

On the Possibility of Kinetic Energy Density Evaluation from the Experimental Electron-Density Distribution

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(Received 18 March 1996; accepted 2 December 1996)

Abstract

A simple new approach for the evaluation of the electronic kinetic energy density, $G(\mathbf{r})$, from the experimental (multipole-fitted) electron density is proposed. It allows a quantitative and semi-quantitative description of the $G(\mathbf{r})$ behavior at the bond critical points of compounds with closed-shell and shared interactions, respectively. This can provide information on the values of the kinetic electron energy densities at the bond critical points, which appears to be useful for quantum-topological studies of chemical interactions using experimental electron densities.

1. Introduction

Bader's quantum-topological theory (Bader, 1990; Tsirelson & Ozerov, 1996) suggests a powerful approach for chemical-bond analysis in a system. This approach does not rely on a reference density and thus is free of some of the uncertainties of the deformation-electron-density approach for electron-rich atoms (e.g. Savariault & Lehmann, 1980; Dunitz & Seiler, 1983; Dunitz, Schweizer & Seiler, 1983). The definition and classification of the chemical bond in topological analysis are based on the existence of a saddle point (bond critical point) of the total electron density, $\rho(\mathbf{r})$, between neighboring atoms, and on the value of the Laplacian of the total electron density at this point (Bader & Essen, 1984). Additional useful information about chemical-bond type can be obtained from knowledge of the electronic kinetic energy density (or local kinetic density) value, $G(\mathbf{r}_c)$ (Bader & Essen, 1984), and total electronic energy density value, $E_c(\mathbf{r}_c)$ (Cremer & Kraka, 1984), at the bond critical point. The ratio $G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$ should be less than unity and $E_c(\mathbf{r}_c)$ should be negative for a shared interaction (covalent bond), while the former is greater than unity for a closed-shell interaction (ionic, hydrogen or van der Waal's bonds). The energy densities can be easily obtained in a quantum-topological study of the

theoretical electron density. However, this is not the case for the application of this approach to the experimental electron densities obtained by X-ray diffraction. The latter field of application is now rapidly developing (e.g. Kapphann, Tsirelson & Ozerov, 1988; Craven & Stewart, 1990; Destro, Bianchi, Gatti & Merati, 1991; Gatti, Bianchi, Destro & Merati, 1992; Destro & Merati, 1995; Iversen, Larsen, Souhassou & Takata, 1995; Tsirelson, 1996; Tsirelson & Ozerov, 1996) owing to the possibility of analytical representation of the experimental electron density by various multipole models (Hirshfeld, 1971; Stewart, 1976; Hansen & Coppens, 1978), which allow analytical or numerical evaluation of the total electron-density Laplacian and gradient vector field. In the present work, an attempt to develop an approach for the evaluation of electronic kinetic energy density at the bond critical-point region from the experimental electron density is described.

2. Approach

2.1. Description of the problem

Taking into account the complexity of the problem under consideration, we should take advantage of all possible simplifications. The specifics of our case are as follows. We are not particularly interested in the proper description of the short-range or long-range behavior of the kinetic energy density. The former is a core region, which is not so interesting from the point of view of the topological study of chemical bonding in the system. The latter is a region of negligibly small values of kinetic energy density relative to the short- or medium-range contributions at this point from other atoms in the crystal. Thus, we are interested in a fairly simple approach that allows relatively accurate description of the medium-range [~ 1 –4 bohr (1 Bohr radius = $5.291\,772\,249 \times 10^{-11}$ m)] behavior of the kinetic energy density. This is this region where bond critical points lie and redistribution of valence density due to chemical bonding takes place. In the general case, the kinetic energy density of a quantum system can be correctly expressed in terms of the first-order density matrix $\rho(\mathbf{r}, \mathbf{r}')$ in two alternative ways† (Bader

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‡ Atomic units (a.u.) are used throughout the paper.

& Preston, 1969; Tal & Bader, 1978):

$$\begin{aligned} G(\mathbf{r}) &\equiv \text{gt}[\rho(\mathbf{r}, \mathbf{r}')] = \frac{1}{2} \nabla \nabla' \rho(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \\ &= \frac{1}{2} \sum_{i=1}^N |\nabla \varphi_i(\mathbf{r})|^2 \end{aligned} \quad (1)$$

or

$$\begin{aligned} K(\mathbf{r}) &\equiv \text{gk}[\rho(\mathbf{r}, \mathbf{r}')] = -\frac{1}{2} \nabla^2 \rho(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \\ &= -\frac{1}{2} \sum_{i=1}^N \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}), \end{aligned} \quad (2)$$

where $\varphi_i(\mathbf{r})$ is a single-occupied Hartree–Fock (HF) spin orbital of a system with N electrons. The two forms of the kinetic energy density are related to each other by the expression (Bader & Preston, 1969)

$$K(\mathbf{r}) = G(\mathbf{r}) - \frac{1}{4} \nabla^2 \rho(\mathbf{r}). \quad (3)$$

According to the Gauss theorem, $\int \nabla^2 \rho(\mathbf{r}) \, d\mathbf{r} = \int_S \nabla \rho(\mathbf{r}) n(\mathbf{r}) \, d\mathbf{r} = 0$, since both $\rho(\mathbf{r})$ and $\nabla \rho(\mathbf{r})$ are equal to zero on the surface S covering the whole many-electron system. Thus, $K(\mathbf{r})$ and $G(\mathbf{r})$ integrate to yield the same value of the total kinetic energy, T . In this sense, the local kinetic energy yielding the correct value of the total kinetic energy is only defined up to $C * \nabla^2 \rho(\mathbf{r})$, where C is an arbitrary constant.

