Binding Entropy and Its Application to Solids

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The concept of binding entropy is introduced and information theoretical approach is combined with orbital-free density functional theory. It is shown that binding entropy expresses the deviation of the molecular electron density from the promolecular density and the deviation of the molecular kinetic energy density from the promolecular kinetic energy density. The change of the kinetic energy density during the chemical bond formation explicitly appears in the binding entropy expression. The binding entropy and binding entropy density are analyzed using experimental electron density for solid germanium, gallium arsenide and dinitrogen tetroxide. It is demonstrated that the binding entropy joined with deformation electron density and "deformation" kinetic energy density, carries information about both the bonding and binding details and provides a deeper insight into the nature of chemical bond. Atomic and global binding entropies also appeared to be useful descriptors giving a compact description of chemical binding.

1. Introduction

Information measures have a growing importance in various fields of science. Shannon,[1] Fisher,[2] and Rényi[3] information has already been applied in atomic and molecular physics.[4−45] Several useful quantities have been introduced on information theoretical backgrounds. In particular, Ghosh, Berkowitz, and Parr (GBP)[46] developed the concepts of local temperature and entropy of electron distribution. Extending the GBP theory, Nagy and Parr[47] gave an alternative proof of Teller's theorem,[48,49] that there is no chemical binding in the Thomas−Fermi theory.[50] In this work, we make a next step: we introduce the concept of binding entropy and describe its application to solids. Our approach unifies the information theory and density functional theory (DFT) and employs the electron density extracted from the accurate X-ray diffraction experiments, as it was suggested ref 51. In this way, we avoid computation of the crystalline wave function by using the orbital-free electron density functionals to compute the local and global binding entropies. Besides, the theoretical and experimental results are maximally combined in our approach. As we will show, that provides a deeper insight into the chemical binding in solids.

The paper is organized as follows. In section 2, the theory of local temperature and local entropy is summarized. Section 3 presents the concept of binding entropy and section 4 describes how the electron density extracted from the accurate X-ray diffraction experiments can be applied to the computations of binding entropy. The last section is devoted to numerical illustrations and discussion.

2. Information Theoretical Approach to Local Temperature and Local Entropy

The GBP theory employs the information theoretical approach. The fundamental quantity of the GBP theory is the electron density, $\rho(\mathbf{r})$. Besides the electron density, there are several local (**r**-dependent) quantities that proved to be very useful in studying the chemical binding. Among them are the local temperature and the local entropy of the electron distribution.

A system of N electrons moving independently in a local external potential $v(\mathbf{r})$ is studied, and the density functionals are considered as averages in the phase space. A phase-space distribution function $f(\mathbf{r},\mathbf{p})$, describing the distribution of electrons over coordinates and momenta, is introduced. It displays the following properties:

$$\rho(\mathbf{r}) = \int d\mathbf{p}\, f(\mathbf{r},\mathbf{p}) \qquad (1)$$

$$\int d\mathbf{r}\, \rho(\mathbf{r}) = N \qquad (2)$$

and

$$t_s(\mathbf{r}) = \int d\mathbf{p} \left(\frac{\mathbf{p}^2}{2}\right) f(\mathbf{r},\mathbf{p}) \qquad (3)$$

$t_s(\mathbf{r})$ is the noninteracting electron kinetic energy density and **p** is an electron momentum. The corresponding global quantity is the noninteracting electronic kinetic energy, E_{kin}:

$$E_{kin} = \int d\mathbf{r}\, t_s(\mathbf{r}) \qquad (4)$$

The entropy density, $s(\mathbf{r})$, associated with the electron distribution, is defined in terms of $f(\mathbf{r},\mathbf{p})$ as

$$s(\mathbf{r}) = -k \int d\mathbf{p}\, f(\mathbf{r},\mathbf{p})[\ln f(\mathbf{r},\mathbf{p}) - 1] \qquad (5)$$

where k is the Boltzmann constant. The corresponding global entropy S is

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$$S = \int \mathrm{d}\mathbf{r}\, s(\mathbf{r}) \tag{6}$$

There are several distribution functions $f(\mathbf{r},\mathbf{p})$ satisfying the marginal conditions.[1-3] The most probable distribution function is obtained by maximizing the entropy subject to the constraints of correct density, eq 1, and correct kinetic energy, eq 3. This distribution function has the form

$$f(\mathbf{r},\mathbf{p}) = \mathrm{e}^{-\alpha(\mathbf{r})}\mathrm{e}^{-\beta(\mathbf{r})\mathbf{p}^2/2} \tag{7}$$

where $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ are $\mathbf{r}$-dependent Lagrange multipliers. The local temperature, $T(\mathbf{r})$, is defined in terms of the kinetic energy density by the ideal gas expression

$$t_s(\mathbf{r},\rho) = \frac{3}{2}\rho(\mathbf{r})kT(\mathbf{r}) \tag{8}$$

This definition implies that the electrons are considered to move independently in a local potential field (noninteracting electron system). Equations 3, 7, and 8 lead to

$$\beta(\mathbf{r}) = 1/kT(\mathbf{r}) \tag{9}$$

and

$$f(\mathbf{r},\mathbf{p}) = [2\pi kT(\mathbf{r})]^{-3/2}\rho(\mathbf{r})\mathrm{e}^{-\mathbf{p}^2/2kT(\mathbf{r})} \tag{10}$$

