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Diatomic interactions in momentum space
Bond polarity

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Some fundamental aspects of bond polarity embedded in diatomic molecular orbitals are studied from the viewpoint of the electron distribution in momentum space. Electron momentum density is expressible as a product of one-center and oscillation terms, and the effect of polarity appears mainly in the latter term. Since the oscillation is not spherically symmetrical, the bond polarity is then related to the anisotropy of momentum distribution. In order to investigate this relation, directional ratios of momentum moments are introduced and their behaviors are examined for a model heteronuclear diatomic system.

Key words: Bond polarity — Electron momentum distribution — Directional moment of momentum

1. Introduction

Momentum and position spaces are complementary each other and wave functions in both spaces are related through the Dirac–Fourier transformation. The problem of electron momentum distribution in molecules was first studied by Coulson and Duncanson in the early 1940's [1]. Succeedingly, a number of studies have been carried out on the molecular momentum distribution because of its importance as a fundamental physical quantity and its close connection to the experimental Compton profile (see *e.g.* Refs. [2–4] for reviews).

We have recently examined the momentum redistribution in diatomic systems focussing upon the problem of chemical bonding in momentum space [5–8]. We have first showed that the reorganization of momentum density during the process

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of an interatomic interaction can be exactly related to the total energy of that system [5]. The results have been applied to the H_2^+ system and the differences between σ and π and bonding and antibonding states have been quantitatively discussed based on the momentum distribution [6, 7]. The roles of the floating and polarization functions have also been analyzed in momentum space, which are often used to improve wave functions [8]. However, these studies have been limited to homonuclear systems.

Here we take up heteronuclear diatomics and discuss some basic features of bond polarity in momentum space. The molecules N_2 and HF, for example, are known to be typical covalent- and ionic-bonded systems, respectively. In position space, it is a measure of polarity whether the electron density casts its major portion into the internuclear bond region or into one of the atomic regions [9]. Henneker and Cade [10] examined momentum densities of the above two molecules in comparison with their position-space counterparts, but they could not draw out definite conclusions about the bond polarity in momentum space. Indeed, in momentum space we are unable to observe the location of the electron density relative to the nuclear positions. However, the momentum wave function and resulting momentum density should contain information about the polarity, since the Dirac–Fourier transformation brings all the information to momentum space.

In the present paper we show that the molecular momentum distribution is characterized by its oscillation and resultant anisotropy and their magnitudes are intimately related to the bond polarity. The oscillatory and anisotropic nature is maximal for the complete covalent bond and decreases as the polarity increases. In the next section, we discuss the oscillatory behavior of the momentum density. The oscillation appearing in diatomic molecular orbitals are analyzed in terms of its period, phase, and amplitude. In the third section, we discuss the anisotropy of diatomic momentum distribution in relation to the bond polarity. Directional ratios of nth momentum moments ($1 \leq n \leq 4$) are introduced as measures of the anisotropy, and their behaviors are examined for the model heteronuclear diatomic system employed by Feinberg and Ruedenberg [11]. The result for the second moment is of our particular interest, since it is directly related to the kinetic energy of the system. Atomic units are used throughout this paper.

2. Bond polarity and oscillatory momentum distribution

In its simplest form, a diatomic molecular orbital can be written in position space as

$$\psi(\boldsymbol{r}) = (1+\lambda^2+2\lambda S)^{-1/2}[\psi_a(\boldsymbol{r}-\boldsymbol{R}_a)+\lambda\psi_b(\boldsymbol{r}-\boldsymbol{R}_b)], \tag{1a}$$

where $\boldsymbol{R}_a$ and $\boldsymbol{R}_b$ are the position vectors of two nuclei a and b, $\psi_a(\boldsymbol{r}-\boldsymbol{R}_a)$ and $\psi_b(\boldsymbol{r}-\boldsymbol{R}_b)$ the atomic orbitals centered on them respectively, and S the overlap integral. The parameter λ represents the relative contributions of ψ_a and ψ_b. The Dirac–Fourier transformation gives the momentum representation of Eq. (1a) as

$$\chi(\boldsymbol{p}) = (1+\lambda^2+2\lambda S)^{-1/2}[\exp(-i\boldsymbol{pR}_a)\chi_a(\boldsymbol{p})+\lambda \exp(-i\boldsymbol{pR}_b)\chi_b(\boldsymbol{p})], \tag{1b}$$