Although the problem of the reconstruction of the one-electron-density matrix $\rho(\mathbf{r}, \mathbf{r}')$ from $\rho(\mathbf{r})$ obtained from the diffraction experiment has been considered before (Aleksandrov, Tsirelson, Reznik & Ozerov, 1989; Tanaka, 1988; Schmider, Smith & Weyrich, 1992; Howard, Huke, Mallinson & Frampton, 1994), we are going to propose here an alternative less accurate but easier approach for the evaluation of the local kinetic energy density at the bond critical point of the multipole-fitted electron density. A simple approximate way of directly relating the kinetic energy density to the electron density was introduced by the semiclassical Thomas–Fermi equation (March, 1957) with gradient quantum corrections (von Weizsacker, 1935; Kirzhnitz, 1957). Rather good results for the total kinetic energy, T , to within an accuracy of less than 1%, can be obtained for free atoms by using the Thomas–Fermi equation with the second gradient correction according to Kirzhnitz (*e.g.* Wang, Parr, Murphy & Henderson, 1976):

$$\begin{aligned} T &= T_0 + T_2 \\ &= (3/10)(3\pi^2)^{2/3} \int \rho(\mathbf{r})^{5/3} \, d\mathbf{r} \\ &\quad + (1/72) \int [\nabla \rho(\mathbf{r})]^2 / \rho(\mathbf{r}) \, d\mathbf{r}. \end{aligned} \quad (4)$$

The second term here is 1/9 of the original von Weizsacker (1935) correction. It is justified in the long-wave limit (Jones & Young, 1971), corresponding to the smoothly varying charge density, as a valence density

near the bond critical point is. At the same time, the spatial behavior of the kinetic energy density, used in (4), agrees poorly with the HF results (Alonso & Girifalco, 1978*b*; Tal & Bader 1978; Murphy & Parr, 1979), displaying large errors at very small and very large distances from the nucleus. The errors in these regions are of a fundamental nature, being due to the breakdown of the main assumptions of the theory such as the presence of a slowly varying potential (not fulfilled near the nucleus) in a volume of high electron density (not fulfilled far from the nucleus). Cancellation of the errors between these two limiting regions yields good results for the total kinetic energies. On the other hand, Alonso & Girifalco (1978*b*) have paid attention to the necessity to consider the total form of Kirzhnitz's (1957) gradient correction $\text{gk}_2[\rho]$ for the kinetic energy density calculations:

$$\text{gk}_2[\rho] = (1/72)[\nabla \rho(\mathbf{r})]^2 / \rho(\mathbf{r}) - (1/12) \nabla^2 \rho(\mathbf{r}). \quad (5)$$

The second term in (5) integrates to zero and thus is usually not considered in the total kinetic energy calculations. However, its inclusion noticeably improves agreement of the calculated kinetic energy density with the Hartree–Fock density $\text{gk}[\rho]$, as defined by (2). Moreover, the best agreement occurs in the medium-range region, which is of the most interest for us. The kinetic energy density equation (5) can be easily transferred to gt form using (3):

$$\begin{aligned} G(\mathbf{r}) &\equiv \text{gt}[\rho] \\ &= (3/10)(3\pi^2)^{2/3} \rho(\mathbf{r})^{5/3} \\ &\quad + (1/72)[\nabla \rho(\mathbf{r})]^2 / \rho(\mathbf{r}) + (1/6) \nabla^2 \rho(\mathbf{r}). \end{aligned} \quad (6)$$

This equation is twice the first three terms of the expression obtained earlier for the semiclassical expansion of the kinetic energy density defined as twice (1), using the partition-function method (Brack, Jennings & Chu, 1976) and Wigner transform of operators (Grammaticos & Voros, 1979).

In Fig. 1, the results of the various forms of the Thomas–Fermi approach for the kinetic energy densities in the He and Ne atoms are compared with the Hartree–Fock results. It is evident that the use of (6) considerably improves the agreement with the HF density in the valence region. The best agreement, to within 25%, occurs at distances 1–3 bohr from the nuclei. The total kinetic energies are not affected by the Laplacian in (6) and thus, according to Wang, Parr, Murphy & Henderson (1976), differ from the HF values by only 0.59 and –0.54% for He and Ne, respectively. The fourth-gradient correction for the kinetic energy density (Hodges, 1973) being taken into account spoils the $G(\mathbf{r})$ behavior in the long-range region and almost negligibly contributes to the medium-range (~ 0.5 – 2.5 bohr) behavior of the local kinetic energy.