Finally, for the entropy density we obtain the Sackur–Tetrode equation[46]

$$s(\mathbf{r}) = -k\rho(\mathbf{r})\ln\rho(\mathbf{r}) + \frac{3}{2}k\rho(\mathbf{r})\ln T(\mathbf{r}) + \frac{1}{2}k\rho(\mathbf{r})[5 + 3\ln(2\pi k)] \tag{11}$$

Note that the local entropy (11) is different from the thermodynamic entropy: thermodynamic properties are zero for the electronic ground state, whereas local function $s(\mathbf{r}) \geq 0$ is $\mathbf{r}$-dependent.

The expression (11) can be rewritten[46,47] as

$$s(\mathbf{r}) = \frac{3}{2}k\rho(\mathbf{r})\left\{\ln\left[\frac{t_s(\mathbf{r})}{t_{\mathrm{TF}}(\mathbf{r})}\right] + c\right\} \tag{12}$$

where the Thomas–Fermi kinetic energy density of electrons is

$$t_{\mathrm{TF}}(\mathbf{r}) = c_{\mathrm{TF}}\rho(\mathbf{r})^{5/3} \tag{13}$$

and the constants are

$$c = \frac{5}{3} + \ln\left(\frac{4}{3}\pi c_{\mathrm{TF}}k\right) \tag{14}$$

and

$$c_{\mathrm{TF}} = \frac{3}{10}(3\pi^2)^{2/3}. \tag{15}$$

From eq 12 we readily obtain for the Thomas–Fermi entropy density

$$s_{\mathrm{TF}}(\mathbf{r}) = \frac{3}{2}kc\rho(\mathbf{r}) \tag{16}$$

and the global Thomas–Fermi entropy

$$S_{\mathrm{TF}} = \frac{3}{2}kcN \tag{17}$$

3. Binding Entropy

When atoms A and B form a molecule AB, the energy of the molecule E^{AB} is smaller than the sum of the energies of the separate atoms $E_{\mathrm{A}} + E_{\mathrm{B}}$. The difference $E^{\mathrm{AB}} - (E_{\mathrm{A}} + E_{\mathrm{B}})$ is the binding energy. Now, we define the binding entropy and the binding entropy density as

$$S_{\mathrm{b}} = \int \mathrm{d}\mathbf{r}\, s_{\mathrm{b}}(\mathbf{r}) \tag{18}$$

and

$$s_{\mathrm{b}}(\mathbf{r}) = s(\mathbf{r}) - s_{\mathrm{prom}}(\mathbf{r}) \tag{19}$$

where $s(\mathbf{r})$ and $s_{\mathrm{prom}}(\mathbf{r})$ are the entropy densities of the molecule and the promolecule, respectively. Using the analogy with the definition of the promolecule (or procrystal),[52] we define $s_{\mathrm{prom}}(\mathbf{r})$ as the sum of the local entropies of the atoms placed in the real atomic positions. From eq 12, the local binding entropy has the form

$$s_{\mathrm{b}}(\mathbf{r}) = \frac{3}{2}k\left[\rho(\mathbf{r})\ln\frac{t_s(\mathbf{r})}{t_{\mathrm{TF}}(\mathbf{r})} - \rho_{\mathrm{prom}}(\mathbf{r})\ln\frac{t_{\mathrm{s,\,prom}}(\mathbf{r})}{t_{\mathrm{TF,\,prom}}(\mathbf{r})} + c\delta\rho(\mathbf{r})\right] \tag{20}$$

where $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_{\mathrm{prom}}(\mathbf{r})$ is called the deformation electron density.[53] The last term does not contribute to the total binding entropy, as both $\rho(\mathbf{r})$ and $\rho_{\mathrm{prom}}(\mathbf{r})$ are isoelectronic and integrate to the number of electrons. Therefore, the global binding entropy (18) can be now presented as

$$S_{\mathrm{b}} = \frac{3}{2}k\int \mathrm{d}\mathbf{r}\left[\rho(\mathbf{r})\ln\frac{t_s(\mathbf{r})}{t_{\mathrm{TF}}(\mathbf{r})} - \rho_{\mathrm{prom}}(\mathbf{r})\ln\frac{t_{\mathrm{s,\,prom}}(\mathbf{r})}{t_{\mathrm{TF,\,prom}}(\mathbf{r})}\right] \tag{21}$$

It is expected[54] that the sum of the global S values for the separated atoms is always greater than their sum when they form the molecule, i.e., S_{b} is always negative. In terms of information theory,[29] that corresponds to the statement that the information related to the electron distribution in a molecule is greater than the information that the promolecule can contain.