where $\chi_a(\boldsymbol{p})$ and $\chi_b(\boldsymbol{p})$ are momentum-space atomic orbitals corresponding to $\psi_a(\boldsymbol{r})$ and $\psi_b(\boldsymbol{r})$, respectively. Then the momentum density becomes a sum of one- and two-center terms;

$$\begin{aligned}\rho(\boldsymbol{p}) = (1+\lambda^2+2\lambda S)^{-1}\{&|\chi_a(\boldsymbol{p})|^2+\lambda^2|\chi_b(\boldsymbol{p})|^2\\ &+2\lambda|\chi_a(\boldsymbol{p})||\chi_b(\boldsymbol{p})|\cos[\boldsymbol{p}\boldsymbol{R}+\arg[\chi_a(\boldsymbol{p})/\chi_b(\boldsymbol{p})]]\},\end{aligned} \tag{2a}$$

where $\boldsymbol{R}=\boldsymbol{R}_b-\boldsymbol{R}_a$ is the internuclear vector. The third term in the braces of Eq. (2a) is intrinsic to molecular systems. In order to know the relative magnitude of the contribution of this term, it is more convenient to express Eq. (2a) as a product of one-center and oscillation terms. That is,

$$\rho(\boldsymbol{p})=\rho_{\text{one}}(\boldsymbol{p})\rho_{\text{osc}}(\boldsymbol{p}), \tag{2b}$$

$$\rho_{\text{one}}(\boldsymbol{p})=(1+\lambda^2+2\lambda S)^{-1}[|\chi_a(\boldsymbol{p})|^2+\lambda^2|\chi_b(\boldsymbol{p})|^2], \tag{2c}$$

$$\rho_{\text{osc}}(\boldsymbol{p})=1+A(\boldsymbol{p})\cos\{\boldsymbol{p}\boldsymbol{R}+\arg[\chi_a(\boldsymbol{p})/\chi_b(\boldsymbol{p})]\}, \tag{2d}$$

$$A(\boldsymbol{p})=2\lambda|\chi_a(\boldsymbol{p})||\chi_b(\boldsymbol{p})|/[|\chi_a(\boldsymbol{p})|^2+\lambda^2|\chi_b(\boldsymbol{p})|^2]. \tag{2e}$$

The molecular momentum density is essentially different from the atomic momentum density in that the former has a oscillation term. The mode of oscillation is characterized by its period, phase, and amplitude.

2.1. Period

We take the p_z axis parallel to the internuclear axis. Then $\boldsymbol{pR}=p_zR$ (where $R=|\boldsymbol{R}|$), and hence the cosine term in Eq. (2d) oscillates with the period $2\pi/R$ along the p_z axis [1], if $\arg[\chi_a(\boldsymbol{p})/\chi_b(\boldsymbol{p})]$ is constant. The period is inversely proportional to the bond length R; a molecule with shorter (longer) bond length has longer (shorter) period. Though this suggests the possibility of estimating the bond length from the period of momentum distribution [3], the result of detailed analysis by Kaijser and Smith [12] is not encouraging.

2.2. Phase

The $\arg[\chi_a(\boldsymbol{p})/\chi_b(\boldsymbol{p})]$ is the phase of oscillation and its extent is determined by a combination of two atomic orbitals. If the spherical harmonic atomic orbital is used, the orbital can be written [13] in momentum space as

$$\chi_{nlm}(\boldsymbol{p})=(-i)^l S_{nl}(p)\Theta_{lm}(\theta_p)\Phi_m(\phi_p),$$

and so the phase is

$$\arg[\chi_a(\boldsymbol{p})/\chi_b(\boldsymbol{p})]=\begin{cases}-(\pi/2)(l_a-l_b), & \text{if } S^a\Theta^aS^b\Theta^b\geq 0,\\ -(\pi/2)(l_a-l_b)+\pi, & \text{if } S^a\Theta^aS^b\Theta^b<0,\end{cases} \tag{3}$$

since atomic orbitals with different m's do not form a molecular orbital from the symmetry condition. Namely the phase is determined by the difference between azimuthal quantum numbers of two atomic orbitals. In momentum space, the density distribution shifts by $-(\pi/2)(l_a - l_b)/R$ to the positive p_z direction. Since $l_a - l_b$ generally dominates the energy difference between the two atomic orbitals when $n_a = n_b$, the phase is expected to have a correlation with that energy difference.

