of the 'perfect transferability' of small fragments are rare and in general they refer to linear unbranched alkanes. Analysis of thermochemical data [48] shows that in the majority of cases the additive schemes for molecular energies belong to the so-called 'compensatory transferability' where the changes in energy and charge for one group coincide with the changes in energy and charge for another, but their signs are opposite.[49] A typical manifestation of compensatory transferability is the fact that the energy of the molecule CH_2F-CH_3 corresponds to the mean algebraic values for the energies of molecules CH_3-CH_3 and CH_2F-CH_2F to within 0.1 kcal mol^{-1}. Naturally, methyl group should respond to the introduction of the electron acceptor and the calculation of $E(|CH_3|)$ and $E(|CH_2F|)$ values shows that the CH_3 group in fluoroethane is 15.5 kcal mol^{-1} more stable than in ethane, while the energy of the CH_2F group is 15.6 kcal mol^{-1} higher than in difluoroethane.

The questions of compensatory and perfect transferability were studied in detail by Mosquera and co-workers for compounds of the type $X(CH_2)_nCH_3$ where X is an electron-withdrawing group. In particular, they have shown that dependences similar to Eqn (11) are fulfilled for fluoroalkanes,[50] aldehydes and ketones,[51,52] ethers,[53,54] nitriles [55] and alcohols [56] upon variation of chain lengths up to 30 carbon atoms. Moreover, by the application of one basis set in quantum chemical calculation using DFT method the mean energy of a methylene group was found to be identical for all studied series. This fact is defined predominantly by the compensatory transferability (as differences in energy between methylene groups in alkyl chains come up to 13 kcal mol^{-1}) and is trivial. However, in investigations of dependences of oxygen atom characteristics on the length of alkyl fragment is was found [57] that the substitution of the trifluoromethyl group for the terminal methyl group unexpectedly changes significantly the energy of the oxygen atom: the value of $\Delta E(\Omega)$ ranges from 6 to 20 kcal mol^{-1}, at the same time, the charge and other characteristics for this atom did not virtually change. A comparison of kinetic energies of oxygen atoms (the actual, integrated properties; see Section II.2) showed that the values of $T(\Omega)$ for oxygen atom were also close in considered molecules. Hence, the error in the energy value appeared at the stage of the transformation of the kinetic energy to the potential by Eqn (5) and was due to the changes in the virial coefficient γ. More detailed investigations of the coefficient γ behaviour showed its distinct dependence on the molecule size.[57] An important consequence of this result is the impossibility of the precise comparison of atomic energies for molecules of different size. Mosquera suggested in such cases to confine to comparson of $T(\Omega)$ values.[57]

Bader responded to this paper by investigating the transferability of atomic properties based on self-consistent virial scaling (SCVS) functions.[58] It was shown that the transferability of atomic properties, energies, in particular, is improved by the application of such functions thus confirming the correctness of Mosquera's conclusions. At the same time Bader noticed that the method of comparison of $T(\Omega)$ values [57] can hardly be applied to the analysis of atomic energies as the summation of $T(\Omega)$ values does not give the full energy of a molecule. This investigation was a kind of justification of the widely used method of kinetic energy scaling by the coefficient $1-\gamma$ as, strictly speaking, it did not show any qualitative difference between atomic energies obtained from the SCVS functions and energies calculated as $(1-\gamma)T(\Omega)$. However, it confirmed that in comparison of atomic energies obtained by a standard procedure for different molecules it is necessary to take account of the possible influence of the coefficient γ. As it was shown later,[59,60] for small differences in structures of compared compounds, especially in comparison of atomic energies for different conformers of a molecule one can neglect the changes in the coefficient γ and compare atomic energies directly.

The postulate of the transferability of atomic energies implies that the differences between energies of molecular fragments in reality are connected with their relative stability and are not artifacts of the method.

IV. Examples of application of atomic energies in structural chemistry

Analysis of atomic charges is applied to a wide range of problems.[1,4] The main area of their application is the estimation of the energies of interatomic interactions (both covalent and weakly bonding) by comparing the atomic energies in bonded and non-bonded structures. But analysis of atomic energies is also applicable for the explanation of conformational preferabilies of molecules, including those caused by the anomeric effect and is an integral part of the criterion proposed by Popellier for hydrogen bonding (see Section IV.3). Examples of the application of atomic energies for the prediction of experimentally observed values are also known, namely for the heats of combustion and acidity constants.

We shall now consider each of the areas of application in detail.

1. Heats of combustion and strain energies of cycloalkanes

The first paper that comprehensively examined atomic energies within the AIM theory was that by Bader mentioned above.[46] In this fundamental paper, methyl and methylene groups were pointed out for the first time as transferable fragments; their energies were obtained independently by the integration of the electron density in agreement with the additive schemes for the heats of combustion already known. Further, on the basis of data on energies and charges for the 'ideal' methyl and methylene groups Bader with co-workers obtained 'standard' values of the energy of the methine group and tertiary carbon atom by subtracting the energy of the methyl groups from the energies of isobutane and neopentane, respectively.[46] The obtained values were used for the calculation of strain energies of cyclic molecules as a difference between the calculated molecular energy and the sum of the energies of 'standard' groups that could be used to form the considered molecule. The results were in good agreement with the experimental data for the heat of combustion of the considered compounds (Table. 1).

Table 1. Atomic characteristics and strain energy (SE) in cyclic alkanes.[46]

Alkane	SE [a]	Characteristics of fragments [b]			Alkane	SE [a]	Characteristics of fragments [b]		
		C1	C2	C3			C1	C2	C3
	28.7 (27.5)	q(C) = −0.010 q(H) = 0.005 q(CH_2) = 0.0 E = 9.6				11.4 (7.4)	q(C) = 0.061 q(H) = −0.040 q(CH_2) = −0.019 E = −7.3	q(C) = 0.101 q(H) = −0.044 q(CH) = 0.057 E = 27.6	
	26.8 (26.5)	q(C) = 0.057 q(H) = −0.029 q(CH_2) = 0.0 E = 6.7				104.2 (98.0)	q(C) = 0.026 q(H) = 0.023 q(CH_2) = 0.072 E = 5.4	q(C) = −0.107 E = 44.0	
	7.1 (6.2)	q(C) = 0.084 q(H) = 0.037 q(CH_2) = 0.010 E = −0.9	q(C) = 0.077 q(H) = −0.040 q(CH_2) = −0.003 E = −0.2	q(C) = 0.068 q(H) = −0.035 q(CH_2) = −0.002 E = 4.2		106.6 (104.0)	q(C) = 0.036 q(H) = 0.019 q(CH_2) = 0.074 E = 11.3	q(C) = 0.103 q(H) = −0.014 q(CH_2) = 0.075 E = 30.6	q(C) = −0.149 E = 11.4
	0.06 (0.00)	q(C) = 0.080 q(H) = −0.040 q(CH_2) = 0.0 E = 0.01				104.6 (105.0)	q(C) = 0.042 q(H) = 0.013 q(CH_2) = 0.069 E = 13.6	q(C) = 0.099 q(H) = −0.020 q(CH_2) = 0.059 E = 34.9	q(C) = −0.152 E = −24.3
	68.6 (63.9)	q(C) = 0.072 q(H) = −0.002 q(CH_2) = 0.068 E = 32.7	q(C) = −0.121 q(H) = 0.054 q(CH) = −0.067 E = 1.6			95.3 (89.0)	q(C) = 0.051 q(H) = −0.023 q(CH_2) = 0.005 E = 20.9	q(C) = −0.016 E = −15.1	
	58.5 (54.7)	q(C) = −0.003 q(H) = 0.002 q(CH_2) = 0.000 E = 2.5	q(C) = −0.043 q(H) = 0.011 q(CH) = −0.032 E = 8.9	q(C) = 0.082 q(H) = −0.025 q(CH_2) = 0.032 E = 17.8		140.8 (140.0)	q(C) = −0.111 q(H) = 0.111 q(CH) = 0.0 E = 35.2		
	69.0 (68.0)	q(C) = 0.043 q(H) = −0.030 q(CH_2) = −0.017 E = −5.2	q(C) = 0.036 q(H) = −0.011 q(CH) = 0.025 E = 42.3			159.1 (154.7)	q(C) = 0.003 q(H) = −0.003 q(CH) = 0.0 E = 19.9		
	15.2 (14.4)	q(C) = 0.058 q(H) = −0.036 q(CH_2) = −0.012 E = −5.1	q(C) = −0.074 q(H) = −0.033 q(CH) = 0.041 E = 30.5	q(C) = 0.036 q(H) = −0.034 q(CH_2) = −0.032 E = −25.4		61.4 (63.2)	q(C) = 0.003 q(H) = 0.007 q(CH_2) = 0.018 E = 12.2	q(C) = −0.072 E = 12.5	

[a] The calculated values are given in kcal mol^{-1}, the experimental values are given in brackets; [b] q is charge on an atom or a group (in a.u.), for the CH_2 groups the mean value q(H) is given; E is the strain energy for a group in kcal mol^{-1}.

This result was quite expected as additive schemes for the calculation of the heats of combustion of hydrocarbons have already been known and the energies of the methyl and methylene groups were close to the corresponding coefficients obtained from the additive schemes. But the main significance of this paper was a completely new approach, for that time, to the rationale of the appearance of the strain energies. Analysis of energies and charges of atoms in the strained molecules unambiguously showed that the charges of 'strained' carbon atoms (*e.g.*, in cyclopropane) increased as compared to those for the acyclic systems and the energies decreased. The destabilization of the system occurred mainly due to hydrogen atoms, for which the energy increased significantly upon onset of the strain.