Using eq 11, the entropy S can be also presented as[46]

$$S = -kN \int g(\mathbf{r}) \ln \frac{g(\mathbf{r})}{f(\mathbf{r})} \, d\mathbf{r} - NK \tag{22}$$

where the distribution functions $g(\mathbf{r})$ and $f(\mathbf{r})$ are normalized to unity:

$$g(\mathbf{r}) = \rho(\mathbf{r})/N \tag{23}$$

$$f(\mathbf{r}) = aT(\mathbf{r})^{3/2} \tag{24}$$

a is defined with the normalization condition

$$a \int T(\mathbf{r})^{3/2} \, d\mathbf{r} = 1 \tag{25}$$

and

$$K = k\left[\ln(\mathrm{Na}) - \frac{3}{2}\ln(2\pi k) - \frac{5}{2}\right] \tag{26}$$

The first term in eq 22 is related with the so-called relative entropy $I(g,f)$[55] (also called cross-entropy or Kullback–Leibler distance) associated with two probability density functions $g(\mathbf{r})$ and $f(\mathbf{r})$:

$$I(g,f) = \int g(\mathbf{r}) \ln \frac{g(\mathbf{r})}{f(\mathbf{r})} \, d\mathbf{r} \tag{27}$$

The relative entropy is a measure of the deviation of function $g(\mathbf{r})$ from the reference density $f(\mathbf{r})$. So the global entropy, an integral of eq 11, can be expressed with the relative entropy (27) as

$$S = -kNI(g,f) - NK. \tag{28}$$

$I(g,f) = 0$ for the homogeneous electron gas. Consequently, I and therefore S measure the deviation of the electron distribution from the homogeneous electron gas.

The binding entropy is the difference of the relative entropies of the molecule and the promolecule:

$$S_b = -kN[I(g,f) - I(g_{\mathrm{prom}},f_{\mathrm{prom}})] \tag{29}$$

$S_b < 0$ and relative entropy, $I > 0$; that implies that the deviation from the homogeneous electron gas increases during the formation of a molecule.

The substitution $\rho_{\mathrm{prom}}(\mathbf{r})$ for $\rho(\mathbf{r}) - \delta\rho(\mathbf{r})$ in the second term of eq 20 yields

$$s_b(\mathbf{r}) = \frac{3}{2}k\rho(\mathbf{r})\left[\ln \frac{t_s(\mathbf{r})}{t_{s,\,\mathrm{prom}}(\mathbf{r})} - \ln \frac{t_{\mathrm{TF}}(\mathbf{r})}{t_{\mathrm{TF,prom}}(\mathbf{r})}\right] + \frac{3}{2}k\delta\rho(\mathbf{r})\left[\ln \frac{t_{\mathrm{s,prom}}(\mathbf{r})}{t_{\mathrm{TF,prom}}(\mathbf{r})} + c\right] \tag{30}$$

Taking into account eq 13, we obtain

$$s_b(\mathbf{r}) = \frac{3}{2}k\rho(\mathbf{r})\left[\ln \frac{t_s(\mathbf{r})}{t_{\mathrm{s,prom}}(\mathbf{r})} - \frac{5}{3}\ln \frac{\rho(\mathbf{r})}{\rho_{\mathrm{prom}}(\mathbf{r})}\right] + \frac{3}{2}k\delta\rho(\mathbf{r})\left[\ln \frac{t_{\mathrm{s,prom}}(\mathbf{r})}{t_{\mathrm{TF,prom}}(\mathbf{r})} + c\right] \tag{31}$$

The first term expresses the deviation of the molecular electron density from the promolecular density and the deviation of the molecular kinetic energy density from the promolecular kinetic energy density. The second term is proportional to the change in the electron density. It is interesting that the change in the kinetic energy density during the bond formation explicitly appears in the binding entropy expression. Of course, in the density functional theory every quantity is a functional of the density; however, the kinetic energy density is an unknown, very complicated functional of the electron density (see, for example, discussion in ref 56). That is why the evident link between the binding entropy and the kinetic energy density change resulting from the bond formation is important. Because the deformation electron density is linked with the electrostatic forces acting on the nuclei,[57] we can conclude that the binding entropy carries information about both bonding and binding effects.

