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Interatomic Interactions in Momentum Space. Momentum Density and Kinetic Energy in Chemical Bonding

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On the basis of the virial theorem for a uniform scaling process of a polyatomic system, the total energy and its gradient are quantitatively related with the behavior of the electron density in momentum space through the kinetic energy of the system. For attractive and repulsive interactions, the behavior of the momentum density distribution and its effect on the stabilization energy and the interatomic force are examined. Some guiding principles are deduced for their interrelation. The results are used to clarify the role of kinetic energy in chemical bonding. Possible energy partitioning in this approach is also mentioned.

Key words: Momentum density – Kinetic energy – Chemical bonding – Virial theorem.

1. Introduction

In molecular quantum mechanics, the electron density $\rho(\boldsymbol{r})$ in the coordinate ($r-$) space has been utilized as a basic physical quantity in understanding and predicting various nuclear displacement processes [1]. Specifically, the Hellmann–Feynman (H–F) theorem [2] connects the behavior of the electron density with the quantum-mechanical force acting on a nucleus in an intuitive and quantitative manner [1, 3, 4]. The integration of the force also enables us to relate the energy of the system directly with the density behavior (integrated H–F theorem [5]).

However, it is shown in quantum mechanics that the position $\boldsymbol{r}$ and the momentum $\boldsymbol{p}$ of a particle are variables which can equally describe states of systems under the commutation condition $[\boldsymbol{r}, \boldsymbol{p}] = i$ [6]. Therefore, the use of the electron density

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$\rho(\boldsymbol{p})$ in the momentum ($p-$) space, instead of $\rho(\boldsymbol{r})$, is expected to give a new or an alternative development for density studies of nuclear displacement processes such as molecular geometries, molecular vibrations, chemical reactions, and long-range forces.

Theoretically, the momentum density $\rho(\boldsymbol{p})$ is derived from the p-space wave function obtained either by the direct solution of the Schrödinger equation in the p-representation [7, 8] or by the Dirac transform of the r-space wave function (see [9–12] for the representation theory). The properties of the p-representation of molecular electronic wave functions were first investigated by Coulson and Duncanson in the early 1940s [13]. The momentum density $\rho(\boldsymbol{p})$ does not mean a distribution in the actual three-dimensional molecular space. Then, it is a merit of the p-space approach that the density distribution is free from the nuclear framework: for example, $\rho(\boldsymbol{p})$ is expected to throw its major part into the region around the origin even for large molecules in their ground and low excited states. The momentum density also has the advantage that it is closely related with the experimental Compton profiles of atoms and molecules [14].

When the momentum density $\rho(\boldsymbol{p})$ is given for a system, it is then necessary for our purpose to connect it with the energy or the force of the system in a simple and yet quantitative manner. In the p-space, the Coulombic potential operator between nucleus A and electron i, $-Z_A/|\boldsymbol{r}_i-\boldsymbol{R}_A|$, is given by

$$-(Z_A/2\pi^2)\int d\boldsymbol{p}\,|\boldsymbol{p}|^{-2}\exp(i\boldsymbol{p}\cdot\boldsymbol{R}_A)\exp(\boldsymbol{p}\cdot\nabla_{p_i}),$$

and the corresponding H–F force operator, $Z_A(\boldsymbol{r}_i-\boldsymbol{R}_A)/|\boldsymbol{r}_i-\boldsymbol{R}_A|^3$, by

$$-i(Z_A/2\pi^2)\int d\boldsymbol{p}\,\boldsymbol{p}|\boldsymbol{p}|^{-2}\exp(i\boldsymbol{p}\cdot\boldsymbol{R}_A)\exp(\boldsymbol{p}\cdot\nabla_{p_i}),$$

where Z_A and $\boldsymbol{R}_A$ are charge and position of nucleus A, respectively. The physical picture of these operators is not clear. Calculations of these expectation values require not only $\rho(\boldsymbol{p})$ but also $\rho(\boldsymbol{p}'|\boldsymbol{p})$, the off-diagonal elements of the momentum density matrix. On the other hand, the kinetic energy operator becomes multiplicative $|\boldsymbol{p}|^2/2$ and $\rho(\boldsymbol{p})$ is sufficient for its expectation value in the p-space.

