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(Journal of the Korean Chemical Society)
Vol. 23, No. 1, 1979
Printed in Republic of Korea

결합공간과 반결합공간 (제 1 보)

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서울대학교 자연과학대학 화학과

(1978. 11. 22 접수)

Bonding and Antibonding Regions (I)

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(Received Nov. 22, 1978)

요 약. Integral Hellmann-Feynman Theorem과 천이밀도의 positive definite한 성질로 부터, 천이 밀도 공간을 "결합공간"과 "반결합공간"으로 구분할 수 있음을 보였고, 이러한 개념의 유용성을 H_2계에 대하여 증명하였다. 핵의 배치의 변화에 기인한 전자 섭동에너지의 본질을 이 개념을 이용함으로써 성공적으로 이해할 수 있으리라는 결론을 얻었다. 천이밀도의 성질에 관하여 논의하였다.

ABSTRACT. The new concept of the Bonding and Antibonding Regions in the transition density space is developed from the Integral Hellmann-Feynman Theorem and the positive definiteness of the transition density. The unility of this concept is fully demonstrated for H_2 system. It is expected that the nature of the electronic perturbation energy due to the change of nuclear configuration can be successfully understood by using this concept. Properties of the transition density is briefly discussed.

INTRODUCTION

To understand the nature of such chemical behavior as internal rotation, the origin of the energy difference between molecules with different nuclear configurations should be sought out. This energy difference has been analyzed from various points of view.[1~6]

Within a scope of the Born-Oppenheimer approximation, this energy difference can be explicitly given by the Integral Hellmann-Feynman Theorem (IHF) of Parr.[7] According to IHF, the total perturbation energy accompanying the the change of nuclear configuration is partitioned into the change of nuclear-nuclear repulsion energy (ΔE_{nn}) and that of electronic energy (ΔE_{el}). And ΔE_{el} is expressed in terms of the perturbation operator of the electron-nuclear attraction and the transition density[8] which is obtained from the wavefunctions of two conformers. Since ΔE_{nn} is a physically definite quantity which can be explained by the classical electrostatic theory, the origin of the energy change induced by the change of nuclear configuration should be investigated through the close examination of ΔE_{el}.

It is the purpose of this paper to develop the idea of bonding region in the transition density space around nuclei. The word "bonding" shall be defined in such a way that it relates to the electronic energy change of molecule due to the change of the nuclear configuration. In this paper, the approach to the electonic energy change shall be essentially qualitative. Some properties of the transition density will be discussed. A definition of the Bonding and Antibonding Regions will then be given, and the utility of this concept will be demonstrated for H_2 system.

BONDING AND ANTIBONDING REGIONS

Within the framework of the Born-Oppenheimer approximation, the energy of a molecule with a fixed configuration is given by the eigenvalue of the (electronic) Schrödinger equation,

$$\begin{aligned} H(R)\Phi_{el}(R) &= (T+V_{ee}+V_{ne}+V_{nn})\Phi_{el}(R) \\ &= E(R)\Phi_{el}(R) \end{aligned} \tag{1}$$

where T, V_{ee}, V_{ne}, and V_{nn} are the kinetic, electron-electron repulsion, nuclear-electron attraction, and nuclear-nuclear repulsion operators, respectively. R may be any nuclear coordinate: a simple internuclear separation or an angle of internal rotation. In general, if the mass center of a molecule or a group of atoms is taken as the origin of a space-fixed coordinate system, a deformation of nuclear framework from R_0 to R induces changes in V_{ne} and V_{nn},

$$\begin{aligned} \Delta V(R_0\to R) &\equiv H(R)-H(R_0) \\ &= \Delta V_{ne}(R_0\to R)+\Delta V_{nn}(R_0\to R) \\ &= \sum_{i=1}^{N}\Delta v(i)+\Delta V_{nn}(R_0\to R) \end{aligned} \tag{2}$$

where N is the total number of electrons.

According to IHF,[7] the corresponding perturbation energy is given by

$$\begin{aligned} \Delta E(R_0\to R) &\equiv E(R)-E(R_0) \\ &= \frac{\langle \Phi_{el}(R_0)\,|\,\Delta V(R_0\to R)\,|\,\Phi_{el}(R)\rangle}{\langle \Phi_{el}(R_0)\,|\,\Phi_{el}(R)\rangle} \\ &= \int \Delta v(1)\rho_{R_0R}(1)\,d\tau_1+\Delta E_{nn}(R_0\to R) \end{aligned} \tag{3}$$

where ΔE_{nn} is the change of nuclear-nuclear repulsion energy, and $\rho_{R_0R}(1)$ is the transition density matrix,[8]

$$\rho_{R_0R}(1)=\frac{N\int \Phi_{el}^*(R_0)\Phi_{el}(R)\,d\tau_2 d\tau_3\cdots d\tau_N}{\int \Phi_{el}^*(R_0)\Phi_{el}(R)\,d\tau_1 d\tau_2\cdots d\tau_N}. \tag{4}$$