2.2. Testing approach (6) at the bond critical points

In the next step, we compared the results for kinetic energy density G calculated by (6) with HF results at the bond critical points in molecules. For this purpose, we used the published (Bader & Essen, 1984) results of an HF study of the electron density, the Laplacian of the electron density and the local kinetic energy G at the bond critical points in some molecules. According to the definition of the critical point, the gradient of the electron density is equal to zero at this point and the first term of the gradient correction in (6) vanishes. The published data (Bader & Essen, 1984) and data calculated by (6) are presented in Table 1. It is clear from Table 1 that the approach used gives quite good results (within 4%) for the kinetic energy densities at the bond critical points of molecules with closed-shell interactions between corresponding atoms. On the other hand, the results for molecules with shared interactions, though improved by comparison with those calculated by (4), still show large errors. The basic source for the observed disagreement for molecules with shared interactions can

be accounted for by the nonlocal rather than local nature of the kinetic energy density functional of $\rho(\mathbf{r})$ (Alonso & Girifalco, 1978a). That is, in general the value of the kinetic energy density at any point of a system cannot be fully determined only by the value of the charge density at this point, as is stated by the local functional (6). In practice, rather than searching for an unknown nonlocal functional, a partitioning of the charge density is usually applied. The most successful partitioning was suggested in the well known Kohn–Sham orbital model (Kohn & Sham, 1965). Among known simpler partitioning schemes (Ashby & Holzman, 1970; Goodisman, 1970, 1971; Tal & Bader, 1978), the latter seems to be the most favorable. In their work, Tal & Bader suggested the partitioning of $\rho(\mathbf{r})$ into rapidly varying and slowly varying terms. This results in noticeable improvement of the local behavior of the kinetic energy, most of all in the short-range and long-range regions. However, it is easy to find that this model also does not lead to a proper description of the local kinetic energy behavior in the medium-range region of molecules with shared interaction.

2.3. Partitioning scheme

Another partitioning scheme is proposed in the present work. It is expected that its application will improve the results of approach (6) for the medium-range behavior of the kinetic energy density in systems with shared interaction between atoms, while it will not spoil the already satisfactory results for compounds with closed-shell interaction. The consideration of the nonlocality of the kinetic energy density functional of $\rho(\mathbf{r})$ in the new scheme fundamentally differs from that in the scheme proposed by Tal & Bader (1978). It arises from the fact that, although the bonding density is dominant in the internuclear region between atoms displaying shared interaction, its contribution to the local kinetic energy in this region is not dominant (Bader & Preston, 1969; Schwarz, Valtazanos & Ruedenberg, 1985). Indeed, according to the second expression for $gt[\rho(\mathbf{r}, \mathbf{r}')] in (1), the contribution to the local kinetic energy density of the highest occupied σ_g bonding molecular orbital (MO), for which the density distribution displays a maximum between two nuclei in compounds with a shared interaction, is low in this region. It even goes to zero at the point of maximum orbital charge density. On the other hand, the contribution of the highest occupied antibonding MO, σ_u , to $gt[\rho(\mathbf{r}, \mathbf{r}')] in the internuclear region is relatively large owing to the presence of a nodal plane, where the wavefunction is zero. For example, the $3\sigma_g$ and $2\sigma_g$ bonding MOs of the F_2 molecule (Cade & Wahl, 1974), which account for almost 100% (0.29 a.u.) of the charge density at the bond midpoint (bond critical point), display no contribution to the local kinetic energy density at this point. Contrary$$

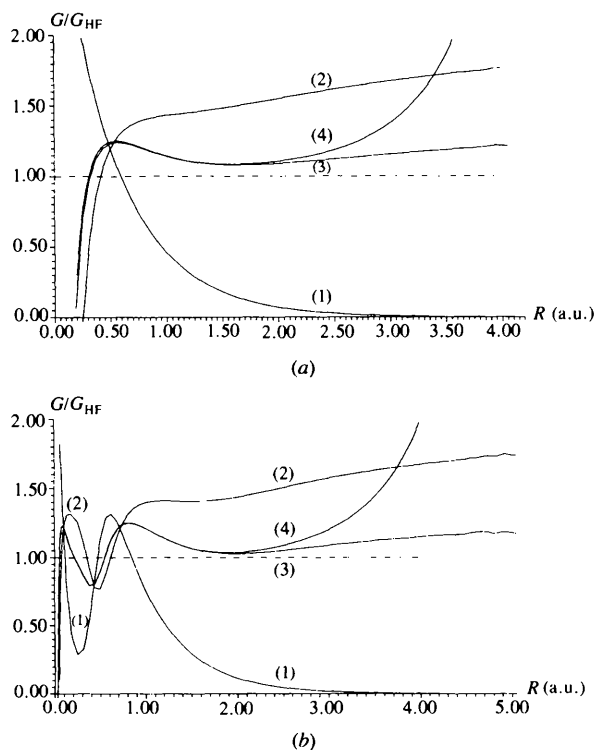


Fig. 1. Comparison of the model kinetic electron energy density distributions, G , with those calculated from Hartree-Fock wave functions, G_{HF} (Clementi & Roetti, 1974) for free (a) He and (b) Ne atoms. (1) $G(\mathbf{r})$ is calculated by the Thomas-Fermi approach; (2) $G(\mathbf{r})$ is calculated by the Thomas-Fermi approach with the second-gradient correction in the form $(1/72)[\nabla\rho(\mathbf{r})]^2/\rho(\mathbf{r})$; (3) $G(\mathbf{r})$ is calculated according to equation (6); (4) $G(\mathbf{r})$ is calculated according to equation (6) with the addition of the fourth-gradient correction according to Hodges (1973).