From this motivation, we here investigate a relationship between the momentum density and the total energy (or the force) through the kinetic energy of a system. As we have developed in r-space by the use of the H–F theorem [37], we are interested in a quantitative study of interaction processes based on the electron density in the p-space. In the next section, the basic equations in this approach are derived and summarized from the virial theorem for a uniform scaling process of polyatomic systems. In Sect. 3, stabilization and destabilization (or attraction and repulsion) of a system are discussed in terms of the behavior of momentum density. Some guiding rules are deduced for the relation of the density behavior to the energy and force. In Sect. 4, a possible energy partitioning is briefly mentioned based on the decomposition of momentum density. In Sect. 5, the present approach is applied to the kinetic explanation of chemical bonding. The reorganization of momentum density during the bonding process is discussed as well as the corresponding behavior of the coordinate density.

2. Theoretical Ground

The virial theorem for a polyatomic system is given by [15]

$$T(\boldsymbol{R})+E(\boldsymbol{R})+\sum_{A} R_A[\partial E(\boldsymbol{R})/\partial R_A]=0, \tag{1}$$

where T is the kinetic energy, E the total energy of the system, and $\boldsymbol{R}\equiv\{R_A\}$ the space coordinates of nuclei. If we consider a uniform scaling process of an arbitrary conformation $\boldsymbol{R}_0$,

$$\boldsymbol{R}_s\equiv s\boldsymbol{R}_0, \tag{2}$$

Eq. (1) is reduced to

$$T(s)+E(s)+s[dE(s)/ds]=0, \tag{3}$$

where the scale factor s varies from 0 (united atom limit) to ∞ (separated atoms limit). Then the solution of this equation is [16, 17]

$$E(s)=(1/s)\int_s^{\infty}\Delta T(t)\,dt-T(\infty), \tag{4}$$

where

$$\Delta T(s)\equiv T(s)-T(\infty), \tag{5}$$

and $T(\infty)$ can be replaced by $-E(\infty)$. The corresponding force F is given by

$$\begin{aligned}F(s)&\equiv -dE(s)/ds\\ &=(1/s^2)\left\{\int_s^{\infty}\Delta T(t)\,dt+s\Delta T(s)\right\}.\end{aligned} \tag{6}$$

Eqs. (4) and (6) are the first set of the desired result which connects energy and force with kinetic energy. Alternatively, application of the kinetic field normalization relation [17]

$$(1/s)\int_0^{\infty}\Delta T(t)\,dt=V_{nn}(s) \tag{7}$$

to Eqs. (4) and (6) yields the second set of equations,

$$E(s)=-(1/s)\int_0^{s}T(t)\,dt+V_{nn}(s), \tag{8}$$

$$F(s)=-(1/s^2)\left\{\int_0^{s}T(t)\,dt-sT(s)-sV_{nn}(s)\right\}, \tag{9}$$

where V_{nn} means the nuclear repulsion potential. Eq. (8) has been also derived by Knöll [18]. If the equilibrium geometry $s_e\boldsymbol{R}_0$ and energy $E(s_e)$ $(=-T(s_e))$ are known, the third set of equations is obtained as

$$E(s) = (1/s)\left\{\int_s^{s_e} T(t)\,dt - s_e T(s_e)\right\}, \tag{10}$$

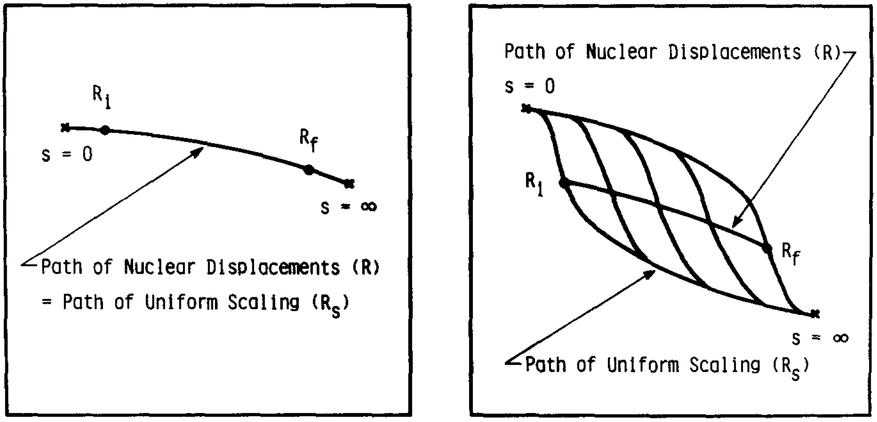
$$F(s) = (1/s^2)\left\{\int_s^{s_e} T(t)\,dt - s_e T(s_e) + sT(s)\right\}, \tag{11}$$

where the relation $F(s_e) = 0$ has been used. Borkman and Parr obtained the corresponding formula for diatomic molecules [19].