We can rewrite the expression (31) in terms of the normalized distribution functions $f(\mathbf{r})$ and $g(\mathbf{r})$. For that, we insert eqs 8 and 13 to the last term in eq 31 and use eqs 23 and 24. The result is

$$s_b(\mathbf{r}) = -kN\left[g\left(\ln \frac{g(\mathbf{r})}{g_{\mathrm{prom}}(\mathbf{r})} - \ln \frac{f_s(\mathbf{r})}{f_{\mathrm{s,prom}}(\mathbf{r})}\right)\right] - N\delta g\left[K + k \ln \frac{g_{\mathrm{prom}}(\mathbf{r})}{g_{\mathrm{s,prom}}(\mathbf{r})}\right] \tag{32}$$

The term $\ln[g(\mathbf{r})/g_{\mathrm{prom}}(\mathbf{r})]$ expresses the surprise of obtaining the final distribution function $g(\mathbf{r})$, provided the distribution $g_{\mathrm{prom}}(\mathbf{r})$ is given. The term $\ln[f_s(\mathbf{r})/f_{\mathrm{s,prom}}(\mathbf{r})]$ has a similar meaning. Because of the different signs, these terms show the opposite trends. Thus, if we integrate eq 32, the first term in eq 30 yields the average of the difference in two surprisals.

4. The Binding Entropy in Terms of Experimental Electron Density

The application of the approach presented above to solids can be realized using two different ways. One of them consists of the calculation of the crystalline wave function in orbital approximation by means of the Hartree–Fock, post-Hartree–Fock, or Kohn–Sham methods followed by computing the entropy. Another one employs the approximate functionals developed in the DFT, which explicitly link the kinetic energy density to the electron density.[58] Unlike the orbital scheme, such an approach avoids the variational determination of the wave function. In particular, the kinetic energy density, which appears in eqs 20 and 21, can be approximated according to Kirzhnits[59] by means of electron density and its derivatives as

$$t(\mathbf{r}) = c_{\mathrm{TF}}\rho(\mathbf{r})^{5/3} + \frac{1}{72}\frac{[\nabla(\mathbf{r})]^2}{\rho(\mathbf{r})} + \frac{1}{6}\nabla^2\rho(\mathbf{r}) \tag{33}$$

This expression is not unique due to the Laplacian term;[60] at the same time, it satisfies a necessary non-negativity condition for the phase-space distribution function $f(\mathbf{r},\mathbf{p})$.[61] The long-range

TABLE 1: Atomic Contributions to the Global Entropy (*37*), the Values of Global Entropy for Selected Crystals/Molecules and Procrystals/Promolecules, Determined from the Experimental Electron Density and Its Derivatives, and the Global Binding Entropy Values S_b (*38*) per Formula Unit (All Values Given in the Units of *S*/*k*)

compound	atom-in-crystal values $S_b(\Omega_i)$(37)	atomic charge $Q = Z - \int_{\Omega_i} d\mathbf{r}\,\rho(\mathbf{r})$	Hartree−Fock atomic values	S_{mol}	S_{promol}	S_b
Ge	202.179	0	218.140	202.179	218.140	−15.961
GaAs						
Ga	187.700	+1.32	211.748	404.551	436.182	−31.631
As	216.851	−1.32	224.434			
N_2O_4						
O	53.725	−0.39	56.321	294.340	324.884	−30.544
N	39.720	+0.78	49.800			

behavior of the approximate density $t(\mathbf{r})$ (33) is correct as the gradient expansion is truncated at the second order term.[62] At the same time, the function $t(\mathbf{r})$ (33) goes to the negative infinity with $\mathbf{r} \to \mathbf{R}_i$ ($\mathbf{R}_i$ denotes the position of i atom) because of the Laplacian term,[51,63] whereas the "correct" kinetic energy density is finite and positive at the nuclei.[64] Fortunately, the size of the negative holes in $t(\mathbf{r})$ around the nuclei is quite small. The maximal hole radius of 0.3 bohr is observed for the hydrogen atom; it is less than 0.04 bohr for atoms with $Z \geq 11$ and reaches the value of 0.01 bohr for $Z = 36$; the radius variation fits a $1/Z$-dependency.[65] These small areas around the nuclei must be excluded from consideration.

Since electron density is now readily obtainable from the accurate X-ray, γ-ray, and synchrotron radiation diffraction experiments,[53] a combination of the DFT formalism and the experimental electron density looks possible for the analysis of the nature of atomic and molecular interactions in solids.[51,66] The electron density is usually reconstructed from the diffraction experiment by means of the multipole model, in which the electron density of a crystal is presented as a sum of aspherical atomic (pseudoatomic) densities, $\rho_{atom}(\mathbf{r})$, each of which is expanded into a convergent series over the real combinations of the spherical harmonics, $y_{lm\pm}$. We used the Hansen−Coppens[67] model

$$\rho(\mathbf{r}) = \sum_{atom} \rho_{atom}(\mathbf{r}) \qquad (34)$$

$$\rho_{atom}(\mathbf{r}) = \rho_c(\mathbf{r}) + P_{val}\kappa^3\rho_{val}(\kappa r) + \sum_{l=1}^{4} \kappa'^3 R_l(\kappa' r) \sum_{m=-l}^{l} P_{lm\pm} y_{lm\pm}(\mathbf{r}/r) \qquad (35)$$

Here ρ_c and ρ_{val} are the atomic core and valence electron densities, correspondingly, described by the wave functions of free atoms,[68] the κ and κ' are atomic valence-shell contraction−expansion parameters, and P_{val} and $P_{lm\pm}$ are the multipole electronic populations. The radial density functions have exponential form $R_l(\mathbf{r}) \sim r^{n_l} \exp(-\kappa' \xi r)$, where n_l is related with the principal quantum number of an atom. The Fourier transformation of (34) and (35) yields the model structure factors; the electronic populations of multipoles as well as the atomic κ-parameters are determined by the least-squares fit of the latter to the experimental structure factors.