Table 1. Comparison of Hartree-Fock and model [equations (6), (15)] kinetic energy densities at the bond critical points

All values are in a.u. One atomic unit of density = $6.748 \text{ e } \text{\AA}^{-3}$ and of $\nabla^2 \rho = 24.10 \text{ e } \text{\AA}^{-5}$. Results of the near-Hartree-Fock calculations are taken from Bader & Essen (1984).

Molecule and interaction	<i>R</i>	Results of the theoretical calculations				Results of the model calculations				Promolecule orbitals†
		$\rho(\mathbf{r}_c)$	$\nabla^2 \rho(\mathbf{r}_c)$	$G(\mathbf{r}_c)$	$G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$	From equation (6) $G(\mathbf{r}_c)^\ddagger$	$G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$	From equations (15), (16)* $G(\mathbf{r}_c)^\ddagger$	$G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$	
Closed-shell interactions										
He ₂	3.000	0.0367	0.2501	0.054	1.47	0.053 (2)	1.44			
Ne ₂	3.000	0.1314	1.3544	0.331	2.52	0.323 (2)	2.46			
Ar ₂	4.000	0.0957	0.4455	0.127	1.33	0.132 (4)	1.38			
LiCl	3.825	0.0462	0.2657	0.064	1.39	0.061 (5)	1.32			
NaCl	4.461	0.0358	0.2004	0.047	1.30	0.045 (4)	1.26			
NaF	3.629	0.0543	0.4655	0.105	1.94	0.100 (5)	1.84			
KF	4.104	0.0554	0.3132	0.078	1.41	0.075 (4)	1.35			
MgO	3.305	0.0903	0.6506	0.169	1.87	0.161 (5)	1.78			
Hydrogen bond										
in (H ₂ O) ₂	3.853	0.0198	0.0623	0.016	0.806	0.015 (1)	0.758			
Hydrogen bond										
in (HF) ₂	3.360	0.0262	0.1198	0.027	1.027	0.027 (1)	1.031			
Shared interactions										
H ₂	1.400	0.2728	-1.3784	0.017	0.062	0.100	0.367	-0.020		
B ₂	3.005	0.125	-0.1983	0.050	0.396	0.057 (13)	0.456	0.056 (12)	0.408	<i>sp-sp</i>
N ₂	2.068	0.7219	-3.0500	0.625	0.866	1.160 (86)	1.607	0.659 (5)	0.913	<i>p-p</i>
								0.551 (13)	0.763	<i>sp^{2.7}-sp^{2.7}§</i>
O ₂	2.282	0.5513	-1.0127	0.485	0.88	0.896 (85)	1.625	0.608 (25)	1.103	<i>p-p</i>
								0.509 (5)	0.923	<i>sp^{6.5}-sp^{6.5}§</i>
F ₂	2.680	0.296	0.233	0.255	0.86	0.416 (64)	1.405	0.299 (12)	1.010	<i>p-p</i>
								0.277 (8)	0.936	<i>sp^{27.7}-sp^{27.7}§</i>
CC bond in ethylene										
	2.489	0.3627	-1.1892	0.139	0.383	0.331	0.913	0.149 (7)	0.411	<i>sp²-sp²</i>
CC bond in benzene										
	2.619	0.3268	-1.0134	0.096	0.293	0.276	0.845	0.122 (27)	0.374	<i>sp²-sp²</i>
CC bond in ethane										
	2.886	0.2523	-0.6615	0.049	0.196	0.179	0.709	0.080 (63)	0.317	<i>sp³-sp³</i>
CH bond in CH ₄										
	2.048	0.2770	-0.9784	0.039	0.141	0.175	0.632	0.059 (50)	0.213	<i>sp³-s</i>

* Bonding geometry and unknown positions of the bond critical points are taken from Wiberg, Bader & Lau (1987). † Moduli of percent errors (less than 100%) relative to the theoretical values are shown in parentheses. ‡ Type of overlapping orbitals of atoms *A* and *B* used for promolecule density $\rho_{\text{hyb}}(\mathbf{r})$ construction along the *A-B* bond. Each orbital is singly occupied. § *sp²* hybrids are taken from Foster & Weinhold (1980).

to that, the $2\sigma_u$ antibonding MO, which has a zero density at the bond midpoint, contributes ~ 0.10 a.u. ($\sim 40\%$) to the local kinetic energy at this point. Thus, the accumulation of the charge density at the bond critical point of the compounds with shared interaction does not contribute to the local kinetic energy at this point. Such behavior cannot be accounted for by the dominant first term of (6). On the other hand, the third term, $(1/6)\nabla^2 \rho(\mathbf{r})$, takes into account these quantum effects only partially, with the values of $G(\mathbf{r}_c)$ being considerably overestimated (Table 1) in the compounds with shared interactions, where the contribution of the bonding density is dominant in the internuclear region.