All the three sets of equations show that one can calculate $E(s)$ and $F(s)$ from the knowledge of $T(s)$. Since $T(s)$ is simply related with the electron density in the p-space, these equations permit us to discuss $E(s)$ and $F(s)$ based on the behavior of the momentum density (see next section). Of these equations, the first (Eqs. (4) and (6)) and the third (Eqs. (10) and (11)) sets have a merit that there is no need to consider the additional nuclear repulsion. The nuclear repulsion has been replaced with the integral term of ΔT by Eq. (7). However, it is a demerit of the present approach that not only $T(s)$ but also $\int T(s)\,ds$ is required for the calculation. From the range of integration, the first set is useful for the study of interaction processes starting from separated atoms. Similarly, the second set may be advantageous in examining the change from the united atom, and the third set the change around equilibrium conformation. Since we are mainly interested in the process of molecular formation from separated atoms, we proceed with our study using the first set of equations in the following sections.

The present equations may be applied to any process of nuclear displacements in any molecular systems (including solids). Let us consider a (totally) symmetric stretching mode described by a symmetry coordinate such as $S = \sum_B R_{AB}$ (A means the central atom, B the terminal one, and R_{AB} the bond length). In this case, the path of nuclear displacements ($\boldsymbol{R}$) coincides with the path of uniform scaling ($\boldsymbol{R}_s$) (Fig. 1a). All the intermediate conformations between the initial and final geometries ($\boldsymbol{R}_i$ and $\boldsymbol{R}_f$) correspond to some s values on the path $\boldsymbol{R}_s$ with common reference conformation $\boldsymbol{R}_0$. Therefore, the behavior of the momentum density along the path $\boldsymbol{R}_s$ (which will be discussed in the next section) is nothing but the behavior along the path $\boldsymbol{R}$. For other modes (such as antisymmetric stretching and bending modes), however, the two paths $\boldsymbol{R}$ and $\boldsymbol{R}_s$ are generally different (see Fig. 1b). The points on $\boldsymbol{R}$ lie on different $\boldsymbol{R}_s$s and have different $\boldsymbol{R}_0$s. We have to employ different $\boldsymbol{R}_s$s to calculate the energies of conformations which are represented by the crossing points of the paths $\boldsymbol{R}$ and $\boldsymbol{R}_s$. Thus the energy of a given conformation is obtained from the momentum density, but the guiding rules for the density behavior (see next section) cannot be directly applied to the latter case unless the two paths are almost parallel.

The three sets of equations summarized above hold for both the exact and approximate momentum densities insofar as their parent wave functions satisfy the virial theorem. If the theorem is not satisfied, the resultant equations are only approximate. In this case, an appropriate rescaling procedure (such as



(a) Symmetric Stretching Mode (b) Other Modes

Fig. 1. Schematic representations for the path of nuclear displacements ($\boldsymbol{R}$) and the path of uniform scaling ($\boldsymbol{R}_s$)

optimization of orbital exponents) is necessary to make the equations valid [20]. This point is similar to the case of the H–F theorem, where the theorem holds only for the stable or floating wave functions [16, 21, 22].

