Diatomic Interactions in Momentum Space. The $2p\pi_u$ and $3d\pi_g$ States of $H_2^+$ System

Toshikatsu Koga*, Minoru Sugawara, and Mutsuo Morita

Departments of Industrial Chemistry and of Applied Science for Energy, Muroran Institute of Technology, Muroran, Hokkaido, 050 Japan

The recently proposed method of momentum electron density for interatomic interactions is applied to the two $\pi$ states of the $H_2^+$ system. The processes of the attractive $2p\pi_u$ and repulsive $3d\pi_g$ interactions are analysed based on the behaviour of the momentum density and Compton profile. The results are compared with the previous ones for the $1s\sigma_g$ and $2p\sigma_u$ states. The guiding principle of contraction and expansion for the energy-density relation in momentum space is shown to be common to both the $\sigma$ and $\pi$ states.

Key words: Momentum electron density – Compton profile – $H_2^+$ System – $\pi$ States of $\sim$.

1. Introduction

In the early 1940s, an investigation of the chemical bond from the momentum ($p$-) space viewpoint was initiated by Coulson and Duncanson [1] based on the Dirac–Fourier transform [2] of the coordinate ($r$-) space wave function. Though the wave functions they employed were far less accurate than those available today, they [1] gave in a series of papers some significant insight into the $p$-space characteristics of the chemical bonding not only in diatomic $H_2^+$ and $H_2$ molecules but also in simple hydrocarbons. However, the $p$-space treatment has received little attention in molecular quantum mechanics, partly because our everyday intuition is more confined to a space of lengths rather than that of velocities. The momentum electron density $\rho(p)$, which is a basic physical quantity in our present approach, has been examined only in relation to the Compton profiles.

* To whom all correspondence should be addressed
of atoms and molecules at their equilibrium conformations. However, the \( r \)- and \( p \)-representations are complementary to one another [2], and a study in \( p \)-space is expected to provide a new or alternative understanding to the bonding problem.

Indeed, there seems to be renewed interests on the use of \( p \)-space concept for several atomic and molecular phenomena in recent years [3]. Especially, we have recently proposed a method of momentum density for interatomic interactions [4] which permits to clarify the origin of nuclear rearrangements (such as molecular geometries and chemical reactions) in terms of the concept in \( p \)-space instead of the usual one in \( r \)-space. Considering a uniform scaling process of an arbitrary molecular conformation \( \mathbf{R}_0 \) with scaling factor \( s \), we have shown that the difference in momentum density \( \rho (\mathbf{p}) \) and its modified forms defined by

\[
\Delta \rho (\mathbf{p}; s) = \rho (\mathbf{p}; s) - \rho (\mathbf{p}; \infty),
\]

\[
\Delta \tilde{\rho} (\mathbf{p}; s) = \left( \frac{1}{s} \right) \int_s^\infty ds' \Delta \rho (\mathbf{p}; s'),
\]

\[
\Delta \tilde{\rho} (\mathbf{p}; s) = \Delta \tilde{\rho} (\mathbf{p}; s) + \Delta \rho (\mathbf{p}; s),
\]

rigorously govern kinetic energy, stabilization energy, and interatomic force of the system, respectively. It has been then suggested that the contraction and expansion observed in these density differences are important concept which characterizes the nature of nuclear rearrangements in \( p \)-space. The method has been applied to the two lowest \( \sigma \) states of the \( \mathrm{H}_2^+ \) system [5]. For the attractive \( 1s\sigma_g \) and repulsive \( 2p\sigma_u \) interactions, the behaviour of momentum density and its effect on the energy and force have been quantitatively examined. Origin of covalent bonding has been also discussed based on the energy partitionings proposed previously [4].

The purpose of this paper is to extend the application of the momentum density approach to the \( \pi \) states of the \( \mathrm{H}_2^+ \) system. For the bonding \( 2p\pi_u \) and antibonding \( 3d\pi_g \) states, the reorganization of \( \rho (\mathbf{p}) \) and its effect on the stabilization/de-stabilization of the system are quantitatively investigated in comparison with the previous results for the \( 1s\sigma_g \) and \( 2p\sigma_u \) states. In the next section, the present theory of momentum density is outlined, and the results are discussed in Sec. 3. Sec. 3.1 provides discussion on the differences between \( \sigma/\pi \) and bonding/anti-bonding states in \( p \)-space on the basis of the momentum density distributions and Compton profiles. The behaviour of momentum density and its energetic contribution during the interaction processes are analysed in Sec. 3.2. Atom-bond partitioning is also examined. Changes in the average and directional Compton profiles and the parallel-perpendicular partitioning of the stabilization energy are discussed in Sec. 3.3.

2. Theoretical Ground

For diatomic systems, the scale factor \( s \) in Eq. (1a–c) can be replaced with internuclear distance \( R \). Then the density differences \( \Delta \rho (\mathbf{p}; R), \Delta \tilde{\rho} (\mathbf{p}; R), \) and