In order to apply this qualitative consideration to the development of a new partitioning scheme, identification of the electron-density term mostly responsible for the discussed nonlocality of the local kinetic energy functional of $\rho(\mathbf{r})$ at the bond critical point is desirable. It is easy to show that this term represents interference

of those atomic orbitals in the molecule that can lead to contributions to the charge density and local kinetic energy in the internuclear region that are opposite in sign, and thus accounts for the nonlocality of the local kinetic energy functional of $\rho(\mathbf{r})$ qualitatively discussed above. Considering for simplicity only two overlapping valence orbitals of interacting atoms, φ_1 and φ_2 , the bonding and antibonding MOs, ψ_b and ψ_a , can be approximated respectively as (McWeeny, 1979)

$$\psi_b = N_b(\varphi_1 + \beta\varphi_2), \quad (7)$$

$$\psi_a = N_a(\varphi_2 - \beta'\varphi_1), \quad (8)$$

where $N_b = (1 + \beta^2 + 2\beta S_{12})^{-1/2}$, $N_a = (1 + \beta'^2 - 2\beta' S_{12})^{-1/2}$ are the normalization coefficients, $S_{12} = \int \varphi_1 \varphi_2 \text{d}\mathbf{r}$ is the overlap integral, β and β' ($0 \leq \beta, \beta' \leq \infty$) measure the 'polarity' of the MOs. The limits $\beta, \beta' \rightarrow 0$ and $\beta, \beta' \rightarrow \infty$ would concentrate MO charge densities entirely on separate atoms: $\psi_b \rightarrow \varphi_1$, $\psi_a \rightarrow \varphi_2$ or $\psi_a \rightarrow \varphi_1$, $\psi_b \rightarrow \varphi_2$, respectively (closed-shell inter-

action). For $\beta, \beta' \approx 1$, the electrons would be equally shared between the two atoms (shared interaction). The corresponding orbital densities and orbital local kinetic energies are

$$\rho_b = n_b |\psi_b|^2 = n_b N_b^2 (\varphi_1^2 + \beta^2 \varphi_2^2 + 2\beta \varphi_1 \varphi_2), \quad (9)$$

$$G_b = \frac{1}{2} n_b |\nabla \psi_b|^2 = \frac{1}{2} n_b N_b^2 (\nabla \varphi_1^2 + \beta^2 \nabla \varphi_2^2 + 2\beta \nabla \varphi_1 \nabla \varphi_2), \quad (10)$$

$$\rho_a = n_a |\psi_a|^2 = n_a N_a^2 (\varphi_2^2 + \beta'^2 \varphi_1^2 - 2\beta' \varphi_1 \varphi_2), \quad (11)$$

$$G_a = \frac{1}{2} n_a |\nabla \psi_a|^2 = \frac{1}{2} n_a N_a^2 (\nabla \varphi_2^2 + \beta'^2 \nabla \varphi_1^2 - 2\beta' \nabla \varphi_1 \nabla \varphi_2), \quad (12)$$

where n_b and n_a are the occupation numbers of the MOs. Taking into account that $\nabla \varphi_1$ and $\nabla \varphi_2$ have opposite signs near the bond critical point along the internuclear vector (Goddard & Wilson, 1972), it is evident from (9)–(12) that in this region the interference term gives a contribution to charge density that is opposite in sign to its contribution to the local electron density for both bonding and antibonding MOs. The total valence-electron kinetic energy density can be represented from (10) and (12) as

$$G = G_b + G_a = \frac{1}{2} [\nabla \varphi_1^2 (n_b N_b^2 + \beta'^2 n_a N_a^2) + \nabla \varphi_2^2 (\beta^2 n_b N_b^2 + n_a N_a^2)] + \nabla \varphi_1 \nabla \varphi_2 (\beta n_b N_b^2 - \beta' n_a N_a^2). \quad (13)$$

Thus, according to (13), the local kinetic energy of the valence electrons in the molecule can be split into two parts. The first term in this equation corresponds to separate contributions from each overlapping atomic orbital before the electrons are spin coupled. The second term corresponds to the net contribution of the constructive interference of these atomic orbitals, leading to molecular-orbital formation. In pure ionic compounds, this term vanishes due to $n_a = 0$ and $\beta \cong 0$ or ∞ , while in the compounds displaying van der Waals bonds or long and intermediate hydrogen bonds this term is negligible owing to the full occupation of both bonding and antibonding MOs and an electrostatic rather than an exchange interaction. On the other hand, in compounds with shared interaction, noticeable contribution of the interference term to the local kinetic energy in the internuclear region takes place.

We propose to take into account approximately the discussed nonlocality of the local kinetic energy functional of $\rho(\mathbf{r})$ at the bond critical point within approach (6) by partitioning the total electron density into a contribution $\rho_{ci}(\mathbf{r})$, arising from the net constructive interference of the overlapping orbitals, and a difference density $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_{ci}(\mathbf{r})$.

$$\rho(\mathbf{r}) = \Delta\rho(\mathbf{r}) + \rho_{ci}(\mathbf{r}). \quad (14)$$