3. Behavior of Momentum Density

Using the momentum density $\rho(\boldsymbol{p})$, we can rewrite Eqs. (4) and (6) as

$$\begin{aligned}\Delta E(s) &\equiv E(s) - E(\infty)\\ &= \int (p^2/2)\,\Delta\bar{\rho}(\boldsymbol{p}; s)\,d\boldsymbol{p},\end{aligned} \tag{12}$$

$$F(s) = (1/s) \int (p^2/2)\Delta\tilde{\rho}(\boldsymbol{p}; s)\,d\boldsymbol{p}, \tag{13}$$

where $p = |\boldsymbol{p}|$. Here, we have introduced two modified density difference functions $\Delta\bar{\rho}$ and $\Delta\tilde{\rho}$, which are defined as

$$\Delta\bar{\rho}(\boldsymbol{p}; s) \equiv (1/s) \int_s^\infty \Delta\rho(\boldsymbol{p}; t)\,dt, \tag{14a}$$

$$\Delta\tilde{\rho}(\boldsymbol{p}; s) \equiv \Delta\bar{\rho}(\boldsymbol{p}; s) + \Delta\dot{\rho}(\boldsymbol{p}; s), \tag{14b}$$

in terms of the (usual) density difference

$$\Delta\rho(\boldsymbol{p}; s) \equiv \rho(\boldsymbol{p}; s) - \rho(\boldsymbol{p}; \infty). \tag{14c}$$

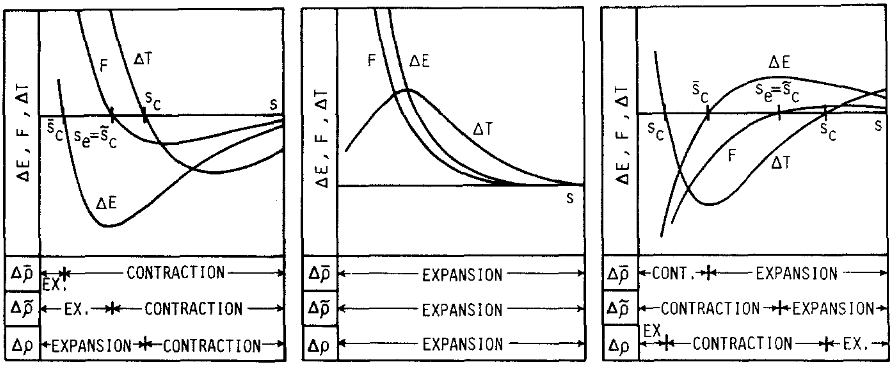
These three density differences must satisfy

$$\int \Delta\bar{\rho}(\boldsymbol{p}; s)\,d\boldsymbol{p} = \int \Delta\tilde{\rho}(\boldsymbol{p}; s)\,d\boldsymbol{p} = \int \Delta\rho(\boldsymbol{p}; s)\,d\boldsymbol{p} = 0 \tag{15}$$

in order to conserve the number of electrons.

Based on Eqs. (12) and (13), we can derive some guiding principles for the effect of the density reorganization in the p-space on the energy and force of a system. Taking the weighting factor $(p^2/2)$ into account, we see in Eq. (12) that the stabilization of the system (i.e. $\Delta E < 0$) occurs only when $\Delta\bar{\rho}$ decreases in a larger p region and increases in a smaller p region under condition (15). Namely, $\Delta\bar{\rho}$ must *contract* to stabilize the system. At stable equilibrium conformation, this contraction should be maximum since ΔE is (locally) minimum at this point (Fig. 2a). For the destabilization of the system ($\Delta E > 0$), the situation is opposite and hence *expansion* must be observed in $\Delta\bar{\rho}$. If the system is monotonously destabilizing, the degree of the expansion will also increase monotonously (Fig. 2b). If there is unstable equilibrium (i.e. local maximum of ΔE), the expansion is maximum at this geometry (Fig. 2c). The critical point ($\bar{s}_c$) for the contraction and expansion of $\Delta\bar{\rho}$ is the point of $\Delta E = 0$. Consequently, the contraction and expansion appearing in the distribution $\Delta\bar{\rho}$ play a determinative role for the density–energy relation in the p-space.

Similarly, we can derive guiding principles for the density difference $\Delta\tilde{\rho}$ from Eq. (13). Since s is non-negative, it is seen that an attractive force ($F < 0$) results only when $\Delta\tilde{\rho}$ shows contraction, whereas a repulsive force ($F > 0$) results only when $\Delta\tilde{\rho}$ shows expansion (see Fig. 2). The critical point ($\tilde{s}_c$) of these density behaviors is the point of $F = 0$, i.e. equilibrium conformation. Maximum reorganizations in $\Delta\tilde{\rho}$ will be found at points of inflection in the ΔE curve, because the forces are extremum at these points. The contraction and expansion in $\Delta\tilde{\rho}$ are critical for the density–force relation in the p-space. When compared with the $\Delta\bar{\rho}$–ΔE relation, the present $\Delta\tilde{\rho}$–F relation seems more convenient since the critical point $\tilde{s}_c$ is identical with the equilibrium point s_e. The concept of the contraction and expansion of $\Delta\tilde{\rho}$ in the p-space may correspond to the concept of the electron-cloud preceding and (incomplete) following [23], which is a guiding principle in the r-space for the density reorganization during interaction processes. It should