2.3. Amplitude

In the oscillation term, the parameter λ which determines the extent of mixing of two atomic orbitals appears explicitly in the amplitude part $A(\boldsymbol{p})$. From Eq. (2e), we have

$$A(\boldsymbol{p}) = \begin{cases} 1 - [|\chi_a| - \lambda|\chi_b|]^2/[|\chi_a|^2 + \lambda^2|\chi_b|^2] \leq 1, & \text{(4a)} \\ -1 + [|\chi_a| + \lambda|\chi_b|]^2/[|\chi_a|^2 + \lambda^2|\chi_b|^2] \geq -1. & \text{(4b)} \end{cases}$$

The amplitude $|A(\boldsymbol{p})|$ is generally a function of $\boldsymbol{p}$ and is large (small) when $\boldsymbol{p}$ diminishes (augments) the second terms of Eqs. (4a, b). When $\lambda = \pm|\chi_a|/|\chi_b|$, $A(\boldsymbol{p})$ takes its extremum values ±1. Since λ is a constant whereas $|\chi_a|/|\chi_b|$ is a function of $\boldsymbol{p}$, this condition is satisfied if $\chi_a = \chi_b$, i.e., a complete covalent bond. In this case, $\lambda = \pm 1$ and the momentum distribution has nodal planes

$$p_z = (2n+1)\pi/R, \quad \text{for } \lambda = 1,$$

$$p_z = 2n\pi/R, \quad \text{for } \lambda = -1,$$

where n is an integer. When $\chi_a \neq \chi_b$, it is possible that $\lambda = \pm|\chi_a|/|\chi_b|$ for some values of $\boldsymbol{p}$, but at the same time $\cos[p_z R + \arg(\chi_a/\chi_b)]$ will not be ∓ 1 for such values of $\boldsymbol{p}$. So the oscillation term does not vanish. Namely, if there is some polarity, nodes from the oscillation term do not appear in the momentum distribution.

In order to obtain an approximate magnitude of $A(\boldsymbol{p})$, we may take the expectation value of $A(\boldsymbol{p})$ over the normalized one-center momentum density $[|\chi_a|^2 + \lambda^2|\chi_b|^2]/(1+\lambda^2)$;

$$\bar{A} = \int A(\boldsymbol{p})[|\chi_a|^2 + \lambda^2|\chi_b|^2]\, d\boldsymbol{p}/(1+\lambda^2) = 2\lambda S_p/(1+\lambda^2), \tag{5a}$$

$$S_p = \int |\chi_a(\boldsymbol{p})||\chi_b(\boldsymbol{p})|\, d\boldsymbol{p} \leq 1, \tag{5b}$$

where S_p is a kind of overlap integral in momentum space, and represents the similarity of two momentum-space atomic orbitals; for example, it is 1 for the same atomic orbitals, 0.507 for $1s$-$2s$ pair, and 0.424 for $1s$-$2p\sigma$ pair, if Slater type orbitals with the same exponents are used. Since the similarity between two atomic orbitals is also reflected in λ, $\bar{A}$ is eventually governed by the polarity. For $\chi_a = \chi_b$ (complete covalent bond), all of $|2\lambda/(1+\lambda^2)|$, S_p, and $|\bar{A}|$ take maximum value 1. As the polarity increases, the value of $|\bar{A}|$ decreases from 1 and the oscillation of $\rho(\boldsymbol{p})$ diminishes. Figure 1 shows several momentum distributions for the bonding state of the model one-electron heteronuclear system used