The model electron density (34) and (35) is quasi-static and it is close to that derived from the wave functions.[66,69] Therefore, this density appears to be suitable for the analysis of binding in solids. It is as precise as $\sim$0.004−0.008 e$\cdot$bohr^{-3} in the main part of a crystal space, excluding the regions around the nuclei with radius of about 0.4 bohr, where the experimental error increases with the atomic number. Thus, an error resulting from the inadequate behavior of the kinetic energy density (33) in the vicinity of the nuclei is within the range of the experimental uncertainty of electron density in this region.

In this work, the kinetic energy density (33) was locally applied in the expression of the entropy density (20); i.e., we accept that the entropy density at each point $\mathbf{r}$ is supposed to be the same as that of a homogeneous electron gas with electron density, which is equal to $\rho(\mathbf{r})$ everywhere.

The position space of a molecule or a crystal may be divided into atomic basins separated by surfaces $S(\mathbf{r})$ satisfying the condition[54]

$$\nabla\rho(\mathbf{r})\cdot n(\mathbf{r}) = 0 \qquad \forall r \in S(\boldsymbol{r}) \qquad (36)$$

These basins, each of which contains only a single nucleus, are identified with bounded atoms.[54] An integral of a binding entropy density, $s_b(\mathbf{r})$, over the volume of atomic basin i, Ω_i, yields an average atomic value of the binding entropy:

$$S_b(\Omega_i) = \int_{\Omega_i} d\mathbf{r}\, s_b(\mathbf{r}) \qquad (37)$$

The sum of atomic contributions (37) yields the value of the binding entropy for the whole system (the global entropy):

$$S_b = \sum_i S_b(\Omega_i) \qquad (38)$$

5. Results and Discussion

We performed numerical calculations of the global binding entropies of electron distribution and binding entropy densities for the covalent germanium, polar-covalent (ionic) gallium arsenide and molecular crystal N_2O_4. The experimental multipole electron-density parameters were taken from the following sources: from ref 70 for germanium, from refs 71 and 72 for GaAs and from ref 73 for N_2O_4. The entropy was calculated from the experimental data with the WinXPRO program.[74] The atomic quantities were computed by using the Hartree−Fock wave functions;[75] the expression (33) has been used for kinetic energy density. The binding entropy densities are presented Figures 1, 2, and 3. Because the binding entropy density expresses both the deviation of the molecular electron density from the promolecular density and the deviation of the molecular kinetic energy density from the promolecular kinetic energy density, the experimental deformation electron density maps and the "deformation" kinetic energy density $\delta t(\mathbf{r}) = t(\mathbf{r}) - t_{prom}(\mathbf{r})$[76] for the same compounds were computed as well. Calculated global binding entropy values (22) refer to atoms, and binding