(a) (b) (c)

Fig. 2. Schematic representations of curves for energy (ΔE), force (F), kinetic energy (ΔT), and corresponding density reorganizations $\Delta\bar{\rho}(p)$, $\Delta\tilde{\rho}(p)$, $\Delta\rho(p)$. (**a**) Attractive interaction with stable equilibrium. (**b**) Repulsive interaction with no equilibrium. (**c**) Repulsive interaction with unstable equilibrium

be stressed that in the present approach, there is no need to consider the nuclear repulsion separately, different from the H–F treatment of the electron density in the r-space.

In Eqs. (12) and (13), the density difference $\Delta\rho$ does not appear explicitly. However, its behavior during interaction processes is deduced from those of $\Delta\bar{\rho}$ and $\Delta\tilde{\rho}$ through the relations (14a) and (14b). Since $\Delta\rho(\boldsymbol{p}; s) \to 0$ as $s \to \infty$, we may expand $\Delta\rho$ as $\Delta\rho(\boldsymbol{p}; s) = \sum_n a_n(\boldsymbol{p})s^{-n}$ for large s[1]. In this approximation, we see that the terms in $\Delta\rho$, $\Delta\bar{\rho}$, and $\Delta\tilde{\rho}$ are proportional, and then the behaviors of the three density differences are expected to be parallel at large s. On the other hand, Eq. (13) shows that at the equilibrium, the contributions from $\Delta\rho$ and $\Delta\bar{\rho}$ must cancel out because of $F(s_e) = 0$ (i.e. no contribution of $\Delta\tilde{\rho}$). Therefore, the behavior of $\Delta\rho$ is first parallel and then opposite to that of $\Delta\bar{\rho}$. The critical point (s_c) lies between $s = s_e$ and $s = \infty$, and is defined as the point of $\Delta T = 0$ since $\Delta\rho$ is directly related with the kinetic energy by $\Delta T = \int (p^2/2)\, \Delta\rho(\boldsymbol{p})\, d\boldsymbol{p}$. During the course to a stable equilibrium, the momentum density $\rho(\boldsymbol{p})$ changes from contraction to expansion (Fig. 2a). In the range of $s > s_c$, $\Delta\rho$ works to accelerate the process in cooperation with $\Delta\bar{\rho}$, while for $s_e < s < s_c$ it works to terminate the process against $\Delta\bar{\rho}$. The reverse change and contribution of $\Delta\rho(\boldsymbol{p})$ will be seen for an unstable equilibrium (Fig. 2c). For monotonous repulsions, $\Delta\rho$ is expected to continue its behavior (i.e. expansion) without s_c (Fig. 2b). However, whether s_c exists or not depends on the states correlated in the united atom and separated atoms limits.

4. Energy Partitioning

We here briefly mention a possible partitioning of the energy in this approach. Application to the partitioning of the force is also straightforward.

By expanding the wave function of a system by an appropriate AO basis, we can separate the density $\rho(\boldsymbol{p}; s)$ into one- and two-center parts.

$$\rho(\boldsymbol{p}; s) = \sum_{A} \rho_A(\boldsymbol{p}; s) + \sum_{A>B}\sum \rho_{AB}(\boldsymbol{p}; s). \tag{16}$$

Since $\rho(\boldsymbol{p}; \infty) = \sum_A \rho_A(\boldsymbol{p}; \infty)$ and $\rho_{AB}(\boldsymbol{p}; \infty) = 0$, $\Delta\rho$, $\Delta\bar{\rho}$, and $\Delta\tilde{\rho}$ can be similarly partitioned. Then using $E(\infty) = \sum_A E_A(\infty)$, we get

$$E(s) = \sum_{A} E_A(s) + \sum_{A>B}\sum E_{AB}(s), \tag{17}$$

where

$$E_A(s) = \int (p^2/2)\Delta\tilde{\rho}_A(\boldsymbol{p}; s)\, d\boldsymbol{p} + E_A(\infty), \tag{18a}$$

$$E_{AB}(s) = \int (p^2/2)\, \Delta\tilde{\rho}_{AB}(\boldsymbol{p}; s)\, d\boldsymbol{p}. \tag{18b}$$