Obviously

$$\begin{aligned} &\int \Delta v(1)\rho_{R_0R}(1)\,d\tau_1 \\ &\quad = \langle \Phi_{el}(R)\,|\,T+V_{ee}+V_{ne}(R)\,|\,\Phi_{el}(R)\rangle \\ &\qquad -\langle \Phi_{el}(R_0)\,|\,T+V_{ee}+V_{ne}(R_0)\,|\,\Phi_{el}(R_0)\rangle \\ &\quad \equiv \Delta E_T(R_0\to R)+\Delta E_{ee}(R_0\to R) \\ &\qquad +\Delta E_{ne}(R_0\to R) \\ &\quad \equiv \Delta E_{el}(R_0\to R) \end{aligned} \tag{5}$$

Perhaps it may be worthwhile to make some comments on the transition density, ρ_{R_0R} (1), since in practice approximations are often built in $\rho_{R_0R}(1)$ of Eq. (4) through $\Phi_{el}(R_0)$ and $\Phi_{el}(R)$. In the present paper, for example, it is assumed that both $\Phi_{el}(R_0)$ and $\Phi_{el}(R)$ are the Hartree-Fock single determinantal wavefunctions. First of all, the transition density is invariant with respect to the (unitary) transformation of orbital bases of $\Phi_{el}(R_0)$ and/or $\Phi_{el}(R)$. For instance, the localized orbital description does not alter $\rho_{R_0R}(1)$ of the original bases. Secondly, although $\rho_{R_0R}(1)$ is a fictitious charge density, having no classical analog, it can be approximated with such real charge densities as $\rho_{R_0R_0}(1)$ and/or $\rho_{RR}(1)$. Namely, $\rho_{R_0R_0}(1)$ may be viewed as the zeroth order approximation, which yields $\int \Delta v(1)\rho_{R_0R_0}(1)d\tau_1 = E_{el}{}^{(1)}(R_0 \rightarrow R)$, the first order energy. On the other hand, the average real charge density, $\frac{1}{2}(\rho_{R_0R_0}(1)+\rho_{RR}(1))$, is the first order approximation to $\rho_{R_0R}(1)$ which produces the perturbation energy up to (and including) the second order. That is, expanding $\Phi_{el}(R)$:

$$\Phi_{el}(R)=\Phi_{el}(R_0)+\lambda\Phi_{el}^{(1)}+\lambda^2\Phi_{el}^{(2)}+\cdots\cdots \tag{6}$$

and taking normality of $\Phi_{el}(R)$ and $\Phi_{el}(R_0)$, and therefore $\langle\Phi_{el}(R)|\Phi_{el}^{(1)}\rangle=0$, into account, it follows from Eq. (4) that

$$\begin{aligned}\rho_{R_0R}(1)&=N\int\Phi_{el}^{*}(R_0)\,\{\Phi_{el}(R_0)+\lambda\Phi_{el}^{(1)}+\lambda^2\Phi_{el}^{(2)}\\&\quad+\cdots\}\,d\tau_2d\tau_3\cdots d\tau_N\\&=\frac{1}{2}[N\int\Phi_{el}^{*}(R_0)\Phi_{el}(R_0)\,d\tau_2d\tau_3\cdots d\tau_N\\&\quad+N\int\{\Phi_{el}(R_0)+\lambda\Phi_{el}^{(1)}+\lambda^2\Phi_{el}^{(2)}\}^{*}\{\Phi_{el}(R_0)\\&\quad+\lambda\Phi_{el}^{(1)}+\lambda^2\Phi_{el}^{(2)}+\cdots\}\,d\tau_2d\tau_3\cdots d\tau_N]+O(\lambda^2)\\&=\frac{1}{2}[\rho_{R_0R_0}(1)+\rho_{RR}(1)]+O(\lambda^2)\end{aligned} \tag{7}$$

The most important thing which Eq. (7) tells us is, however, that the transition density $\rho_{R_0R}(1)$ is positive definite since both $\rho_{R_0R_0}(1)$ and $\rho_{RR}(1)$ themselves are positive definite.[8] The fact thus implies that the sign of $\Delta v(1)\cdot\rho_{R_0R}(1)d\tau_1$ is determined solely by that of $\Delta v(1)$. Therefore if one divides the transition density space into two regions: the Bonding Region where $\Delta v(1)<0$ and the Antibonding Region where $\Delta v(1)>0$, one has

$$\begin{aligned}\Delta E_{el}(R_0\rightarrow R)&=\underset{\Delta v(1)<0}{\int}\Delta v(1)\,\rho_{R_0R}(1)\,d\tau_1\\&\qquad\text{(negative)}\\&\quad+\underset{\Delta v(1)>0}{\int}\Delta v(1)\,\rho_{R_0R}(1)\,d\tau_1\\&\qquad\text{(positive)}\end{aligned} \tag{8}$$