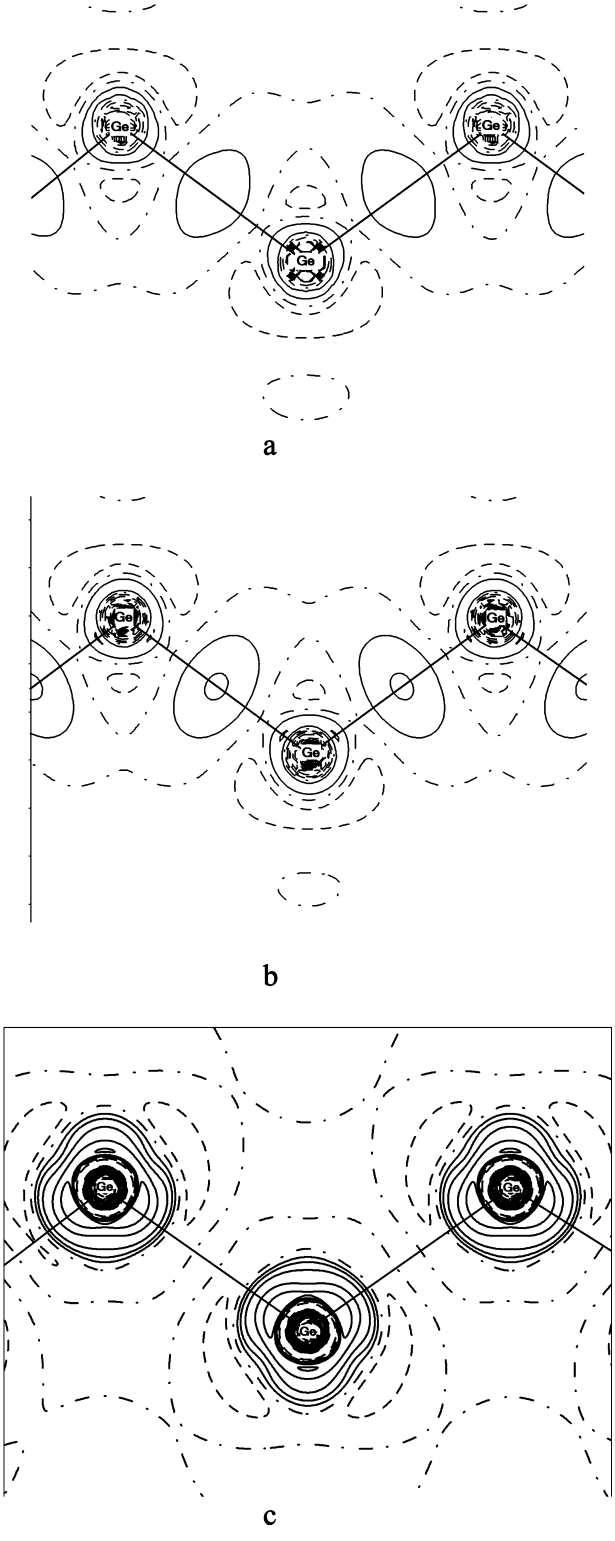

Figure 1. Germanium: binding entropy density, $s_b(\mathbf{r})$, (a), deformation electron density, $\delta\rho(\mathbf{r})$ (b), and "deformation" kinetic energy density, $\delta t(\mathbf{r})$ (c) in the (110) plane of the unit cell. The line intervals are 0.05 s/k (k is the Boltzmann constant) (a), 0.02 e/bohr^3 (b), and $\pm(2, 4, 8) \times 10^n$ hartree/bohr^3 ($-3 \leq n \leq 3$). (c) The solid lines correspond to positive values of functions s_b, $\delta\rho$, and δt, while the chain lines indicate zero values of these functions.

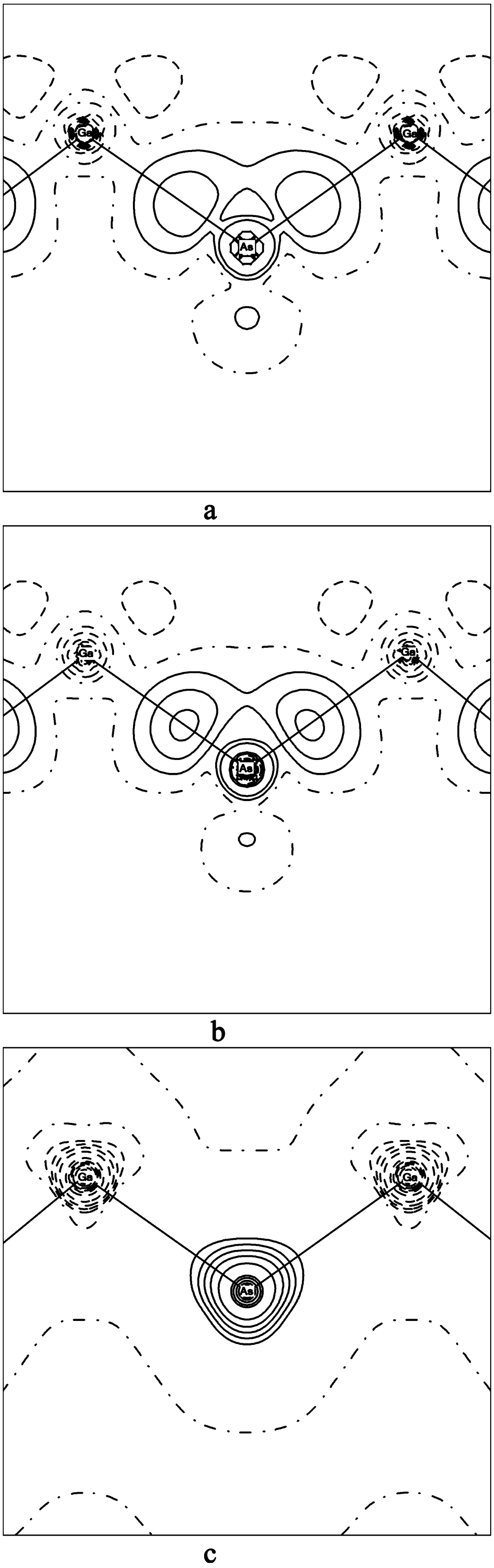

Figure 2. Gallium arsenide GaAs: binding entropy density, $s_b(\mathbf{r})$, (a), deformation electron density $\delta\rho(\mathbf{r})$ (b), and "deformation" kinetic energy density, $\delta t(\mathbf{r})$ (c) in the (110) plane of the unit cell. For details see the caption to Figure 1.

entropy values (38) corresponding to the formula unit are listed in Table 1 (the global entropy values are given throughout the paper in the units of S/k).