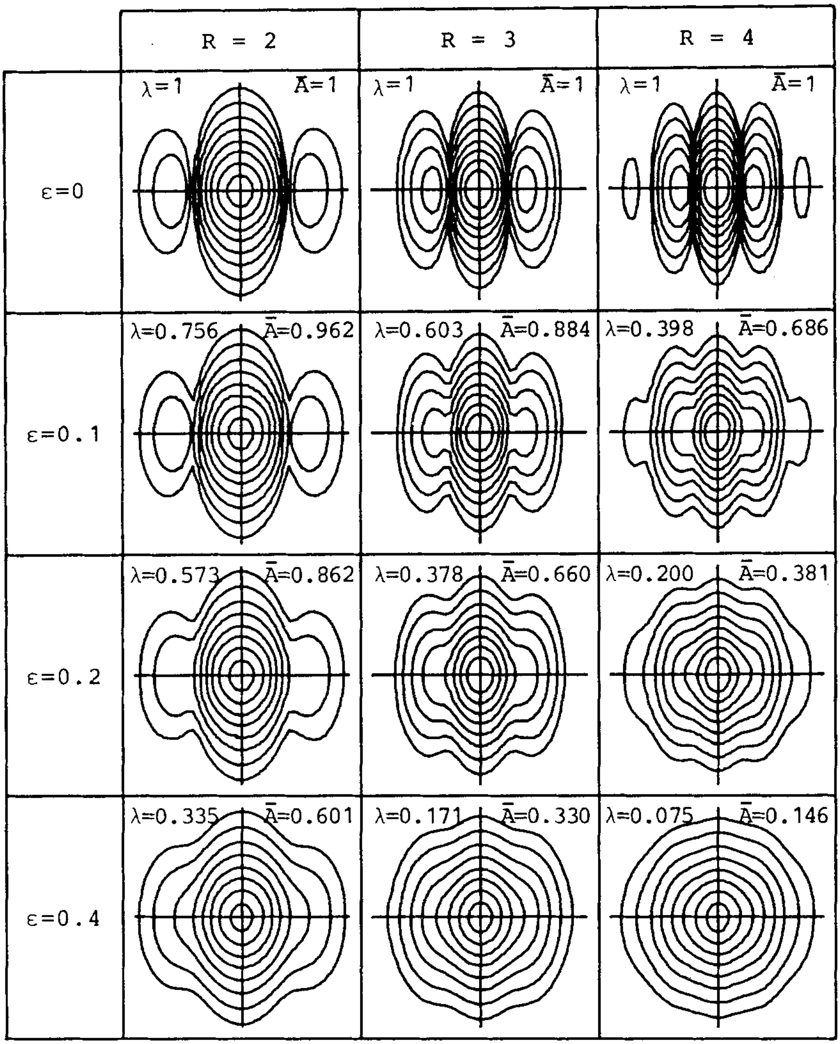

Fig. 1. Contour maps of electron momentum density for the $1s\sigma$ bonding state of the model one-electron heteronuclear system. Contour values are 0.3, 0.1, 0.03, 0.01, 0.003, 0.001, 0.0003, and 0.0001 from the innermost contour. The p_z and p_x axes are taken as the horizontal and vertical axes, respectively. Square region containing each contour map is $|p_z| \leq 4$ and $|p_x| \leq 4$. Refer to Sects. 2.3. and 3.2. for the meaning of parameters

by Feinberg and Ruedenberg [11]. (Nuclear charges Z_a and Z_b are fractional and $Z_a + Z_b = 2$, $\varepsilon = (Z_a - Z_b)/2$ (≥ 0). See Sect. 3.2. for detailed description.) In the H_2^+ system ($\varepsilon = 0$, $\lambda = \bar{A} = 1$), the oscillation is largest and nodes from the oscillation are clearly observed. As R increases or as ε increases, both λ and $\bar{A}$ decrease. After all, the augmentation of polarity (ionic character) results in the diminution of oscillatory behavior of momentum density.

3. Bond polarity and anisotropic momentum distribution

3.1. A measure of anisotropy

Since the oscillation part $\cos[p_z R + \arg(\chi_a/\chi_b)]$ depends explicitly on the z component of momentum vector $\boldsymbol{p}$, the oscillation of momentum distribution is not spherically symmetrical. Consequently, the molecular momentum distribution $\rho(\boldsymbol{p})$ has an anisotropy. Since the oscillation arises along the internuclear axis, we can use ratios Q_n of nth directional moments of momenta ($1 \le n \le 4$) that are parallel and perpendicular to the bond axis;

$$Q_n = \langle |p_z|^n \rangle / \langle |p_x|^n \rangle, \tag{6a}$$

$$\langle |p_z|^n \rangle = \int |p_z|^n \rho(\boldsymbol{p})\, d\boldsymbol{p} = 2 \int_0^\infty p_z^n J_z(p_z)\, dp_z, \tag{6b}$$