At first sight, this result can seem strange as the deviation of the carbon atom geometry from the tetrahedral one should be manifested first of all in the carbon atom. However, the results obtained by Bader were logically explained in terms of hybridization: the distortion of the tetrahedral geometry of the carbon atom should lead to the increase in the p-character of C–C bonds and, consequently to the increase in the contribution of s-orbital to the C–H bond. As is known by the example of alkenes and alkynes, the increase in s-character of the C–H bond leads to the increase in electronegativity of the carbon atom and as a consequence in its charge. The variation of the atomic charge is usually opposite to the change in its energy.

Although considerations given above are quite convincing, experimental proof of the increase in the s-character of carbon atoms in the strained systems based on NMR data (the values of spin–spin coupling constants $^{13}C-H$)[61] and pK_a for these hydrocarbons was also presented.[46]

This paper by Bader became a *de facto* standard for such type of investigations and largely defined the subsequent development of application of the AIM theory.

2. Acidity constants of organic acids

Since the acidity of a compound is defined by the ease of proton abstraction, attempts have been undertaken to link pK_a values with different integral properties of acidic hydrogen atom, see, *e.g.*, Ref. 62.

The possibility of a linear correlation between pK_a values for organic acids and the energy of acidic hydrogen atom has been demonstrated. It was also shown that the precision of the correlation increases with the model improvement describing the molecule of an acid in solution. Thus the correlation improved in the calculation of an acid as a monohydrate or dihydrate compared to the calculation in which the solvent was modeled by the PCM method (polarized continuum model). This correlation was verified for aliphatic carboxylic acids, substituted benzoic acids, anilinium and pyridinum ions.

This result at first glance seems interesting, but the detailed consideration of the calculation method and, in particular, underlying theoretical grounds allows considering it inadequate.

The obtained correlation was explained using the doubtful suggestion that the ΔG value of the dissociation process of the acid HA is equal to the difference between electronic energies of the acid HA and the anion A^-. The question on how could this correlation be combined with the fact that for many carboxylic acids the enthropy component gives the main contribution to ΔG of dissociation was avoided by the author. Nor the solvation processes were discussed. Considering the concept of transferability quite freely the author suggests that the energy of A^- is numerically equal to the difference between the energy of the acid HA and the energy of acidic hydrogen atom. At the same time for the fulfillment of this suggestion it is required that no charge redistribution occured in the anionic fragment upon proton detachment, *i.e.*, that the atomic basin would simply vanish. In particular, this requires that the acid anion would acquire a non-integer charge equal to the population of the hydrogen atom basin, which is evidently not the case.

As was mentioned above, back in 1987 Bader noted[46] the relation of atomic characteristics to pK_a values. In the general case, it is evident that the acidity of a group X–H described by the equilibrium

$$X-H = X^- + H^+,$$

is directly connected with the capability of the atom X to stabilize the negative charge. This is the higher the greater is its electronegativity in a given compound. The increase in electronegativity of the atom X in a series of related compounds in turn leads to the increase in charge transfer from the hydrogen atom to the atom X and consequently to the increase in positive charge on the hydrogen atom and increase in its energy. This rationale seems a more reliable ground for the correlation described.[62]

3. Hydrogen bonds

As the investigation into different types of chemical bonding is one of the main applications of the AIM theory, the creation of criteria for the hydrogen bond formation within this theory was, naturally, of great interest.

The first papers on this topic were the papers by Boyd and Choi of 1985–1986[63,64] in which it was shown that the AIM theory can be applied for the analysis of a hydrogen bond. Complexes of the wide range of acceptors of the hydrogen bond with HF and HCl were chosen as subjects of investigation. In 1987–1988, Caroll and Bader considered this topic; in their papers the hydrogen bond was investigated first by the example of H_2O and NH_3 dimers[65] and later by a series of complexes of the type B···H–F where B designates the hydrogen bond acceptor.[66] Bader considered for the first time the changes in the integral atomic properties upon the formation of a hydrogen bond. Later the applicability of the created approaches for the investigation of both inter- and intramolecular hydrogen bonds[67–70] including π-type hydrogen bonds was demonstrated.[71]

Eight different criteria of a hydrogen bond were generalized by Koch and Popellier.[72] All considered criteria were tested in the same paper by the example of C–H···O hydrogen bonds, which are usually weak but can exert significant influence on the conformational preferabilities and crystal packing of molecules.

We shall now examine these criteria in more detail. Strictly speaking, as it will be clear from the following discussion, not all of them can be applied for the localization of hydrogen bond, which has also been mentioned.[72] If an A–H···B bond does not satisfy any of these criteria, it can rather be the reason of doubts wether it should be called 'hydrogen bond'. At the same time, conclusions on the characteristics of the C–H···O hydrogen bonds[72] are in agreement with the data obtained independently.[73]

Criterion 1. Topology of the function $\rho(\mathbf{r})$. According to the AIM theory the presence of CP (3,−1) in the electron density distribution function $\rho(\mathbf{r})$ is a necessary and sufficient condition for the existence of a chemical bond.

Apparently, the hydrogen bond is not an exception. If such a critical point between atoms H and B can be found in the function $\rho(\mathbf{r})$ in the region of the A—H···B-bond and the bond paths from this critical point to atoms B and H can be constructed, then by definition there is a binding between atoms H and B. In zero approximation, the presence of CP (3,−1) is necessary and sufficient for the hydrogen bond to be found, but criteria discussed below allow characterizing this interaction more precisely.

Criteria 2 and 3. The values of $\rho(\mathbf{r})$ and Laplacian of $\rho(\mathbf{r})$ in critical point (3,−1). Usually hydrogen bonds represent the so-called closed-shell interactions (see above) in contrast to covalent bonds, which are of shared type. Quantitative criteria allowing for the distinction between these bond types are $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ values in the critical point (3,−1). The value of the electron density function $\rho(\mathbf{r})$ in a point is an indirect measure of the charge shared by the nuclei, although it depends not only on the interaction strength but also on the nature of the interacting atoms. The values of the Laplacian of $\rho(\mathbf{r})$, in turn, allow determining whether this point corresponds to the region 'concentration' of the electron density. For covalent bonds A—H, significant charge accumulation in the internuclear region is typical, which corresponds to the rather high $\rho(\mathbf{r})$ values and higher absolute value of negative $\nabla^2\rho(\mathbf{r})$ in the critical point (3,−1). Typical cases are $2.42\,e$ Å^{-3} for $\rho(\mathbf{r})$ and $-46.7\,e$ Å^{-5} for the Laplacian in the case of N—H bond in ammonia and $2.64\,e$ Å^{-3} for $\rho(\mathbf{r})$ and $-58.89\,e$ Å^{-5} for the Laplacian of the O—H bond in the water molecule.[65] Closed-shell interactions, which include the majority of weak intermolecular contacts, correspond to significantly smaller accumulation of the electron density between the nuclei, so small $\rho(\mathbf{r})$ values and slightly positive $\nabla^2\rho(\mathbf{r})$ values are typical of them.

On the basis of a broad range of calculated data for the systems with hydrogen bonds, it was concluded[72] that the $\rho(\mathbf{r})$ value in CP (3,−1) should lie in the range from 0.002 to 0.035 (a.u.) (0.013–0.236 e Å^{-3}), and a rather accurate correlation exists between the value of the energy of a hydrogen bond and the value of $\rho(\mathbf{r})$. It should be noted that for the strong hydrogen bonds (see, *e.g.*, Ref. 74) the values of $\rho(\mathbf{r})$ can come up to $0.5\,e$ Å^{-3}. The values of $\nabla^2\rho(\mathbf{r})$ vary over a wider range, from 0.024 to 0.139 (a.u.) (0.578–3.350 e Å^{-5}) for conventional hydrogen bonds; at the same time, for the H···O bond in $H_5O_2^+$ the value of $\nabla^2\rho(\mathbf{r})$ is equal to −0.011 (a.u.) ($-0.265\,e$ Å^{-5}). The values of the Laplacian depend on the used basis set, consequently they cannot serve as reliable criteria for the hydrogen bond, although a recourse to them has also been made to justify the conclusion that C—H···Cl bonds cannot be regarded as hydrogen bonds.[72]

Criterion 4. Interpenetration of a hydrogen atom and the hydrogen bond acceptor. For the description of this criterion of hydrogen bond, which was stated for the first time by Caroll, Chang and Bader,[68] it is necessary to introduce the definitions of the bonded and non-bonded radii for the atomic basins of the hydrogen atom and a hydrogen bond acceptor. The bonded radius (r_H^0 or r_B^0) is the distance between the nuclear attractor of the hydrogen atom or an acceptor to the CP (3,−1), which corresponds to the supposed hydrogen bond, while non-bonded radius (r_H or r_B respectively) is the distance from a nucleus to an outer contour with the charge density of 0.001 (a.u.) (0.007 e Å^{-3}). This value of density for the contour was chosen since the non-bonded radii defined in such a way do well agree with the gas-phase van der Waals radii.[75,76] For the analysis of interpenetration of atoms upon the formation of hydrogen bond, the non-bonded radius is estimated in the direction of the 'future' hydrogen bond.