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[1] According to the long-range perturbation theory, it seems to be reasonable to write $\Psi(\{\boldsymbol{r}_i\}; s) = \Psi(\{\boldsymbol{r}_i\}; \infty) + \sum_n b_n(\{\boldsymbol{r}_i\})s^{-n}$ for large s in the r-space. Then the Dirac–Fourier transform results in $\Psi(\{\boldsymbol{p}_i\}; s) = \Psi(\{\boldsymbol{p}_i\}; \infty) + \sum_n b'_n(\{\boldsymbol{p}_i\})s^{-n}$ and hence $\Delta\rho(\boldsymbol{p}; s) = \sum_n a_n(\boldsymbol{p})s^{-n}$.

In these equations, the energy of a system is partitioned into an atomic contribution E_A and an interatomic (or bond) contribution E_{AB}. Since the localization (towards nuclei) and delocalization (into bond regions) of the electron density $\rho(\boldsymbol{r})$ may be predominantly reflected by the terms ρ_A and ρ_{AB}, respectively, the partitioned energies E_A and E_{AB} are expected to give energetic contributions of these density behaviors (see also the atom-bond partitioning due to Ruedenberg et al. [30]). Although the present decomposition is basis dependent, it holds for both the exact and approximate momentum densities. This point is different from the similar formula found in approximate MO methods like CNDO [24].

In addition, it is also possible to decompose the energy based on the kinetic energy operator. By separating $(p^2/2)$ into several directional parts, the energy is represented as the sum of the directional contributions. For example, the partitioning into the parallel and perpendicular components, $(p^2/2) = (p_{/\!/}^2/2) + (p_\perp^2/2) + (p_\perp'^2/2)$, seems interesting for molecules with symmetry axis.[2]

5. Kinetic Energy in Chemical Bonding

There are two viewpoints for the origin of chemical (covalent) bonding. One is the potential explanation which emphasizes the potential lowering due to the density accumulation in the internuclear region as a result of electron sharing (exchange) or in-phase overlap of the relevant orbitals (see e.g. [25]). The other is the kinetic explanation which attaches importance to the lowering of the kinetic energy caused by the extension of the space of the electron movement from atoms to molecule and hence the decrease of the kinetic pressure [26, 27]. The virial theorem [15] shows the relative importance of the kinetic contribution for a larger separation and of the potential contribution for a shorter separation [28, 29].

However, several authors have reported the significance of the kinetic energy. Ruedenberg and Feinberg [30] analyzed the H_2^+ system in detail and emphasized the critical role of $T_{/\!/}$ (parallel component of the kinetic energy) in the bonding process (see also [31]). Wilson and Goddard [32] defined the exchange kinetic energy T^x from the difference between the Hartree and $G1$ [33] wave functions and showed the importance of T^x (and then the contragradient nature of orbitals) as the origin of bonding. Bader and Preston [34] discussed the relation between the kinetic energy and the electron density in the r-space by examining the kinetic energy density.

Though these studies were carried out in the r-representation, we can treat this subject in a direct manner by use of the p-representation of the electron density and the kinetic operator as has been developed in the preceding sections. Some insight on a relationship between the kinetic and total energies is also obtained.

For the sake of simplicity, let us consider the process of covalent bond formation between two atoms. Typical changes in ΔE and ΔT curves derived from an empirical potential function [35] are depicted in Fig. 2a as a function of s.[3]

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[2] We can always choose one axis in the p-space parallel to some axis in the r-space.

[3] For diatomic systems, the scale factor s can be replaced by the internuclear distance R.