First, we analyze the atomic and global binding entropies. Table 1 shows that S_b is always negative; thus the entropy diminishes during the formation of a crystal from separated atoms, as anticipated in ref 77. We also observe that the binding

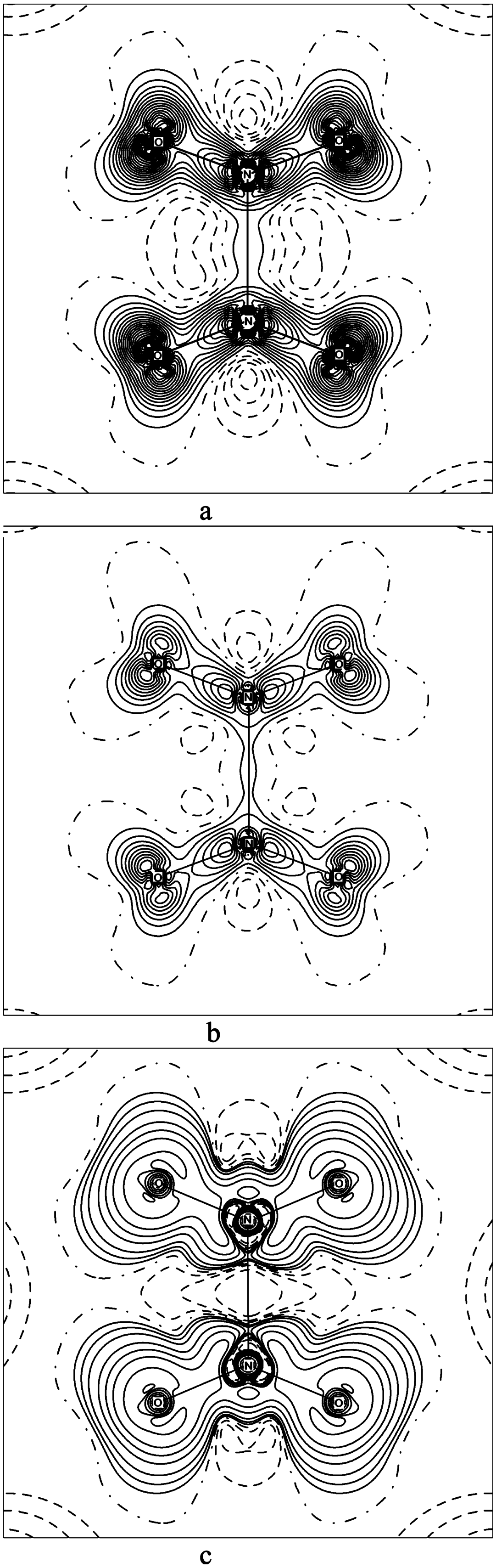

Figure 3. Dinitrogen tetroxide N_2O_4: binding entropy density, $s_b(\mathbf{r})$ (a), deformation electron density $\delta\rho(\mathbf{r})$ (b), and "deformation" kinetic energy density, $\delta t(\mathbf{r})$ (c) in the plane of the molecule. For details see the caption to Figure 1.

entropy of Ga atom $S_b(\mathrm{Ga}) = -24.048$, which is the donor of electrons in GaAs, is much more significant as compared with the binding entropy of the As atom $S_b(\mathrm{As}) = -7.583$ (acceptor of electrons). In molecular crystal N_2O_4, we see a similar picture: the binding entropy of the donor N atom $S_b(\mathrm{N}) = -10.080$ is more noticeable than that of the acceptor O atom $S_b(\mathrm{O}) = -2.596$. Thus we can conclude that the crystal (and molecule) formation is accompanied by more significant reorganization of less electronegative atoms.

We also computed the net atomic charges, Q_i, in GaAs and N_2O_4 by using Bader's procedure:

$$Q_i = Z - \int_{\Omega_i} \mathrm{d}r\, \rho(r) \tag{39}$$

Comparing Q_i and $S_b(\Omega_i)$ (Table 1), we can note that these quantities in coordination reflect the interatomic shift of electrons from Ga to As atoms in GaAs and from N to O atoms in N_2O_4.