This criterion can hardly be formalized but can be easily described at the qualitative level: the criterion for the formation of a hydrogen bond is partial 'embedding' of the hydrogen atom into the electron shells of the acceptor atom. Analysis of a wide range of compounds shows that in the formation of a hydrogen bond the value of Δr defined as the difference between non-bonded and bonded radii is positive for both the hydrogen and acceptor atoms. Interestingly, the relationship between Δr_H and Δr_B depends on the nature of the hydrogen bond donor and acceptor: for 'soft' acid A—H and 'hard' base B $\Delta r_H > \Delta r_B$ and *vice versa*.[68]

The following four criteria are integral properties of the hydrogen atom.

Criterion 5. Increase in the positive charge on the hydrogen atom. This criterion was fulfilled for all compounds chosen by Carroll and Bader,[66] which in principle could be expected, since in the NMR spectra the main sign for the formation of a hydrogen bond is a downfield shift of a hydrogen atom signal, which corresponds to the depletion of electron density on this atom.

Criterion 6. Increase in the energy of the hydrogen atom. This criterion was also fulfilled for all analyzed compounds. Possibly, the increase in the energy of the hydrogen atom is to a great extent due to the depletion of a charge on the atom, since for the hydrogen atoms the changes in the energy and charge are as a rule oppositely directed.

Criterion 7. Decrease in polarization of a hydrogen atom. Similarly to criterion 6, this criterion is due to the charge depletion on a hydrogen atom: the decrease in the electron density in the hydrogen atom basin leads to the decrease in its polarizability and consequently to the decrease in the modulus of the dipole moment of this atom, which was the case for all compound analyzed.[66]

Criterion 8. Decrease in a hydrogen atom volume. This effect was found by Bader and co-workers,[67] although it cannot serve as a reliable criterion for the hydrogen bond as it is not fulfilled for dimer HCl···HF.

Charge transfer. Although changes in the charges of atomic basins of non-hydrogen atoms were not formulated as a separate criterion for the hydrogen bond, they are rather significant and present certain interest. First of all, upon formation of a hydrogen bond A—H···B is usually accompanied charge transfer from the hydrogen bond acceptor to the donor. This is comparable in absolute value with the decrease in the charge on the hydrogen atom or even exceeds it. Second, the charge of the atom B, the hydrogen bond acceptor, decreases by a magnitude comparable to the total charge that is transferred. The charge acquired by the acid is in general localized on the atom A. However, the charge transfer upon formation of the hydrogen bond can be compensated by other effects and consequently cannot serve as a criterion for the presence of the hydrogen bond.

Among compounds that have been used[72] for the investigation of C—H···O interactions, complexes of chloroform with acetone and formaldehyde were present with critical points for contacts H···Cl in addition to the critical points (3,−1) corresponding to the hydrogen bond H···O. These contacts which could not be classified as a real hydrogen bond from geometrical considerations, were compared with

the hydrogen bonds C—H···O and their attribution to hydrogen bonds, strictly speaking, was prevented only on the basis of criteria 4 and 7 (interpenetration of hydrogen and acceptor atoms and the change in the hydrogen atom volume) which are apparently influenced by the geometrical characteristics of the interaction to the greatest extent.

Thus, one cannot conclude that unambiguous criteria for the hydrogen bond were formulated by Koch and Popelier [72] that would allow distinquishing it based on the AIM theory. However, the data presented above give an idea on how such binding manifests itself in the topology of the electron density distribution function $\rho(\mathbf{r})$; they can be used for the analysis of different bonds involving hydrogen atoms. It should be noted that the variations of the integral properties of hydrogen atoms, energy in particular, are more clear and can easier be analyzed than the properties of critical points.

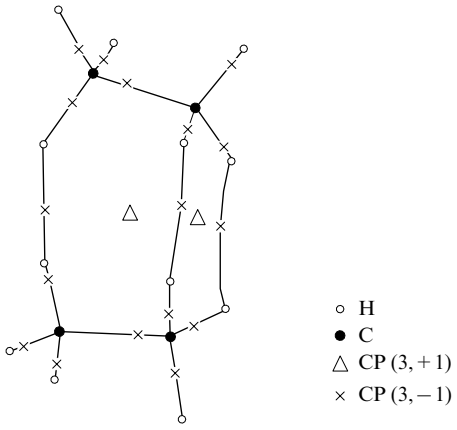


Figure 1. Molecular graph for the dimer $(BH_3NH_3)_2$.[79]

4. H···H interactions

The listed criteria of a hydrogen bond can be applied for the analysis of H···H contacts and the estimation of their energetics

Strictly speaking, H···H contacts can be divided in two main classes: (1) the so-called dihydrogen bonds, which correspond to the interaction $A-H^{\delta+}\cdots H^{\delta-}-B$ [77] and are classified as a special type of hydrogen bonds both by spectroscopic methods and according to Popelier criteria; (2) the so-called van der Waals interactions,[10–12] which correspond to the interaction between the spatially close hydrogen atoms possessing similar or equal charges.

Dihydrogen bonds are substantially more rare than the van der Waals contacts H···H, they were discovered only in the 1990s.[78] However, from the point of view of the logic of explanations, it is more convenient to discuss them first, because it was shown [79] that they meet all criteria of a hydrogen bond described in Section IV.3.

Dihydrogen bonds were considered by an example of dimer $(BH_3NH_3)_2$. The choice of this compound as a model was not occasional: BH_3NH_3 is one of the most widely studied examples of the dihydrogen bond of the $A-H^{\delta+}\cdots H^{\delta-}-B$ type. This compound was considered in detail in a fundamental crystallographic paper on dihydrogen bonding.[80] It was shown that the energy of this bond in the dimer can be estimated at $\sim$6 kcal mol^{-1}. The presence of strong intermolecular interactions in BH_3-NH_3 is also justified by its abnormally high melting point, which is 285° higher than that of isoelectronic ethane.

Thus, if the description of dihydrogen bonds in the dimer $(BH_3NH_3)_2$ were impossible using the criteria of a hydrogen bond suggested by Popelier, this would suggest, first of all, the inadequacy of the criteria. But the detailed analysis of interactions in the dimer confirmed the applicability of these criteria and the possibility of establishing a correlation between the strength of the interaction and the extent of changes in the integral properties of hydrogen atoms, since the dimer (Fig. 1) contains two types of dihydrogen bonds of different strengths. For example, for a stronger dihydrogen bond the energy of the acidic hydrogen atom increased by 30.4 kcal mol^{-1}, while for the weaker one, only by 17.7 kcal mol^{-1}.

Another type of H···H interactions, which can be called, in contrast to the dihydrogen bonds, attractive van der Waals interaction of hydrogen atoms, was considered in detail.[81] Intramolecular H···H-interactions of this type are present predominantly in aromatic compounds and in the cited paper they were also studied by the example of fused aromatic systems (Fig. 2). It should be mentioned that the attractive character of such interactions was often put in doubt by critics of Bader's theory (see for example, Ref. 82). The most doubtful case is the planar biphenyl molecule where the repulsion of hydrogen atoms seems evident from the positions of the 'chemical logic'.

However, analysis of the integral properties of hydrogen atoms testifies to decrease in energy (by 4–6 kcal mol^{-1}) and in charge (by 0.02–0.03 e) on both hydrogen atoms involved in the H···H-interaction. We should also notice that it is this characteristic of the van der Waals contacts H···H that fundamentally distinguishes them from the dihydrogen bonds where the charge on, and the energy of, one of the hydrogen atoms decrease.

The doubts about the attractive character of the H···H interaction in planar biphenyl and similar compounds can be solved by the following considerations: although the approach of hydrogen atoms is energetically unfavourable, the optimized molecular geometry has, by definition, zero forces on atoms. Consequently, the repulsion between the *ortho*-hydrogen atoms is apparently absent. On the contrary, according to the analysis of the atomic energies, these hydrogen atoms make a significant (20.8 kcal mol^{-1} for planar biphenyl in total) contribution to stabilization of such structures. The main increase in energy in planar biphenyl is attributed to the atoms of the single C—C bond (C1 and C7) and is manifested in the elongation of this bond by 0.0086 Å compared to the equilibrium geometry (torsion angle 44°). The sum of all changes in the atomic energies in the molecule leads to the increase in energy by 2.1 kcal mol^{-1} compared to the equilibrium geometry. Thus, Bader's theory does not predict the increased relative stability of biphenyl, it only allows partitioning the energy difference between structures into components and obtaining a more precise understanding of the nature of intramolecular interactions in them.

The results obtained on the intramolecular H···H contacts and the experimental data can be used for the analysis of similar interactions in more complex structures.