$$\langle |p_x|^n \rangle = \int |p_x|^n \rho(\boldsymbol{p})\, d\boldsymbol{p} = 2 \int_0^\infty p_x^n J_x(p_x)\, dp_x, \tag{6c}$$

where $J_z(p_z)$ and $J_x(p_x)$ are directional Compton profiles [2-4]. Q_1 represents the directional ratio of electron velocity. Q_2 affords the anisotropy of the kinetic energy, since the sum of second moments along the three axes is just twice the kinetic energy. Generally, Q_n is positive, is unity for spherically symmetrical distributions, and deviates from unity as the anisotropy increases. As a result, larger polarity corresponds to smaller deviation of Q_n from the value unity. On the other hand, Matcha et al. [14] have proposed $\Delta J(0) = J_z(0) - J_x(0)$, the difference between the directional Compton profiles at zero momentum, as a measure of the anisotropy. In the following, we analyze the anisotropy of momentum distribution for the model one-electron diatomic system using Q_n in comparison with $\Delta J(0)$.

3.2. Analysis of Model One-Electron System

The model employed here is the one-electron heteronuclear diatomic molecule with non-integral nuclear charges introduced by Feinberg and Ruedenberg [11]. Namely, the sum of the nuclear charges is restricted to 2 and ε is defined as $(Z_a - Z_b)/2$ (≥ 0). Slater type $1s_a$ and $1s_b$ orbitals have been considered and their exponents and λ have been determined variationally as a function of ε and R.

Results for Q_n are given in Fig. 2a-d. The behaviors of Q_n ($1 \le n \le 4$) on the variation of R are similar to one another: In the bonding $1s\sigma$ state, $Q_n \le 1$ and in the united atom ($R = 0$) and separated atoms ($R = \infty$) limits Q_n becomes unity reflecting isotropic momentum distributions. In the so-called molecular region, $1 \lesssim R \lesssim 3$, Q_n takes a minimum value and the anisotropy becomes largest. In the energy language, the directional imbalance of the kinetic energy is maximal in this R range. In the bonding state, the increase of ε reduces the internuclear distance where Q_n is the minimum and the well-depth of that minimum. These

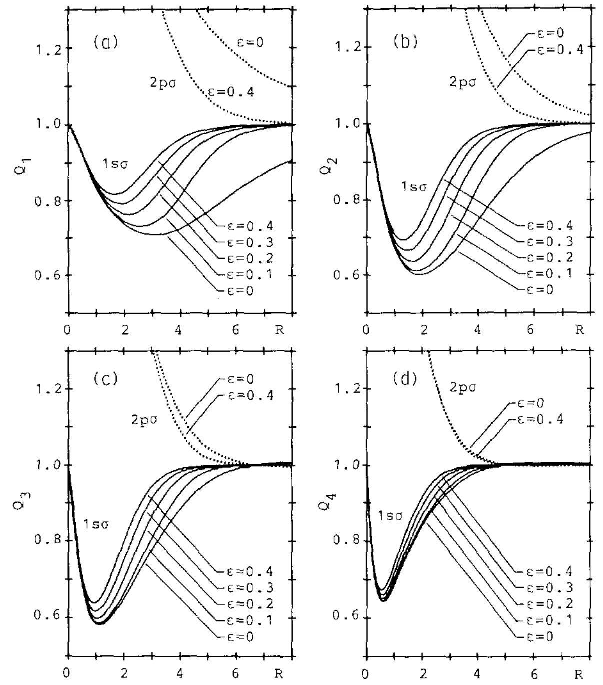

Fig. 2. Directional ratios of momentum moments $Q_n = \langle |p_z|^n \rangle / \langle |p_x|^n \rangle$ $(1 \leq n \leq 4)$ versus internuclear distance R for the model one-electron system