The boundary surfaces of two regions are given by the solutions of $\Delta v(1)=0$. The transition charge element $\rho_{R_0R}(1)d\tau_1$ in the Bonding Region contributes to the lowernig of energy, and $\rho_{R_0R}(1)d\tau_1$ in the Antibonding Region acts in the opposite way during the change of the nuclear framework from R_0 to R.[9] Lastly, it may be pointed out that although $\Delta E(R_0\rightarrow R)=\Delta E_{el}(R_0\rightarrow R)+\Delta E_{nn}(R_0\rightarrow R)$ or $\Delta E_{el}(R_0\rightarrow R)$ itself does not change as the internuclear separations, R_0 and R, are fixed (Born-Oppenheimer approximation), the transition density $\rho_{R_0R}(1)$ may have different feature depending on the relative spatial arrangement of the initial and final nuclear frameworks, as will be seen in *Figs.* 2(B) and 3.

In any diatomic system, which forms a stable molecule in a certain internulear separation, say, R_{eq}, it is true that $\Delta E_{nn}(R_0\rightarrow R)>0$, $\Delta E_{el}(R_0\rightarrow R)<0$, and $\Delta E(R_0\rightarrow R)<0$ as long as $R_0>R>R_{eq}$. The situation may be best illustrated by *Fig.* 1 in which two hydrogen atoms initially separated by $R_0=4.726$ a.u. has moved toward each other to $R=3.088$ a.u. The dominance of the negative part in Eq. (8) to such an extent that $\Delta E_{el}=-97.10$ kcal/mole[10] can be understood through the observation of the transition density as depicted in *Fig.* 2, where the the contour map of $\Delta v(1)$:

$$\Delta v(1)=\underset{\text{(protons at R)}}{\left\{-\sum_{k=1}^{2}\frac{1}{r_{k1}}\right\}}\;-\;\underset{\text{(protons at }R_0\text{)}}{\left\{-\sum_{m=1}^{2}\frac{1}{r_{m1}}\right\}} \tag{9}$$

is plotted together with the transition density and its first order approximation. The large (absolute) values of $\Delta v(1)$ in the vicinity of the protonic sites manifest the extraordinary gravity of the transition density near these sites. If the internuclear separation changes from R_0 to R, P region is the Bonding Region and Q regions are the Antibonding Regions for $R_0>R$ and *vice versa* for $R_0<R$. The protonic sites are denoted by "+" and "×" in *Fig.* 2(B) and

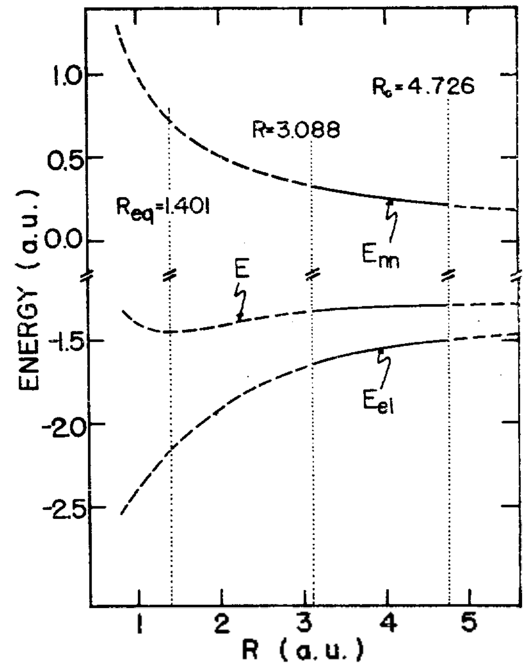

Fig. 1. Energy *vs.* internuclear separation of H_2 calculated by McLean *et al.* R_{eq} is the equilibrium separation of H_2, and R_0 and R correspond to the internuclear separations of two protons of *trans* and *cis* H_2O_2, respectively.