One of the most recent paper of this type was the investigation of 4-methyl-[4]helicene.[83] Judging from the

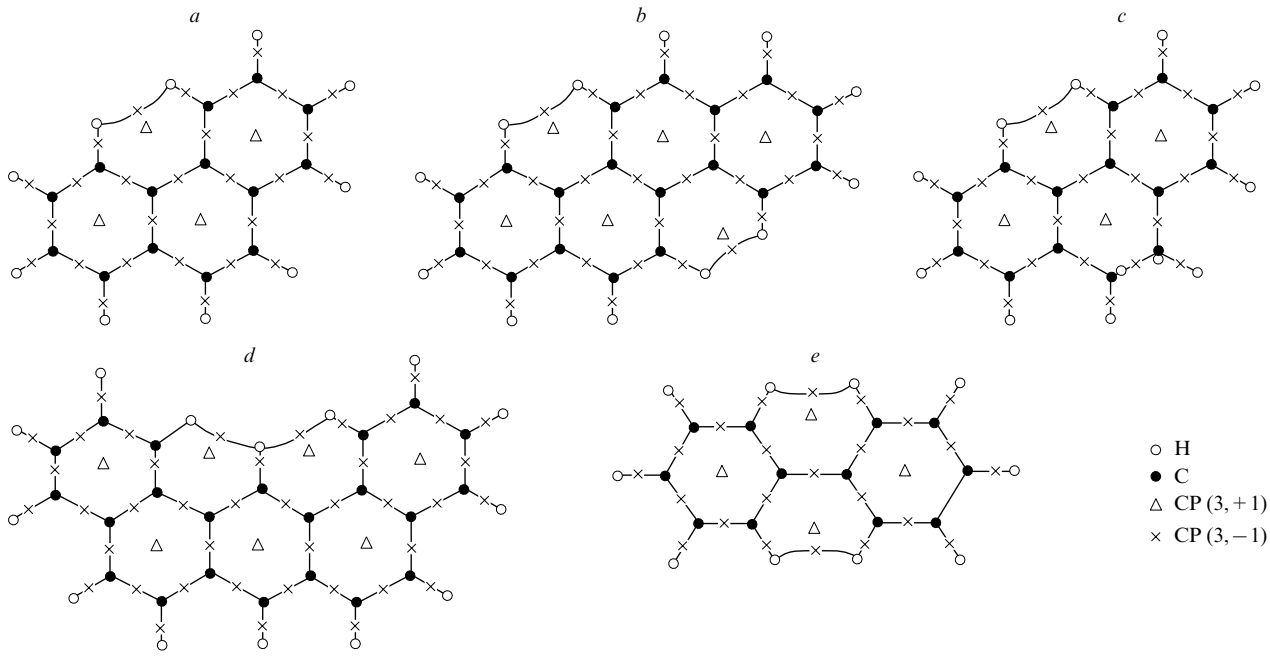


Figure 2. Molecular graphs of phenanthrene (*a*), chrysene (*b*), 9,10-dihydrophenanthrene (*c*), dibenzo[*a*,*j*]anthracene (*d*) and planar biphenyl (*e*).[81]

structure of this compound (Fig. 3) one can suggest the presence of an H···H interaction between the atoms H1 and H12 in close proximity. As these hydrogen atoms have similar environment, their interaction cannot be classified as a dihydrogen bond (as was stated above, in the dihydrogen bond symbolized by $A-H^{\delta+}\cdots H^{\delta-}-B$ one hydrogen atom acts as a hydrogen bond acceptor while another, as a donor). The gas-phase calculation of the molecule confirmed this suggestion and predicted that the energies of the atoms H1 and H12 should be lower by 4.2 and 3.6 kcal mol^{-1}, respectively, with respect to other hydrogen atoms in the molecule, which allowed estimating the local energy of stabilization due to the H···H interaction at 7–8 kcal mol^{-1}. The accuracy of the mutipole refinement of the electron density of 4-methyl-[4]helicene by high-resolution X-ray diffraction study, unfortunately, was insufficient for obtaining reasonable charge parameters of hydrogen atoms, so, the investigators had to confine themselves to the comparison of topological characteristics in CP (3, −1) corresponding to the H···H contact. These data showed good agreement between the theory and experiment. In the crystal, several weaker intermolecular interactions C–H···H–C were found.

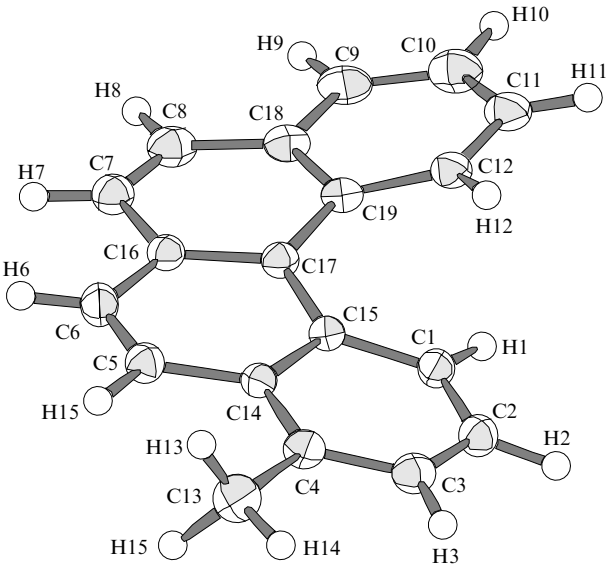


Figure 3. The structure of 4-methyl-[4]helicene molecule.[83] Atoms are represented with thermal ellipsoids.

Thus numerous additional parameters, can be obtained whithin the AIM theory and investigation of the integral properties of atomic basins. It was possible to characterize the chemical bonding and, in particular, differentiate geometrically similar, but different in the nature, types of interatomic interactions.

5. Investigation of the bond dissociation process

The problem of the bond dissociation energy calculation is encountered quite often; however for its solution one should apply quite demanding calculation methods[84] such as CCSD(T),[85,86] MP2 and MP4 with large basis sets[87] and G*n* protocols.[88,89] With the increase in size of a molecule, the application of such methods quickly becomes unreasonable. Therefore, DiLabio[90] and Wright with co-workers[91–93] have developed the application of the Locally Dense Basis Set (LDBS) method[94] for the calculation of bond energies. LDBS method consists of the application of different basis sets for the atoms of the same molecule. Evidently, for the atoms in the part of the molecule that is of the greatest interest, a larger basis set is used than for the other atoms. This method was effectively applied for the correction of chemical shifts and spin–spin coupling constants in ^{1}H, ^{13}C, ^{15}N, ^{17}O, ^{19}F and ^{31}P NMR spectra[95,96] and its application for the estimation of the bond cleavage energy seems evident: it was suggested[93] that the main contribution to the dissociation energy is made by the atoms that form the bond to be cleaved. However, no

attemps were undertaken to confirm this suggestion theoretically. At the same time, the reliable approval (or rejection) of this suggestion can be obtained by means of the AIM theory by analyzing the changes in atomic energies in the bond dissociation.

This problem was studied in detail [97] by the example of linear alkanes and *trans*-alkenes with even number of carbon atoms ($n = 2, 4, 6, 8$). Analysis of the distribution of ΔE for the homolytic bond dissociation over the atomic basins lead to unexpected results: it turned out that for alkanes beginning with the butane the dissociation of the central bond does not influence the energy of carbon atoms participating in this bond (Fig. 4). The most significant variation upon the dissociation occurs for energies of atoms directly linked to the atom Cl, namely, two hydrogen atoms and one carbon atom. In the case of alkenes, as a result of homolytic bond dissociation biradicals are formed, the atom Cl turns out to be destabilized, which leads to a more predictable ΔE distribution over the chain: ΔE(C1) has more than a half of the total value of ΔE for the bond dissociation. But in this case too, one cannot neglect the contributions of H1 and C2 atoms since their overall contribution is comparable to that of the atom C1.

Thus, it was shown that the changes in the molecular energy upon bond dissociation are in fact localized, but not necessarily at the site expected on the basis of 'chemical intuition'. Although the LDBS approach is quite correct for the estimation of bond dissociation energy its correct application requires the use a extended basis set not only for the atoms of the bond to be dissociation, but also (at least) for their nearest environment. Strictly speaking, the choice of atoms for which the extension of the basis set is required demands investigations similar to those reported.[98]

It was shown [98] that the analysis of ΔE distribution over the atoms in a molecule can be interesting itself. However, in this case all calculations were performed at the MP2(full) level of theory, which becomes quite demanding upon the increase in the number of atoms in a system. Thus, to prove the applicability of the DFT method and investigate the possible applications of Atomic Partitioning of the Bond Dissociation Energy method (APBDE), Matta, Arabi and Keith have undertaken the investigation of the P−OH bond dissociation in the anion HPO_4^{2-} and the influence of the complex formation of the anion with Mg^{2+} on the energetics of this process.[42] This problem was interesting as it can be regarded as a model for the study of P−O bond dissociation in ATP in a living cell. Since it was investigation of biochemical processes by the APBDE method that was the final goal, the practical verification of the applicability of the B3LYP method for the solution of this problem was required.

It was shown [42] that the results of APBDE-analysis obtained by the B3LYP method coincide on the qualitative level with the analogous data obtained by the MP2 method. An interesting peculiarity of the complexation process involving the hydrophosphate anion and magnesium cation was considered: although the P−OH bond in the complex is 0.112 Å shorter and stronger (according to the values of force constant obtained from the analysis of vibration frequencies), the dissociation energy of this bond upon interaction of the anion with the cation Mg^{2+} is significantly lower. (The enthalpies of the reactions

$$HPO_4^{2-} \longrightarrow (PO_3^{\bullet})^{2-} + {}^{\bullet}OH$$

and

$$MgHPO_4 \longrightarrow MgPO_3^{\bullet} + {}^{\bullet}OH$$

were compared, respectively.)

Although the APBDE method was used so far only for the model compounds with a rather simple structure, it is evident that its usage can provide new information on the properties of more complex structures.

6. The use of atomic energies in conformational analysis

The classical conformational analysis is the investigation of the dependence of the energy of a molecule on the changes in the inner coordinates, *e.g.*, torsion angles. As a rule, such analysis allows decomposing the total change of the molecular energy into some individual contribution and obtaining new information on the nature of intramolecular interactions in the system studied.