In the proposed model of the kinetic energy density functional G based on this partitioning scheme, both components of the charge density, $\Delta\rho(\mathbf{r})$ and $\rho_{ci}(\mathbf{r})$, are considered separately in the first term of (6), while Kirzhnits's gradient quantum correction [terms 2 and 3 of (6)] is applied to the total electron density $\rho(\mathbf{r})$:

$$G(\mathbf{r}) \equiv \text{gt}[\rho] = (3/10)(3\pi^2)^{2/3} [\Delta\rho(\mathbf{r})^{5/3} + \rho_{ci}(\mathbf{r})^{5/3}] + (1/72)[\nabla\rho(\mathbf{r})]^2/\rho(\mathbf{r}) + (1/6)\nabla^2\rho(\mathbf{r}). \quad (15)$$

2.4. Approximate isolation of the net constructive interference contribution to the total charge density

Low & Hall (1990) isolated the net contribution of constructive interference of bonding orbitals to the total charge density by subtracting the generalized valence-bond (Cooper, Gerratt & Raimondi, 1987) pair promolecule from the total charge density of the molecule. Such a promolecule is believed to preserve the orientation, polarization, electron promotion, orbital hybridization and delocalization (including charge transfer) effects of atomic charge density in the molecule. The earlier use of a promolecule constructed from valence-state hybrid atoms (Kunze & Hall, 1986, 1987) did not preserve the delocalization effect.

A thorough approach for construction of a reference procrystal density from the optimally orientated, occupied and shaped degenerate or quasidegenerate atomic ground states by adjusting to experimental structure-factor data was developed by Ruedenberg & Schwarz (1990). The difference between experimental and procrystal densities, which reflects the orbital interference effect in the interatomic region, was called the chemical deformation density.

We propose that, for our task of semi-quantitative evaluation of the local electronic kinetic energy at the bond critical point from the experimental electron density, the use of a promolecule $\Delta\rho(\mathbf{r}) \equiv \rho_{hyb}(\mathbf{r})$ constructed from the superposition of maximum-overlap hybrid atoms (Pauling, 1961) is the most favorable for the isolation of the net constructive interference contribution to the electron density at this point:

$$\rho_{ci}(\mathbf{r}) = \rho(\mathbf{r}) - \rho_{hyb}(\mathbf{r}). \quad (16)$$

The following method of procrystal (promolecule) construction is suggested for atoms with sp valence states:

(i) The non-equivalent hybrid orbital model should be applied for atoms in the general form

$$h_\lambda(\theta) = N(s + \lambda^{1/2}p_\theta), \quad (17)$$

where $h_\lambda(\theta)$ is the sp^λ hybrid atomic orbital, p_θ is any normalized combination of the three p orbitals pointing in the direction θ , N is a normalizing constant and

λ (generally noninteger) reflects the degree of s and p orbital mixing. The type and order of the orbital hybridization can be determined by the angles between aspherical valence atomic densities (Coulson, 1952). Zero atomic orbital hybridization displaying only oriented ($\lambda \sim 100$) atomic valence-density distribution can occur as a particular case as well. However, for simplicity, the notation 'hybrid' will be applied below for any valence orbital of atoms in the procrystal (promolecule).

(ii) The procrystal valence density can be constructed from the corresponding sp^λ 'hybrid' atomic orbitals using tabulated atomic (ionic) wavefunctions (Clementi & Roetti, 1974). An sp^λ 'hybrid' model of an atom in the crystal can be introduced in terms of the refined multipole model (Takazawa, Ohba & Saito, 1989) as well and occupation of the 'hybrid' orbitals can be determined from the multipole parameters obtained (Okuda, Ohba, Saito, Ito & Shibuya, 1990). However, one should remember that, although the multipole model expresses the crystal charge density with a linear combination of one-center real spherical harmonics, it describes two-center contributions, such as the constructive interference density, together with all other (orientation, polarization, hybridization and delocalization) contributions. That is why the use of tabulated average free-atom orbital exponents ξ (Clementi & Raimondi, 1963) appears to be more favorable for one-center 'hybrid' model construction than refined values, which are affected by the orbital interference density.

(iii) Delocalization (charge-transfer) effects can be approximately induced in the procrystal density through the setting of the occupation numbers of the 'hybrid' orbitals. This can be done by taking into account the tendency of the charge transfer reflected by the atomic monopole populations obtained from the multipole refinement, independent results, chemical intuition and general considerations. For example, the occupation of the promolecular 'hybrid' orbitals, describing the lone-pair charge density in a molecule or crystal, should be equal to $2e$; the joint occupation of the two overlapping 'hybrid' orbitals of neighboring atoms should not be more than $2e$ and the electroneutrality condition should be preserved for the whole crystal.

It is evident that for crystals with closed-shell interactions, where the asphericity of the charge density should be small, the promolecule charge density constructed according to (i)–(iii) above is close to the crystal density. In this case, according to (16), $\rho_{ci}(\mathbf{r})$ is negligible relative to the total charge density and one can directly use (6) for kinetic energy density evaluation.