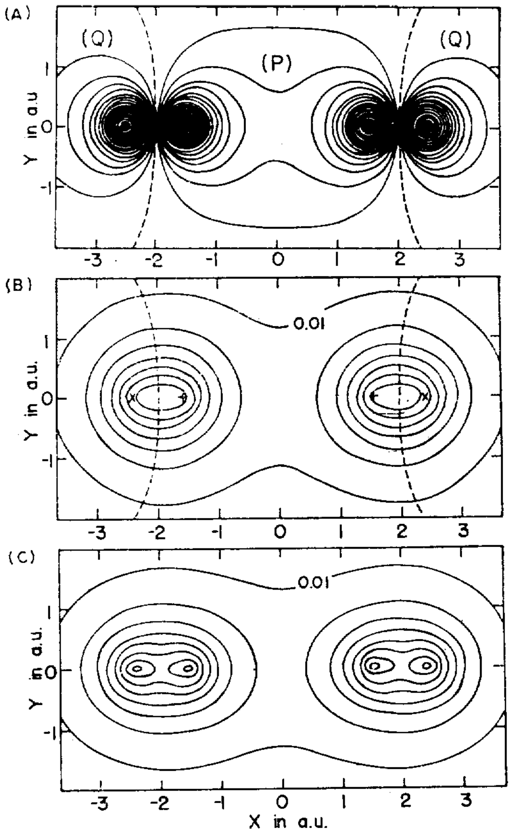

Fig. 2. (A) Contour lines of $\Delta v(1)$ accompanying the change of internuclear separation of H_2 between $R_0=4.726$ a.u. and $R=3.088$ a.u. along x-axis. Dotted lines denote the sections of the boundary surfaces $\Delta v(1)=0$. Contour intervals are 0.2 in the region of $\Delta v(1)>0$, and -0.2 in the region of $\Delta v(1)<0$, respectively. For the change from R to R_0, $\Delta v(1)>0$ in P region and $\Delta v(1)<0$ in Q regions, and for the change from R_0 to R, *vice versa.* (B) Transition density of H_2 in xy-plane calculated by using the McLean's wavefunctions. The positions of the nuclei are denoted by "+" and "×" (C) First order approxiamation of the transition density, $\rho_{R_0R}(1)=\frac{1}{2}(\rho_{R_0R_0}(1)+\rho_{RR}(1))$. Contour interval is 0.02 a.u. both in (B) and (C).

the hyperbola-like boundary sections (surfaces) between two regions justify the dominance of the negative part in Eq. (8) as stated above. Moreover, since the transition density is approximated to the average real charge density as stated earlier, the heavier transition density distribution in P region can be understood from the generally accepted fact that the electron build-up between two protons should become greater as the internuclear separation, R, of a diatomic molecule becomes shorter as long as $R>R_{eq}$. The first order approximation of $\rho_{R_0R}(1)$ depicted in *Fig.* 2(C) may serve, together with *Fig.* 2(B), to demonstrate the positive definiteness of the transition density as stated above with Eq. (7). The average real charge density seems to be poorest in the vicinity of the protonic sites. Yet, it seems to be a good approximation in the other part of the space, and thus would be useful in guessing a general nature of the transition density from an empirical picture of the real charge distribution.

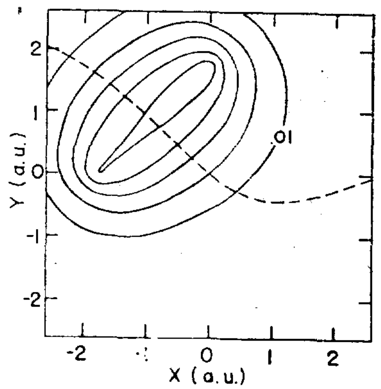

Fig. 3. Transition density of H_2 in the plane including protons when the protonic configurations are the same as those of *trans* and *cis* H_2O_2. Internuclear separations change from $R_0=4.726$ a.u. to to $R=3.088$ a.u. Contour interval is 0.01 a.u.

CONCLUDING REMARKS

The main objective of this paper is to develop the new concept of the Bonding and Antibonding Regions in the transition density space, whose boundary surfaces are given by the solutions of $\Delta v(1)=0$. It is shown that the transition density, which is the essential part of the perturbation energy expression, is positive definite and can be approximated to the average real charge density in all space except the vicinity of nuclear sites.

It was pointed out by Fink and Allen[11] that IHF failed to give the exact perturbation energy from approximate wavefunctions. However, IHF should predict correctly at least the sign of the perturbation energy,[11] so it should be sufficient to our puprose of qualitative analysis.

It is concluded that, in H_2 system, the nature of the electronic perturbation energy due to the change of nuclear framework may be understood in terms of the transition density distribution — in turn, the real charge density distributions of different nuclear configurations — over the Bonding and Antibonding Regions. It is expected that the origin of the barrier to internal rotation around single bond can be successfully sought through this concept.

ACKNOWLEDGEMENT

This research was supported by grant from the Ministry of Science and Technology under contract No. STF-77-39. The authors was much indebted to professor Y. S. Kim and professor C. W. Pyun of the Seoul National University for their helpful discussions and suggestions.

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