The application of the methods of the AIM theory, first of all the investigation of the variations of the atomic charges and energies in different conformers leads to the decomposition of the difference in energy (ΔE) between conformers into the contributions of the individual atoms. It is evident that the possibility to obtain such data opens completely new horizons for the conformational analysis, as it allows localizing unambiguously the changes in the molecular energy.

These problems are being studied mainly by Mosquera and his research group. Their first paper [98] dedicated to the applications of Bader's theory to the conformational analysis contained the investigation of the evolution of atomic characteristics and bonds in the hydrogen peroxide molecule upon rotation around the central bond. This paper did not provide any fundamentally new results, but it was shown that the general features of the energy and charge redistributions in the molecule depend to a small extent on the chosen calculation method for the optimization of the molecular geometry and energy calculation. Therefore, in the later papers by this group, solely B3LYP functional was used for obtaining the electron density distribution function.

Typical examples of the conformational studies can be found in some recent papers on the estimation of the hydrogen bond energy in diols [99] and of the strain energy in perfluorocycloalkanes.[100]

The calculation of the ring strain energy in perfluorocycloalkanes is difficult, first of all, because of the absence of common criteria for the estimation of this quantity. A widespread theoretical method for the calculation of the ring strain energy is at present the analysis of ΔE of the so-called homodesmotic reactions [101] where each carbon atom of the initial ring passes into the carbon atom of the linear product with the same environment and hybridization as in the initial ring. In particular, the homodesmotic 'reaction' of the ring opening of a perfluorocycloalkane can be represented as follows:[100]

$$(CF_2)_n + n\,CF_3(CF_2)_mCF_3 \longrightarrow n\,CF_3(CF_2)_{m+1}CF_3\,.$$

It is evident that it is possible to suggest many processes of this type and different 'reactions' will lead to slightly different ring strain energies (SE^H). At the same time, within the framework of AIM theory the energy of the ring strain of $(CF_2)_n$ should be defined as the difference between the energy of the molecule and the sum of n energies of the

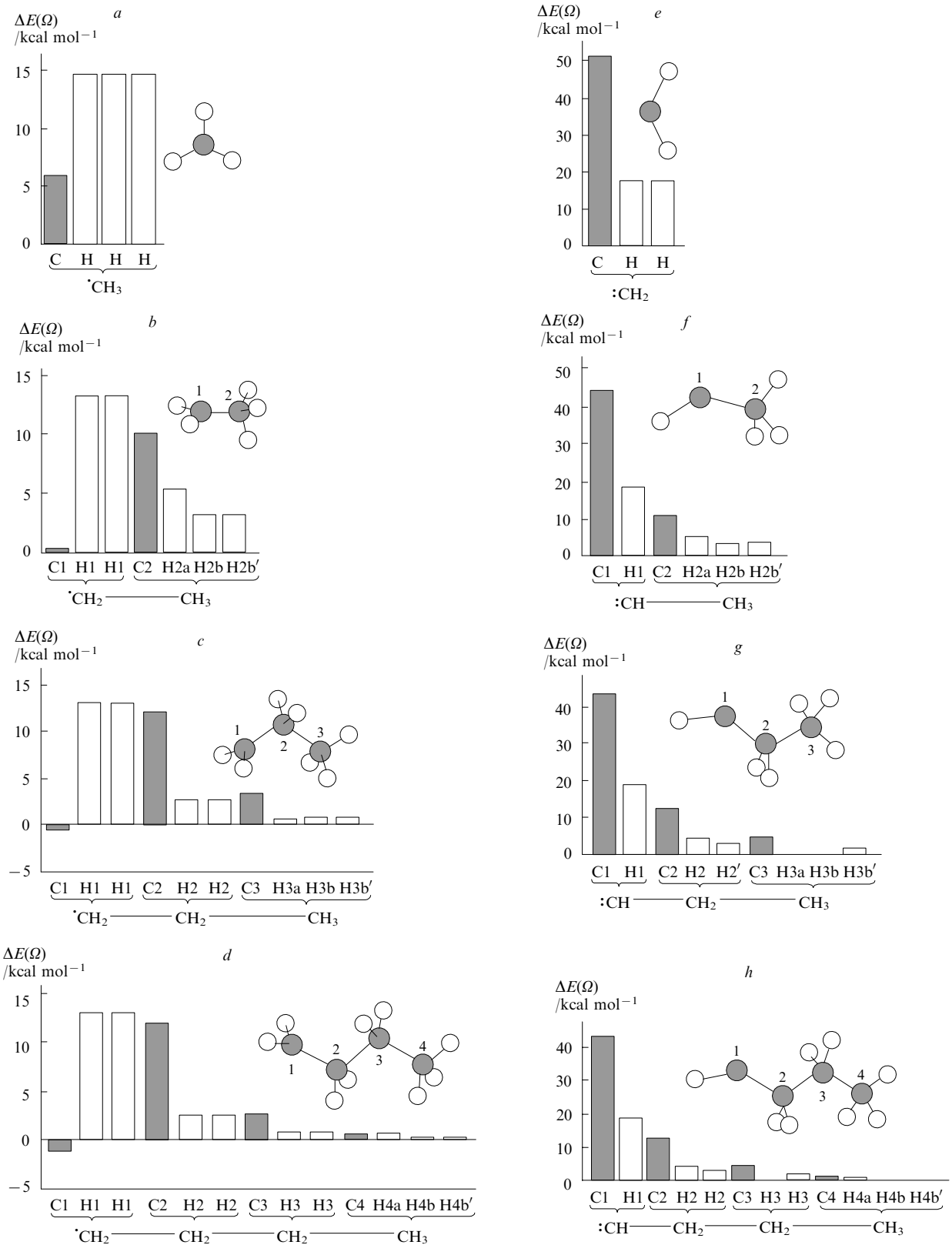


Figure 4. Distribution of the bond dissociation energy of the central bond over the atomic basins [$\Delta E(\Omega)$] in linear alkanes (*a*–*d*) and alkenes (*e*–*h*) with the following number of carbon atoms $n = 2$ (*a*, *e*), 4 (*b*, *f*), 6 (*c*, *g*), 8 (*d*, *h*).[97]

'transferrable' group CF_2 (the central groups in n-C_8F_{18} can be roughly considered to be of such a kind). This value was designated by Mosquera as SE^Q. The values of SE^H and SE^Q do not merely disagree, but may even have different signs. Moreover, the value of SE^Q monotonically increases with the n, which contradicts the general concepts for the ring strain energy. One can suggest that this SE^Q value has no sense, but it is not the case. The analysis of the atomic energies in the products of the homodesmotic reactions shows that the SE^Q value is close in modulus to the total change of the energy of the CF_2 groups, which are as if transferred from the cyclic molecule to the centre of the linear products (Fig. 5), and has the opposite sign. This change in energy corresponds to the energy expences for the ring opening (ΔE^{RO}) and is always positive. As one can see from Fig. 5, this energy can be compensated for by the canges in energy of the remaining atoms in the linear products (ΔE^{NC}).

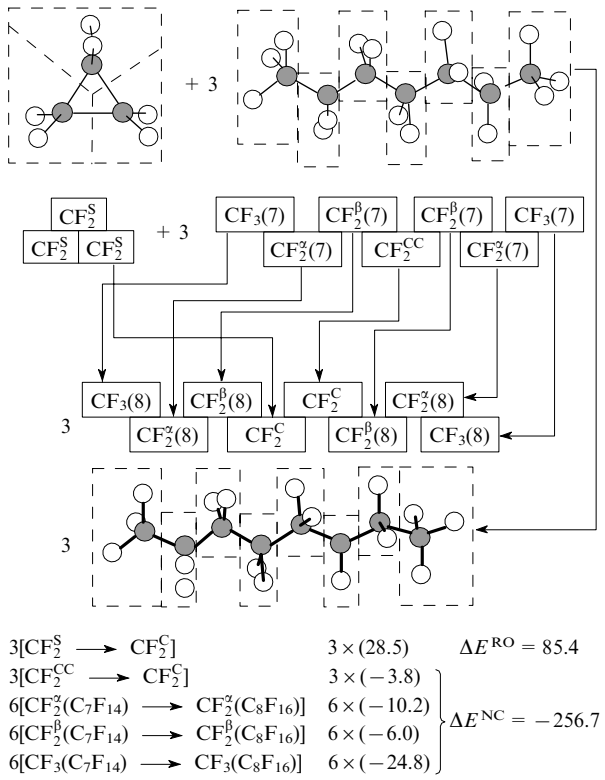


Figure 5. Scheme of the homodesmotic ring opening of perfluorocyclopropane, which illustrates different contributions to the total energy of the ring strain (in kJ mol^{-1}).[100]

Dividing the SE^Q value by the number of atoms in the ring, one can obtain the mean value of the energy stabilization for the CF_2 group in the ring, which is the individual characteristics of this ring and gives correct idea of the relative stability of different perfluorocycloalkanes.

Thus, although the physical sense of SE^Q is not very evident, it can be applied for the estimation of the ring stabilization energy.