Now, our basic equation is Eq. (4), which shows that ΔE is given by the product of the integral term of ΔT and the factor $1/s$. Therefore, the integral term is expected to make ΔE be parallel to ΔT, if the sign of the latter remains unchanged. Indeed, this parallelism is observed for $s > s_c$ in Fig. 2a (and also in Figs. 2b and c). Namely, both ΔE and ΔT are negative in this range, as expected from the contraction of $\Delta\bar{\rho}(\boldsymbol{p})$ and $\Delta\rho(\boldsymbol{p})$ (see Sect. 3) and from the virial relation [15, 28–31] at large s. The contraction of $\rho(\boldsymbol{p})$ (and the resultant decrease in ΔT) seem to reflect the accumulation of $\rho(\boldsymbol{r})$ in the bond region, since it gives rise to a smoothed density distribution in the bond direction with a concomitant decrease in the gradient of the r-space wave function in that direction. This may result in a predominant decrease in the component $T_{/\!/}$ as pointed out by Ruedenberg et al. [30]. In this stage, the wave function has become less compact than that of the separated atoms with decrease of the kinetic pressure.

For an intermediate value of s (i.e. $s \sim s_c$), the wave function (in the r-space) becomes compact as compared to large s, in part due to the shrinkage of the nuclear framework and in part to the increase of promotional hybridization. As a result, $\rho(\boldsymbol{p})$ expands and ΔT increases. (For example, an increase in p-character of an sp hybridization leads to a density increase at high momentum.) The analyses of the $1s\sigma_g$ state of the H_2^+ system [30] suggest that $T_\perp$ (the component of the kinetic energy perpendicular to the bond axis) is primarily responsible for this increase. As shown in Fig. 2a, ΔT is just zero at $s = s_c$ and positive for $s < s_c$.[4] However, ΔE continues decreasing even for $s_c > s$ ($> s_e$) where ΔT has been already positive. This is explained by the term $1/s$ which enhances the integral term as s diminishes. In the range of $s_c > s > s_e$, this contribution is larger than the partial cancellation in $\int \Delta T(s)\, ds$ due to the positive ΔT, resulting further lowering of ΔE.[5]

When s diminishes further ($s \lesssim s_e$), the compactness of the wave function grows rapidly with simultaneous expansion of $\rho(\boldsymbol{p})$. The resultant increase in ΔT is then enough to increase ΔE through the integral term. Thus the positive ΔT works to terminate the process of the bond formation (or the chemical reaction) at $s = s_e$. On bonding, the spherical atomic momentum density becomes an ellipsoid with its shortest axis along the bond direction [13, 36].

During the process, the change in ΔE seems to follow after the change in ΔT due to the term $1/s$. Though further investigations are needed, it is suggested that the behavior of ΔT may predict the succeeding behavior of ΔE, except for the small s region where $\Delta T \to$ const. but $\Delta E \to \infty$. In this sense, the substantial role of the kinetic energy in chemical bonding is suggested in the present approach. However, we expect from the density point of view that the kinetic explanation will be an aspect of chemical bonding and will be complementary to the potential explanation, since the electron densities $\rho(\boldsymbol{p})$ and $\rho(\boldsymbol{r})$ are two aspects of the single fact.

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[4] In the r-space, the critical point s_c may be understood as the point where the delocalization of $\rho(\boldsymbol{r})$ over the molecular space just counterbalances with its localization towards the nuclei.

[5] If the term $1/s$ is absent, the equilibrium point s_e obviously coincides with the critical point s_c.

6. Summary

In this article, we have developed a quantitative method which enables us to connect the behavior of momentum density with the energy and force of a system. This has been achieved through the kinetic energy by using the virial theorem for a uniform scaling process. The predominant origins of stabilization (attraction) and destabilization (repulsion) are shown respectively to be contraction and expansion of the momentum density observed in the modified density differences $\Delta\bar{\rho}(\boldsymbol{p})$ and $\Delta\tilde{\rho}(\boldsymbol{p})$. Reorganization of the momentum density and its effect on the total and kinetic energies have been discussed for the process of bond formation. A decrease of the kinetic energy is important to initiate a reaction, while an increase is important to terminate it at equilibrium geometry. The present study seems to give a clue for interrelation between the kinetic and potential explanations of chemical bonding, since the behaviors of $\rho(\boldsymbol{p})$ (i.e. contraction/expansion) are closely related with those of $\rho(\boldsymbol{r})$ (i.e. delocalization/localization) through the Dirac–Fourier transform. Quantitative analyses for some systems are now in progress.

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