The application of the described partitioning scheme to compounds displaying shared interaction results in a generally significant improvement of the calculated kinetic energy densities at the bond critical points (see Table 1). Two different 'hybrid' promolecule models were independently applied for the diatomic molecules N_2 , O_2 and F_2 . The first model is simply an oriented-

atom model with no sp hybridization. In this case, the configuration of the atomic orbitals oriented along the internuclear bond is $2p^1$. The other model uses results of a published (Foster & Weinhold, 1980) theoretical study. The sp hybridization in this model reflects the non-bonded Pauli repulsion acting on the occupied atomic $1s$ and $2s$ orbitals in the molecule. As a result, the bonding hybrid orbital has high p character and the lone pair behind the nuclei has high s character in the molecules. It can be seen from Table 1 that the use of the oriented-atom approximation without hybridization for promolecule construction leads to satisfactory agreement with the HF values for G at the bond critical points. However, the use of the 'hybrid' O_2 and F_2 promolecules results in a qualitative improvement of the $G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$ values. The largest disagreement with the theoretical data for the shared interaction occurred in the cases of the C—C bond in ethane and the C—H bond in methane. The latter case is quite understandable, taking into account that the light H atom is the worst object for the application of the statistical approach (6).

3. Some experimental results and discussion

The suggested method of the evaluation of the local kinetic energy at the bond critical point of the experimental charge density was applied to the NaF, MgO, C_2H_4 and C_2H_2 molecules, constructed using the model parameters obtained from the multipole refinement of X-ray single-crystal diffraction experiments. Only spherically symmetric terms of the pseudoatom charge densities are significant for the NaF and MgO crystal models. In this series of compounds, the chemical bond displays both the closed-shell (NaF and MgO) and the shared (C_2H_4 and C_2H_2) nature. A bond critical-point search and calculation of the properties of charge density at these points in the NaF and MgO molecules was performed using the program *LSPROP* (Howard & Mallinson, 1992). Experimental charge density and its Laplacian at the bond critical points in the C_2H_4 and C_2H_2 molecules were taken from Kapphann, Tsirelson & Ozerov (1988). The results obtained are compared, along with the results for the independent-atom (IAM) and independent-ion (IIM) models, with the published theoretical calculations for corresponding molecules in Table 2. Theoretical and experimental values of charge density and its Laplacian show quantitative and semi-quantitative agreement, respectively, at the critical points of all molecular densities studied. The worst agreement is observed for ethylene. The calculated local kinetic energies at the bond critical points appeared to be in the quantitative (within 6% for MgO) and semi-quantitative (within 15% for NaF, 20% for C_2H_4 and 27% for C_2H_2) agreement with the theoretical values. This is in general accordance with the observed accuracy of the suggested method in application to the theoretical molecular densities (Table 1).

Table 2. Comparison of bond critical-point properties of experimental and theoretical molecular charge densities

Experimental molecular charge densities are constructed using model parameters received from the multipole refinement of single-crystal X-ray data. Only spherically symmetric terms of the pseudoatom charge densities are significant for the NaF and MgO density models. All values are in a.u.

Molecule	Bond	R	$\rho(\mathbf{r}_c)$	$\nabla^2\rho(\mathbf{r}_c)$	$G(\mathbf{r}_c)$	$G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$	Model for $G(\mathbf{r}_c)$ calculation*
NaF, theory†	Na—F	3.629	0.05	0.47	0.11	1.94	
NaF, exp.‡	Na—F	3.629	0.05	0.41	0.09	1.69	Equation (6)
NaF, IAM§	Na—F	3.629	0.06	0.41	0.09	1.64	Equation (6)
MgO, theory†	Mg—O	3.305	0.09	0.65	0.17	1.87	
MgO, exp.¶	Mg—O	3.305	0.09	0.65	0.16	1.80	Equation (6)
MgO, IAM	Mg—O	3.305	0.08	0.64	0.15	1.88	Equation (6)
Mg ⁺ O ⁻ , IIM**	Mg—O	3.305	0.09	0.64	0.16	1.80	Equation (6)
C ₂ H ₄ , theory††	C=C	2.489	0.37	-1.22	0.15	0.41	
C ₂ H ₄ , exp.‡‡	C=C	2.525	0.32	-0.69	0.18	0.56	Equations (15), (16) sp^2-sp^2
C ₂ H ₄ , IAM	C=C	2.525	0.24	-0.21	0.21	0.85	Equations (15), (16) sp^2-sp^2
C ₂ H ₂ , theory††	C≡C	2.239	0.42	-1.28	0.33	0.79	
C ₂ H ₂ , exp.‡‡	C≡C	2.236	0.42	-1.30	0.24	0.57	Equations (15), (16) $sp-sp$
C ₂ H ₂ , IAM	C≡C	2.236	0.30	-0.59	0.26	0.84	Equations (15), (16) $sp-sp$

*Types of overlapping singly occupied orbitals used for promolecule density $\rho_{\text{hyb}}(\mathbf{r})$ construction along the bond are presented for model (16). †Bader & Essén (1984). ‡Su & Coppens (1995). §Independent atomic model. ¶Abramov, Avilov, Belokoneva, Kitaneh, Feil, Tsirelson & Okamura (1995); Tsirelson, Avilov, Abramov, Belokoneva, Kitaneh & Feil (1997). **Independent ionic model. The IIM model of the NaF molecule almost coincides with the experimental multipole model and is not considered separately here. ††Cremer & Kraka (1984). ‡‡Kapphann, Tsirelson & Ozerov (1988).

The values of $\rho(\mathbf{r}_c)$, $\nabla^2\rho(\mathbf{r}_c)$, $G(\mathbf{r}_c)$ and $G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$ obtained from the experimental charge density (Table 2) adequately reflect the change of the nature of the chemical interaction in this series of molecules: from the ionic Na—F and Mg—O to the strong covalent C=C and C≡C.