A scheme for the estimation of the hydrogen bond energy in diols based of the AIM theory was proposed;[99] it does not require the calculation of $\Delta E_{OH\cdots O}$ value for itsapplication. Ethane-1,2-diol, propane-1,3-diol and butane-1,4-diol were chosen as subjects of investigation. Within the framework of classical concepts, the difference in energy (ΔE) between different conformers of these molecules can be split into several main components, *viz*., hydrogen bond energy ($\Delta E_{OH\cdots O}$), *gauche*-stabilization due to the stereoelectronic interactions of the electron lone pairs of the oxygen atoms with C—C and C—H bonds [$\Delta E_{g(H)}$ and $\Delta E_{g(C)}$ respectively], and destabilization energy due to the repulsion of hydrogen atoms in the adjacent methylene and OH groups ($\Delta E_{CH\cdots HO}$). The topological analysis of the electron density distribution in ethane-1,2-diol conformers shows (Fig. 6) that in contrast to the homologues none of its conformers has CP (3, −1) corresponding to the OH···O hydrogen bond. Hence, using ΔE value for ethane-1,2-diol one can separate components corresponding to $\Delta E_{g(H)}$, $\Delta E_{g(C)}$ and $\Delta E_{CH\cdots HO}$. Further, using the assumption that these three components depend little on the length of the carbon chain they are considered equal for all three studied compounds. Thus, $\Delta E_{OH\cdots O}$ for propane-1,3-diol and butane-1,4-diol can be obtained by subtracting $\Delta E_{g(H)}$, $\Delta E_{g(C)}$ and $\Delta E_{CH\cdots HO}$ from ΔE. The $\Delta E_{OH\cdots O}$ values obtained by this method for propane-1,3-diol and butane-1,4-diol were equal to 4.40 and 5.79 kcal mol^{-1} respectively.

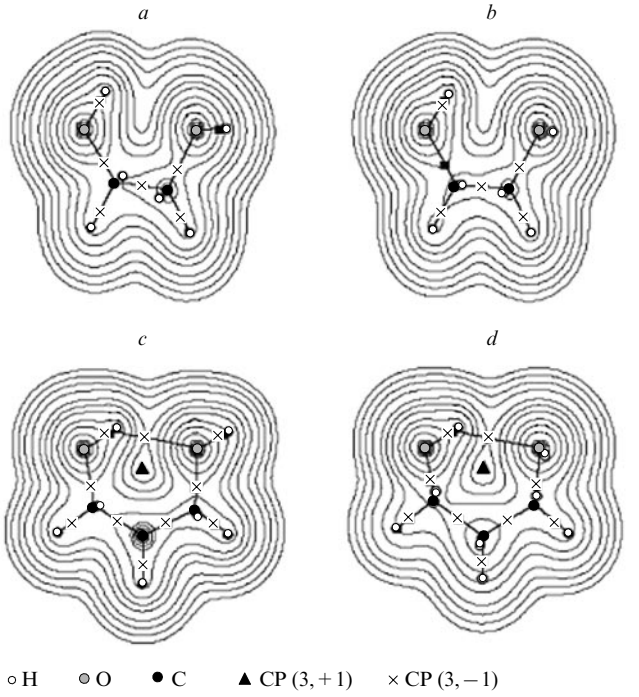


Figure 6. Maps of the electron density distribution in the OH···O plane for different conformers of ethane-1,2-diol (*a*, *b*) and propane-1,3-diol (*c*, *d*).[99]

The works of Mosquera's group on the interpretation of the anomeric effect in terms of the AIM theory are of significant interest.[59, 60] Thus a new interpretation of the conformational preferences in methanediol derivatives based on the analysis of atomic energies and charges in different conformers of these compounds containing the

fragment $O-CH_2-O$ has been proposed.[59] It was shown that the energy gain for *gauche*-conformers is primarily due to the repulsion of the electron lone pairs (LP) of the oxygen atoms with the hydrogen atoms of the methylene fragment (through-space interaction). In *gauche*-conformers, this interaction manifests itself in the most pronounced way and leads to the charge transference from hydrogen atoms to the central carbon atom and other non-hydrogen atoms of the system. In turn, the increase in the electron population for the non-hydrogen atoms leads to the gain in energy, which is higher than the losses in energy for hydrogen atoms. Thus, although the stereoelectronic interaction $LP-O-C-O$ is present in the $O-CH_2-O$ system (this results in the increase in the electron population of the oxygen atoms and the decrease in the electron population of the carbon atom), its contribution to the stabilization of *gauche*-conformer turns out to be insignificant.

The $N-C-N$ system was investigated[60] using analogous method. The results turned out to be similar to those obtained,[59] however, investigation of the methanediamine molecule showed that the transference of the electron density from the hydrogen atoms of the CH_2 group, in contrast to methanediol, proceeds not to the non-hydrogen atoms, but rather to the hydrogen atoms of the NH_2 group, which in turn leads to the overall lowering of the system energy.

Thus, it was shown that the stereoelectronic interactions $LP-O-C-O$ or $LP-N-C-N$ do not exert significant influence on the conformational preferences of $O-CH_2-O$ and $N-CH_2-N$ systems, although the most stable conformers in these systems can be predicted based on the stereoelectronic model. This conclusion seems odd, but in 1993 von Schleier[102] made similar conclusions upon the investigation of the methanediol conformers by NBO methods in combination with Fourier analysis of the dependence of potential energy function of the molecule on the $H-O-C-O$ torsion angle. However, the classical methods could not provide unambiguous explanation for stabilization of methanediol *gauche*-conformers and hence the AIM theory allows a deeper insight into the observed dependences.

V. Atomic energy calculations using experimental data

Unfortunately, to our knowledge, at present the only programme package supporting the atomic energy calculations based on the experimental function $\rho(\mathbf{r})$ is the WinXPRO package,[103] and small occurrence of this programme limits the number of investigations on the considered topic. Nevertheless, a considerable number of papers have already been published to point out two main directions in the investigation of the $E(\Omega)$ experimental values. Within the framework of one of them,[104, 105] the attention is focused on the absolute energies of atoms and the derived total molecular energies; the second direction mainly deals with the relative values of atomic energies.

1. The absolute values of atomic energies

The possibility of obtaining directly the energy of a molecule in a crystal based on experimental data seems quite attractive. This value can be used for the estimation of the crystal packing energy, comparison of polymorphs and investigation of the properties of energetic materials. However, the development of investigations on this topic revealed the drawbacks of this approach.

Attempts to interpret the sum of atomic energies in the molecules of biguanidinium dinitramide[104] and pentaerythrital tetranitrate[105] as the experimentally obtained energy of these molecules were undertaken. Moreover, in the crystals of biguanidinium dinitramide where one can point out the anion and cation the sums of atomic energies for the cation and anion are considered as the true energies of these species in crystal. However, the values obtained by this method are not valuable themselves as the accuracy of the measurement is not known and attempts to compare them with each other allowed only qualitative conclusions to be drawn. In particular, it was shown[104] that the energy of the dinitramide anion in the crystal of diprotonated biguanidinium bis(dinitramide) $[(BIGH_2)(DN)_2]$ [−465.368 (a.u.)] is lower than in the crystal of monoprotonated biguanidinium dinitramide [(BIGH)(DN)] [−462.563 (a.u.)]. However, if one goes on in making conclusions and tries to estimate quantitatively the difference in energy for the anion in two different crystals based on these data, the stabilization energy for dinitramide is equal to 1760 kcal mol^{-1}. It is difficult to imagine that different environment in the crystal exerted such a pronounced influence on the stability of the anion. In a similar way, a comparison of the molecular energy with that obtained by the periodic calculation of the crystal shows that for (BIGH)(DN) the calculated value is lower than the experimental one by 320 kcal mol^{-1}, while for $(BIGH_2)(DN_2)$, on the contrary, it is higher by 2140 kcal mol^{-1}. No reasoning on the calculation method choice in any way was made and the discussion of the fact that the energies obtained by these so different methods in general should not correlate was avoided. This comparison is equivalent to the comparison of the molecular energies obtained by different methods of quantum chemistry and in different basis sets. In the analysis of pentaerythritol tetranitrate molecule analogous problems arose.[105]

It should be noted, however, that in the mentioned papers the detailed analysis of the intra- and intermolecular interactions has been carried out for the considered compounds, the phenomena of the charge transfer and the topological characteristics of the experimental function $\rho(\mathbf{r})$ have been studied. Only the approach to the interpretation of atomic energies based on the experimental data casts doubts.

2. Relative values of atomic energies

An approach that is being developed by the authors of the present review[106, 107] is also based on the calculation of atomic energies from experimental data by the integration of the function $h_e(\mathbf{r})$ over the atomic basin, but implies only consideration of the differences between the energies of atoms in the same crystal, which allows avoiding the mistakes necessarily emerging in the comparison of the results of different experiments. Indeed, as it was shown earlier (see Section II.2), the ambiguity in the comparison of atomic energies emerges even in the comparison of results of the quantum chemical calculations performed by the same method and with the same basis sets.

Wihin the framework of this method the change in the copper atom energy in azurite $[Cu_3(CO_3)_2(OH)_2]$ upon the change in the coordination polyhedron has been determined[106] (Fig. 7). In the unit cell of azurite, two nonequivalent copper atoms are present, which are bound

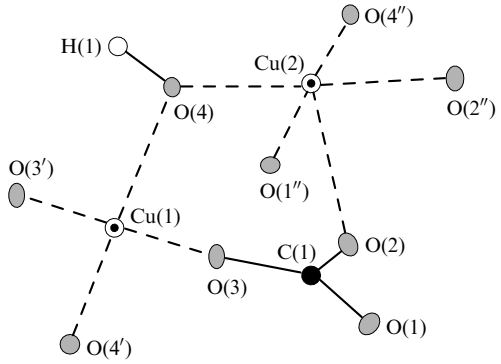


Figure 7. The general view of the crystal structure of azurite.[106]
Atoms are represented with thermal ellipsoids.