To treat the binding entropy density, $s_b(\mathbf{r})$, let us imagine the formation of a molecule or a crystal from free atoms as a result of a few simultaneous actions.[22] These are the valence orbital hybridization and promotion (polarization), contraction/expansion of the atomic-like electron densities (atomic cores), the interatomic charge transfer and valence electron delocalization. These mental changes destroy the order imposed by a promolecule and reflect the opposite trends. For example, the formation of the homoatomic covalent bond can be viewed as atomic promotion and valence electron delocalization due to interference of the atomic wave functions and a contraction of the atomic cores. The first two effects lead to the more diffuse electron distribution in the middle-bond region and the local entropy enhancement here in comparison with a promolecule. The last effect decreases the local entropy in the atomic cores. Along the lines of the ionic or polar covalent bonds, the interatomic valence electron transfer locally diminishes the entropy in the basin of the contracted donor atom and locally increases it in the vicinity of the expanded acceptor atom. It shows the enhancement and reduction in the attraction of the electron to corresponding nuclei. The atomic hybridization, i.e., the valence orbital reorganization accompanied the bond formation, locally increases the entropy both along the bond line and in the regions of the lone pair locations.

The total distribution of the binding entropy reflects the synergetic manifestation of all the factors mentioned above; thus the sign of the binding entropy density shows which of the effects dominate in the position points of the many-electron system under consideration.

These speculations are supported by the binding entropy density maps. The net effect of the formation of the homoatomic covalent bond in Ge (Figure 1a) consists of the entropy enhancement in the middle-bond region and appearance of the $s_b(\mathbf{r})$ oscillations reflecting the orbital contraction/expansion in the valence electronic shells of bounded Ge atoms. The general distribution of the binding entropy resembles the deformation electron density map (Figure 1b). However, the "deformation" function $\delta t(\mathbf{r})$, which exhibits the changes in kinetic energy density of electrons caused by formation of a molecule or a crystal from the atoms, shows (Figure 1c) that main alterations take place within atomic basins. The function $\delta t(\mathbf{r})$ changes sign inside atomic cores (areas close to the nuclear positions are omitted) and shows a typical atomic hybridization picture, which can be associated with the penultimate Ge electronic shell. The $\delta t(\mathbf{r})$ at the middle-bond point between Ge atoms is only 0.005 hartree/bohr.[3] Therefore, we can conclude that electron density accumulation and its reflection in the binding entropy density resulted from the orbital interference effect.

In GaAs, different electronegativity of atoms manifests itself in the shift of the binding entropy density peak along the Ga−As line to the As atom (Figure 2a). The same picture is seen in the deformation electron density (Figure 2b). The kinetic energy density slightly increases along the bond line during the bond formation; at the same time, it significantly diminishes within the Ga atomic core and enhances in the As atom basin (Figure 2c). The oscillations due to the orbital contraction/expansion in the electronic shells of bounded Ga atom do not appear in the $s_b(\mathbf{r})$ function, whereas they are seen around the As atom. We can conclude that factors related with the energy change of atoms and the interatomic charge transfer at the bond formation in GaAs act more evidently in the atomic basins, while the orbital interference and valence electron delocalization become apparent in the interatomic region. In general, the Ga atom is more deformed in agreement with more noticeable value of S_b(Ga) mentioned above.

In molecular crystal N_2O_4, we restrict ourselves by consideration of the intramolecular bonding features. The net binding effect locally increases the entropy both along the bond lines and in the regions of the lone pair locations (Figure 3a). The deformation electron density (Figure 3b) shows that the atomic hybridization yields the most significant effect in binding along the strong covalent N−O bond lines and in the region of electron lone pairs of O atoms, where significant $s_b(\mathbf{r})$ enhancement is observed and where $s_b(\mathbf{r})$ marks the lone-pair electron concentrations. In contrast, the very weak N−N bond (1.76 Å) exhibits a small excess in $s_b(\mathbf{r})$. It correlates with the fact that, according to B3LYP/cc-pVDZ calculation, this bond is mainly formed by means of exchange and correlation electronic effects and is described by the highest occupied molecular orbital; it also has the Cioslowski−Mixon bond order of 0.51.[73] The "deformation" kinetic energy map (Figure 3c) shows a visible kinetic energy drop at the middle of N−N bond and oscillates within the N atom basins. Thus, the N−N bond cannot be identified as a common covalent bond.

6. Concluding Remarks

In this work, we introduced the concept of binding entropy. This quantity expresses the deviation of the molecular electron density from the promolecular density and the deviation of the molecular kinetic energy density from the promolecular kinetic energy density. We stress that the change in the kinetic energy density during the bond formation explicitly appears in the binding entropy expression; it is in the spirit of the general idea of the density functional theory. We also demonstrated that combination of the information theoretical approach and the orbital-free density functional theory presented here provides a useful tool for study of the binding mechanisms in molecules and solids. Jointly with deformation electron density and "deformation" kinetic energy density, the binding entropy density provides a deeper insight into the nature of chemical binding. In addition, our approach combines theoretical and experimental (in the form of the electron density derived by the X-ray diffraction) results to obtain a simple way of gaining knowledge on bond formation in solids. The atomic and global binding entropies also appear to be useful descriptors, which help us understand chemical binding.

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