The calculated values of the electronic kinetic energy density at the bond critical points of the IAM and IIM charge densities (Table 2) appear to be rather close to the corresponding experimental and theoretical values. The agreement between IAM and theoretical values of $G(\mathbf{r}_c)$ is worse by $\sim 6\%$ (for MgO) and by $\sim 20\%$ (for C₂H₄) and better by $\sim 6\%$ (for C₂H₂) than that between corresponding experimental and theoretical values. The IAM value of $G(\mathbf{r}_c)$ in the NaF molecule is almost the same as the experimental one.

The reason for such behavior of the calculated local kinetic energies at the bond critical points of IAM (and IIM for MgO) charge densities is different for ionic and covalent molecules. In the former case, the position of the (3, -1) critical point, the charge density and its Laplacian at this point of IAM and IIM densities are close to the corresponding experimental and theoretical values (Table 2). Consequently, the calculated [by (6)] experimental and IAM or IIM values of $G(\mathbf{r}_c)$ appear to be also close to each other. This is not the case for molecules with shared interaction where charge density and its Laplacian at the bond critical points of IAM densities differ noticeably from those values in the experimental and theoretical molecular charge densities (Table 2). Resulting rather close correspondence of the IAM values of $G(\mathbf{r}_c)$ to those obtained from the experimental charge densities and from the theoretical calculations can be accounted for by the cancellation

of the contributions from the underestimated values of $\rho(\mathbf{r}_c)$ and the overestimated values of $\nabla^2\rho(\mathbf{r}_c)$ (Table 2) in (15). However, the obtained semi-quantitative agreement between theoretical and IAM values of $G(\mathbf{r}_c)$ for compounds with shared interactions should be considered as accidental. For example, for F₂ and N₂ molecules, the disagreement between the IAM values of $G(\mathbf{r}_c)$ calculated by (15), using $F[p_x^2p_y^2(sp_{-z}^{0.04})^2(sp_z^{27.7})^1]$ and $N(s^2p_x^1p_y^1p_z^1)$ promolecular densities, and the corresponding theoretical values (Table 1) is 93 and 138%, respectively.

It is necessary to note that the molecular experimental charge density constructed from the multipole parameters obtained from the diffraction experiment is already affected by the crystal-field effect and by the intramolecular interactions. This means that the most correct study of the applicability of the suggested model of the evaluation of the local electronic kinetic energy at the bond critical point should be performed by comparison of the results for the experimental crystal charge densities with those derived from the accurate theoretical study of the corresponding periodic systems. This will be the subject of following studies.

Careful consideration of the error analysis in the $G(\mathbf{r}_c)$ values derived from the multipole charge density by the suggested method will be the subject of the forthcoming study. Here we should like to outline the following aspects of this problem. The biggest contribution to the systematic error in $G(\mathbf{r}_c)$, equations (6) and (15), is expected to be due to the $\nabla^2\rho(\mathbf{r}_c)$ term. Indeed, in the reciprocal space, the Laplacian of the charge density displays dependence on $(\sin\theta/\lambda)^2$ (Stewart, 1979). Thus, the use of the truncated observed structure-factor set would affect the multipole parameters (and the Laplacian

of the charge density derived from these parameters) through the least-squares fitting. However, this is mostly important for the proper description of the regions with the rapidly varying Laplacian, *i.e.* core regions, while for our task only the valence region is of main interest. Another source of error in the experimental charge density and especially in its Laplacian is that these values are affected by thermal atomic motions in crystals and in fact refer to the mean thermal nuclear distribution (Tsirelson & Ozerov, 1996). This is most pronounced for the covalent interactions, which are worst described by the rigid-atom model usually used for X-ray diffraction refinement. However, comparative topological studies of the theoretical and experimental charge densities of the compounds displaying shared interactions (Abramov & Okamura, 1996; Tsirelson, 1996) revealed that atomic thermal-motion effects are not crucial for the possibility of quantitative and semiquantitative evaluation of the respective charge density and its Laplacian at the bond critical point from a highly accurate X-ray diffraction experiment. Such accuracy does not seem to be limiting for the semiquantitative evaluation of the local kinetic energy at the bond critical point of the accurate experimental charge density by the suggested method.

4. Conclusions

A new approach for determination of the electronic kinetic energy density G based on the partitioning of electron density is proposed in the present study. The application of this method to the theoretical and experimental (multipole) charge densities shows that it allows a quantitative and a semi-quantitative description of G in the internuclear regions, in particular at the bond critical points, of compounds displaying closed-shell and shared interatomic interactions, respectively. This information appears to be important for chemical-bond study by the quantum-topological analysis of experimental charge densities in, for example, a series of related compounds.

The error analysis in $G(\mathbf{r})$ as derived from experimental data by (6) and (15) and comparative study of the results of the suggested method for the experimental charge densities and those obtained by an accurate theoretical study of the corresponding periodic systems will be the subjects of forthcoming studies.

Support of this work by the Science and Technology Promotion Fund is gratefully acknowledged. The author is also grateful to anonymous referees for helpful comments.

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