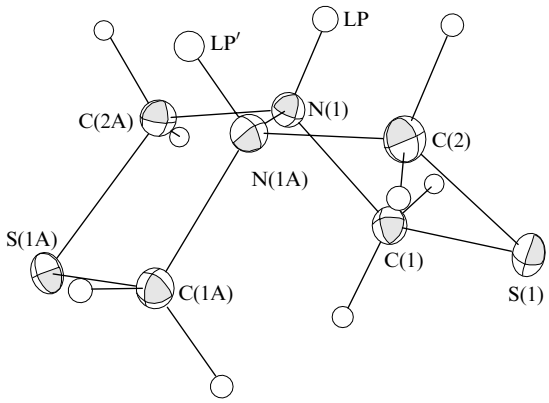


Figure 8. The structure of tetrahydro[1,3,4]thiadiazolo-[3,4-*c*][1,3,4]-thiadiazole molecule.[107]
Atoms are represented with thermal ellipsoids ($p = 50\%$). Hypothetical position of the electron lone pairs are shown as LP and LP′.

todifferent number of oxygen atoms. The coordination polyhedron of the atom Cu(1) is a flat square while that of Cu(2) atom is a distorted tetragonal pyramid with the following Cu – O distances:

Bond	Length /Å	Bond	Length /Å
Cu(1) – O(3)	1.9283(5)	Cu(2) – O(1″)	1.9410(5)
Cu(1) – O(3′)	1.9283(5)	Cu(2) – O(2)	2.3451(5)
Cu(1) – O(4)	1.9440(5)	Cu(2) – O(2″)	1.9338(5)
Cu(1) – O(4′)	1.9440(5)	Cu(2) – O(4)	1.9625(5)
		Cu(2) – O(4″)	1.9861(5)

The multipole refinement of azurite allowed estimating the charge transfer to copper atoms and the energies of their interactions with the oxygen atoms; the copper atoms were found to be similar in these characteristics. However, they differed significantly in the energy: the energy of the penta-coordinated Cu(2) atom was lower by 138.2 kcal mol^{-1}. Although no theoretical investigations of the atomic energy dependence on the coordination polyhedron have been carried out, this value seems to be quite reasonable. It should be noted that the differences in the experimental energies for oxygen atoms in the carbonate anion are also significant (ranging from 30 to 90 kcal mol^{-1}) and follow the same tendency as the total values of the spatial contacts estimated according to the Espinosa – Lecomte scheme.[108, 109]

Another subject for which the relative values of atomic energies have been studied experimentally was tetrahydro[1,3,4]thiadiazolo[3,4-*c*][1,3,4]thiadiazole (Fig. 8).[107] In this compound two topologically equivalent carbon atoms C(1) and C(2) differ in the extent to which they are involved in the stereoelectronic interaction LP – N – C – S, which leads to the differences in their charges and atomic energies. The differences observed in the experiment were semiqualitatively reproduced by the calculation of the molecule in the isolated state. Apparently, the possibility of such an analysis of the experimental data is due to, first of all, the absence of the strong intermolecular interactions in the crystal of the studied compound. Also, a detailed calculation of different conformers of this molecule within the framework of the AIM theory has been carried out, which allowed distinguishing different effects on the energy characteristics and atomic charges in the system. The most significant factor, apart form the stereoelectronic interaction mentioned above, was the repulsion of the electron lone pairs of the nitrogen atoms. It was shown that the methods of the AIM theory can complement the analysis of natural orbitals usually employed for the investigation of the stereoelectronic interactions.

In general, as was shown above, the experimental values of atomic energies can successfully be obtained using high-resolution X-ray diffraction data, while the relative values of atomic energies observed in the experiment can also be reproduced by calculations. However, the peculiarities of the crystal packing also influence the atomic properties in a crystal, which should be taken into account in the analysis.

VI. Atomic electronic moments

Although the atomic volume (V_Ω) is the easiest for calculation of atomic properties

$$V_\Omega = \int_\Omega \mathrm{d}\tau,$$

its interpretation is not evident in the general case. The changes in the molecular volume are typical, for example, of the hydrogen atom upon formation of the hydrogen bond, but steric factors also exert great influence on the atomic volume, which in general makes the discussion of the obtained data difficult.

At the same time the calculation of the atomic charge according to Eqn (2) is also not very complicated, as it assumes just the integration of the function $\rho(\mathbf{r})$ over the atomic basin. The majority of chemists got used to obtaining atomic charges as a result of quantum chemical calculations, hence, the charges calculated by the integration of atomic basins (hereinafter, AIM charges), are much more often mentioned in the literature than any other integral properties of atoms. However, since AIM charges are calculated using different considerations than those according to Mulliken or obtained using decomposition of the wave function of a molecule using natural bond orbital scheme (NBO scheme), their interpretation also sometimes turns out to be not entirely correct.

As it is impossible to cover the entire spectrum of the application of atomic charges in one review, we confine ourselves solely to the most important aspects of the use of

AIM charges and consider some example of the incorrect interpretation of these parameters.

The application of the electron density integral over the volume for the calculation of atomic charge was suggested for the first time by Bader in 1971,[75] but only for the linear molecules: no reliable method to partition the electron density function of complicated molecules into the fragments corresponding to separate atoms existed at that time. However, later Bader suggested and developed the AIM theory, which made such partitioning unambiguous. Back in 1971 he underlined [75] that the obtained charges correspond to the charge transfer solely, while for the description of the molecule behaviour in the external electric field one should account for the electric eigenmoment of atoms as fragments of the electron density function. Thus, for example, the dipole moment of a molecule is made of the 'intrinsic' dipole moments of all atoms and the term responsible for the appearance of the dipole moment in the result of the charge transfer. The contributions of the intrinsic dipole moments of atoms go to zero only in those cases where the electron density distribution around the nuclei is very close to the spherically symmetric one, which corresponds to the case of the ideal ionic compounds. A typical example of such species is the molecule LiF in the gas phase.

The problem of the atomic dipoles was later considered in more detail by Bader *et al.*,[110] who presented the expression for the calculation of the molecular dipole moment based on atomic charges and dipole moments has the form:

$$\mu = \sum_{\Omega} q(\Omega)\mathbf{X}_{\Omega} - \sum_{\Omega} \mu(\Omega),$$

where

$$q(\Omega) = Z_{\Omega} - \int_{\Omega} \rho(\mathbf{r})\mathrm{d}\tau,$$

$\mathbf{X}_{\Omega}$ are the coordinates of the atomic nucleus,

$$\mu(\Omega) = \int_{\Omega} (\mathbf{r} - \mathbf{X}_{\Omega})\rho(\mathbf{r})\mathrm{d}\tau.$$

It is important to mention that such partitioning of the dipole moment of a molecule into the atomic contributions is accurate rather that approximate, in contrast to the fitting of the point charges on atoms for the reproduction of dipole moment.[111] It is most clearly manifested by the investigation of the change in the molecular dipole moments during vibrations since the description of a molecule as a system of the point charges immediately becomes too rough. Moreover, during molecular vibrations the dipole moments and atomic charges also vary; the changes in the charge and atomic dipole moments in silane, methane and ethylene in the harmonic vibrations were considered.[110] On the one hand, the contribution of the changes in atomic properties to the induced dipole moment is not high, but, on the other hand, it cannot be correctly described without recourse to the AIM theory. A traditional scheme for the analysis of stretching vibrations is the decomposition of the molecular dipole moment into the sum of the atomic point charges and the binding dipoles but such decomposition poorly describes the systems with a larger amount of the so-called non-bonded charge density (NBCD). NBCD includes the fragments of the molecular electron density situated at a certain distance from the nuclei and bond lines, in particular, corresponding to the electron lone pairs. From this point of view, the electron density of the π-bond in ethylene is also considered to be non-bonded. The non-bonded electron density can have its own polarization (for example, in the case of ethylene, one is perpendicular to the molecular plane), which cannot be described by the contributions of the bond dipoles.

Problems concerning NBCD are also discussed in a paper,[111] the title of which so precisely reflects the contents that we should cite it: 'Atomic Charges Are Measurable Quantum Expectation Values: A Rebuttal of Criticisms of QTAIM Charges'. Here, in particular, it is underlined that the consideration of AIM charges as 'too big', which can still be found in the literature (see, for example, Refs 112–114), is caused, first of all, by misunderstanding of their nature. Many critics of the AIM charges are trying to interpret them in the same manner as the conventional point charges and state that, for example, these high positive charges lead to the significant overestimation of the quadruple moment of the BF_3 molecule.[115] AIM charges correspond to the charge transfer with in the molecule solely and, as was shown above, cannot be separated from the atomic multipoles upon consideration of the electric moments of a molecule. For example, the atomic charges in CO molecule calculated by QCISD (Quadratic Configuration Interaction with Single and Double Excitations) method according to Bader's theory are equal to $+1.22$ and $-1.22\,e$ respectively, which would lead to the dipole moment of 1.024 D, but the contributions of atomic dipole moments are equal to -0.659 (C) and -0.380 (O) D, which in total leads to an almost zero (0.016 D) dipole moment.[111] As can be seen, the NBCD of the carbon atom in the carbon monoxide is highly polarized and to a great extent defines the dipole moment of the molecule as a whole. The importance of its contribution can be seen by the example of the formaldehyde molecule (CH_2O) in which the charges of the oxygen and carbon atoms are close to those in CO ($\pm 1.24\,e$), but the electron density on the carbon atom is predominantly associated with the hydrogen atoms. This leads to the decrease in the dipole moment of the carbon atom down to -0.35 D and, consequently, to the dramatic increase and even sign reversal for the dipole moment, which is equal to 0.44 D for formaldehyde. Thus, the dramatic increase in the dipole moment of the formaldehyde molecule compared to CO is due not to the increase in the degree of charge transfer, but rather to the reduction in the atomic polarization.