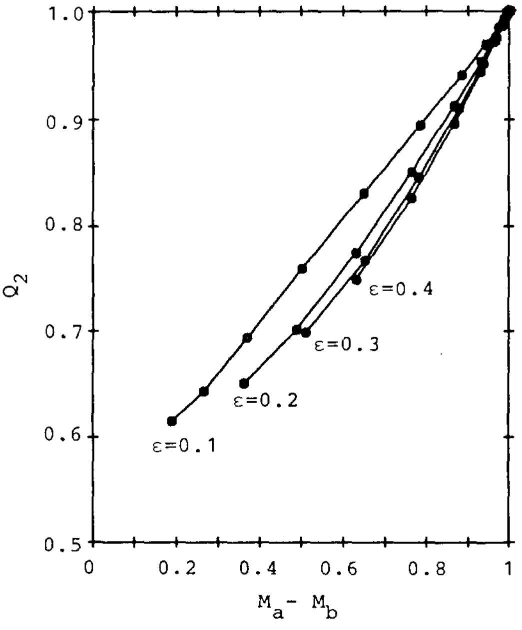

Fig. 3. Relations between the directional ratio Q_2 and the difference in Mulliken atomic populations $M_a - M_b$ for internuclear distance $R \geq 2$. Each ε line is marked by ● at the half integer values of R starting from 2 (bottom) and ending at 10 (top)

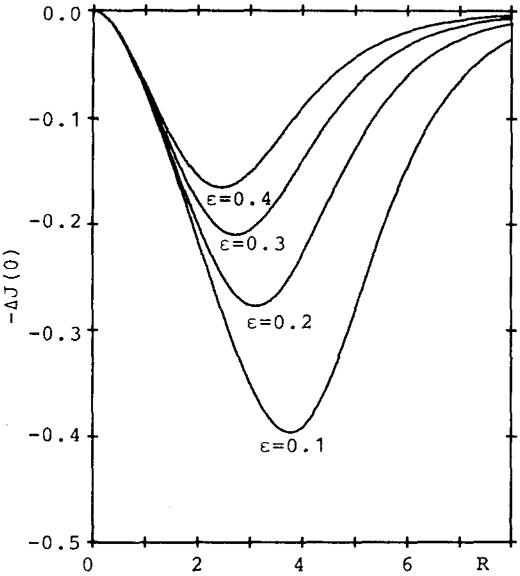

Fig. 4. Difference in the directional Compton profiles at zero momentum $-\Delta J(0) = -(J_z(0) - J_x(0))$ versus internuclear distance R.

correspond to the fact that as the difference in nuclear charges increases, the electron distribution is more strongly bound by one nucleus and hence the covalent character decreases. As an example, Fig. 3 shows the relation of Q_2 to the difference in Mulliken atomic populations, $M_a - M_b$, for the bonding state. It is seen that the unbalanced electron distribution and the anisotropy in momentum density are well correlated. For the antibonding $2p\sigma$ state, $Q_n \geq 1$ and increases monotonically as R decreases. The increase in ε again reduces the anisotropy of momentum distribution in the antibonding state. As n becomes larger, the distance R where Q_n begins to deviate from 1 becomes smaller. Since higher order moments emphasize the contribution from large momentum region, this represents that the anisotropy of momentum distribution is small in the high momentum region and that the anisotropy due to bond polarity occurs mainly in the low momentum region. Since the variation of Q_n against the nuclear charge difference becomes small as n increases, Q_1 or Q_2 is a more suitable measure of the anisotropy than Q_3 or Q_4.

In Fig. 4, the difference between directional Compton profiles at their zero momenta is plotted against R. The behavior of $-\Delta J(0)$ is similar to that of Q_n. The ε dependence of minimum positions and depths is also similar. Though we could not find definite difference between the measures Q_n and $\Delta J(0)$, the present measure of Q_n will be better, since Q_n refers to the whole momentum distribution while $\Delta J(0)$ examines only one local point. Particularly, Q_2 has a merit that the oscillation and anisotropy of electron momentum distribution, and hence the bond polarity, are closely related to the directional imbalance of the kinetic energy. We note that the directional kinetic energy appears in the directional virial theorem [15, 16] derived from the non-uniform scaling.

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Note added in proof

Very recently, Ch. V. Rama Rao and A. K. Chandra [Chem. Phys. Lett. 113, 391 (1985)] have used the directional kinetic energy for the analysis of the bonding in HeH^+. Through the partial-wave analysis of the momentum density, A. M. Simas, V. H. Smith, Jr., and A. J. Thakkar [Int. J. Quantum Chem. S18, 385 (1984)] have shown that a quantitative manifestation of the different bonding situations in the isoelectronic molecules N_2, CO, and BF occurs in the anisotropy of the kinetic energy.