Higher electric moments of atoms are not often discussed in the literature as they are more complicated for the interpretation than the atomic dipoles. One can point out only the fundamental paper by Bader *et al.*[116] devoted to the origin of the rotational barriers and papers by Liem and Popelier [117, 118] on calculations of liquids. Analysis of the quadrupole moments of carbon atoms in ethane showed [116] that the barrier to the rotation in this molecule is caused by the change in the quadrupole polarization of the C–C bond in the eclipsed conformation (E) compared to the staggered one (S). In the E conformation the field of the hydrogen atoms is more pronounced, which results in the shift of the electron density from the C–C bond, weakening of the binding and, consequently, in the elongation of the C–C bond and increase in the energy of the conformer.

Liem and Popelier, in turn, used the decomposition of the molecular electric moments into atomic multipoles (up to hexadecapoles) obtained from the AIM theory for the calculation of the molecular dynamics of liquid HF (Ref. 117) and liquid H_2O (Ref. 118). In these calculations for HF and H_2O molecules the rigid-body approximation was used, while the energy of interaction between molecules was calculated using electrostatic considerations as the Ewald summation containing all possible components of the atomic electric moments of the interacting molecules. This approach allowed reproducing a number of macroscopic properties of these liquids with very high accuracy, for example, the dependence of the density on temperature and pressure and also studying the peculiarities of their three-dimentional structure under different conditions. The developed approach was also applied for the analysis of intramolecular interactions to create new force fields for macromolecules.[119]

VII. Practical aspects of the calculations of integral properties of atoms

The progress of the Bader AIM theory in the recent years followed two main directions: first of all, the development of the theoretical backgrounds, in particular, the development of new methods for the analysis of the electron density distribution in a molecule (*e.g.* the method of localization and delocalizaton indexes[120]), and the development of the calculation methods which facilitate or accelerate gaining information about the molecule.

The calculation of integral properties of atoms of a molecule consists of two stages: derivation of the electron density distribution function $\rho(\mathbf{r})$ and its analysis. As, as a rule, these two stages are performed with different programmes; we shall consider each of them separately.

1. Derivation of the function $\rho(\mathbf{r})$

A standard format for the storage of the function $\rho(\mathbf{r})$ in the analytical representation is the WFN format, which, at present, can be generated by the majority of the programme packages for *ab initio* calculations: in particular, Gaussian (using output = wfn command),[121] Gamess [$control(AIMPAC = .T.) instruction],[122] and also JAGUAR,[123] ADF,[124] QChem,[125] Turbomole[126] and others. Unfortunately, as far as we know from the available documentation, the programme Priroda does not support the export of wave functions into the WFN format, which makes its application virtually impossible for the analysis of molecules by methods of the AIM theory. The majority of programmes for the analysis of wave functions beginning with the original AIMPAC package[127] are oriented to the work with the WFN format. It is necessary to keep in mind that by obtaining the WFN file from the post-Hartree–Fock calculations (in particular, by the MP2 method) Gaussian gives the value of virial for the molecular energy in the Hartree–Fock approximation, which leads to the appearance of 'errors' in the atomic energy values calculated with account of scaling.

However, the derivation of the function $\rho(\mathbf{r})$ in the WFN format requires the preliminary self-consistent field calculation and, ideally, the optimization in the full-electron basis set, which is possible far not for all the systems. It is well known that for systems with a large number of atoms and those containing heavy atoms it is often impossible to avoid using pseudo-potentials. At the same time, there is no unified format of representation of $\rho(\mathbf{r})$ containing pseudopotentials. The only solution is the transition from the analytical representation of $\rho(\mathbf{r})$ to numerical. The most popular format of representation of $\rho(\mathbf{r})$ in the numerical view is CUBE, which contains $\rho(\mathbf{r})$ values in the knots of a three-dimensional network. Analogous formats are, as a rule, convertible into CUBE and the data output in this format is supported by almost all programme packages for quantum chemical calculations. One should specially note that the representation of results in CUBE and related formats is often the only solution in the calculation of crystals by the plane-waves method, in particular, by VASP programme.[128–131]

In the general case, the periodic calculation of crystals can be performed by completely different methods, their diversity is defined by the specifics of this type of calculations, which is not related to the topic of the present review. The most significant programmes for the periodic calculations are TB-LMTO-ASA,[132–135] VASP, Abinit,[136] Wien2k[137] and Crystal.[138] The output formats for all listed programmes differ, and each of them has its own programme for the AIM analysis. These packages differ in the extent of the AIM theory support, but all of them provide basic opportunities, *viz.*, analysis of critical points and integration of the function $\rho(\mathbf{r})$ over the atomic basins. An alternative approach for the derivation of the functions $\rho(\mathbf{r})$ in the crystal calculation is the calculation of the structural factors (which becomes particularly simple in the calculation with the plane-wave method) in combination with the subsequent multipole refinement of the structure using theoretical structural factors and analysis of the function $\rho(\mathbf{r})$ obtained in the multipole approximation (see, *e.g.*, Ref. 139).

2. Analysis of the function $\rho(\mathbf{r})$

The ancestor of all programmes for the analysis of the function $\rho(\mathbf{r})$ by means of Bader's theory is with no doubt the AIMPAC package.[127] The references to this package can also be found in later papers by Bader, but for more than a decade the most developed and effective programme for the analysis of wave function by means of the AIM theory has been the programme package AIMAll written by Keith.[140] Since this package is a logical continuation and development of the AIMPAC package, one can suppose that references to AIMPAC in Bader's papers correspond to the use AIMAll; no separate publications are devoted to it, although it is mentioned *e.g.* in Ref. 42. It should be noted that the usage of the programme AIMAll, which has recently become free, allows the integration over the atomic basins in reasonable time even with weak personal computers. For example, analysis of the acetone molecule by the AIMAll package on a computer with a clock rate of $\sim$2.8 GHz takes no more than 10 min. Such an acceleration (more than 10-fold compared to the AIMPAC package) is due to, first of all, improvements in the algorithm of determination of the atomic basins. AIMAll is capable to calculate virtually all integral properties of atoms described in the literature. In addition, using the input files with the FCK format (an internal format of Gaussian), AIMAll calculates the values of the atomic energies on the basis of correct values of the virial coefficient γ, and can also analyze the results of calculations using f-functions, which cannot be represented in the WFN format. Speaking about programmes that work with WFN format, one should also mention the programme MORPHY98 by Popelier,[141] which

is slower than AIMAll and has not been updated for more than five years, but is more efficient than AIMPAC and AIM2000 packages.[142] The main goal of the latter is the visualization of critical points and a molecular graph obtained by means of Bader's theory; its usage for the integration of atomic basins is also possible but requires unacceptable CPU times.

Programmes that integrate the electron density in numerical form also exist (DGrid,[143] first of all), but one should admit that they all have substantial limitations: they usually allow only search for the critical points and calculation of atomic charges. Programme 'bader' for the calculation of atomic charges based on data in CUBE format also exists, which makes use of an alternative and very effective algorithm allowing determination of charges and atomic basins without the analysis of critical points when the grid of $\rho(\mathbf{r})$ values is sufficiently small [no more than 0.05 (a.u.)].[144]

The programmes working with the experimental function $\rho(\mathbf{r})$ are standing apart. First of all, for the multipole refinement and subsequent analysis, one can use the XD programme package.[145] Second, for a more detailed interpretation of the results of the multipole refinement within the AIM theory one can use the WinXPRO programme,[103] which is substantially more effective, powerful and easy in use than the corresponding module of XD. Both programmes allow calculating the atomic charges and properties in critical points, but in the WinXPRO programme, as was mentioned above, there is a unique function for the calculation of atomic energies.

Summing up, it is possible to conclude that owing to the state-of-the-art hardware and software, analysis of critical points and the calculation of atomic charges within the AIM theory are no longer a problem, regardless of the method used. At the same time, the atomic energies, higher electron moments and other properties of atoms can still be calculated only using the results of calculation with full electron basis sets. Unfortunately, although AIM is widely used for the investigation of organic molecules in the isolated state, there is very little literature examples of the theoretical analysis of organic molecules in crystal with recourse to the AIM theory (see, *e.g.*, Refs 146 – 148).

* * *

Thus, analysis of the integral properties of atoms is a powerful and universal method for the investigation of molecular properties, providing information that is unavailable by other methods.

At the same time, the development of the experimental and theoretical methods, the improvement of the algorithms for the atomic basin determination and integration of atoms alongside with the progress in computers gradually remove any limitations to the application of this method, which gives hope for a substantial increase in the number of both theoretical and experimental papers in this area, in particular, devoted to the analysis of atomic energies.

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