

Zero virial reaction processes. Reactions of Si and Mg atoms with H₂ and HF molecules

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By adopting the bond angle as a reaction coordinate and imposing on appropriate conditions, we determine a reaction path named the zero virial path starting from the reactant and arriving at the product via the transition state. At every point on this path, the polyatomic virial theorem is reduced to the simple atom-like form, and within the LCAO framework the total energy including the nuclear repulsion is partitioned exactly into the one center (atomic) and two center (bond) terms through the negative kinetic energy. Using these advantages of the zero virial path, the processes of bond formation and fission are examined in detail for the reactions of Si and Mg atoms with H₂ and HF molecules.

Key words: Zero virial reaction path—energy partitioning scheme

1. Introduction

The investigation of processes of bond formation and fission during chemical reactions is a fundamental subject in quantum chemistry. For this purpose, the change in the electronic structure is pursued along some reaction path starting from the reactant and arriving at the product via the transition state (TS). It is particularly important for the elucidation of the driving forces of reactions to discuss the electron rearrangement during the reaction process in connection

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with the changes in the total energy and the geometrical parameters. Although the molecular orbitals (MO's) themselves contain all the information for the electronic structure of the system, the bond indices such as the population and the bond energy are considerably useful not only to facilitate the analysis and interpretation of electronic structures but also to clarify some common features among different systems. In the *ab initio* MO theory, however, the energy partitioning scheme is rather complicated because of the three and four center interactions among the atomic orbitals (AO's).

In this paper, the polyatomic virial theorem (PVT) is applied to the study of reaction processes of atoms and diatomic molecules, and a new simple energy partitioning scheme is presented. By the use of the bond angle as a reaction coordinate, the zero virial path (ZVP) is obtained which connects the reactant and the product through the TS. The ZVP approach enables us to determine a path starting from a stable point and arriving at a TS, if exists. (Except for the equilibrium points, this path is generally inconsistent with other reaction paths such as Intrinsic Reaction Coordinate [1], Steepest Descent Path, and Minimum Energy Path [2].) Furthermore on the ZVP, the total energy of the reaction system is exactly partitioned into the one center (atomic) and two center (bond) terms, which seems very useful to discuss the chemical reaction from the viewpoint of bond interchange. The present study is a natural extension of a previous study [3], where the same approach has been successfully applied to the structural problem of triatomic molecules in relation to the redistribution of the electron momentum density.

The reactions of Si and Mg atoms with H₂ and HF molecules are examined and compared with each other. Considering the Si and Mg atoms as representative atoms of their solid surfaces, we may regard these reactions as model processes for chemisorption onto the semiconductor and metal surfaces, respectively. For the SiH₂ system, many experimental data [4–6] and theoretical calculations [7–9] have been reported. The MgH₂ system has attracted considerable attention from the viewpoint of hydrogen storage, but only a few theoretical studies are known [10, 11]. The adsorption of HF is less extensively investigated compared with that of H₂ [9, 12]. However, the comparison of these molecules will be useful to discuss general features of the interactions.

2. Theoretical background

According to Nelander [13] and others [14, 15], the PVT can be written as follows:

$$T(\mathbf{R}, \Theta) + E(\mathbf{R}, \Theta) + \sum_{i=1}^n R_i [\partial E(\mathbf{R}, \Theta) / \partial R_i] = 0. \quad (1)$$

$\{\mathbf{R}, \Theta\}$ are the minimal set of internal coordinates consisting of n bond lengths $\mathbf{R} = \{R_1, R_2, \dots, R_n\}$ and m bond angles $\Theta = \{\Theta_1, \Theta_2, \dots, \Theta_m\}$ which are sufficient to specify the conformation of a given molecular system. $T(\mathbf{R}, \Theta)$ and $E(\mathbf{R}, \Theta)$ represent the kinetic and total energies of the system, respectively. It is easily

recognized that at equilibrium points (i.e. stable points and TS), Eq. (1) is reduced to the simplest form of $E = -T$. However, if all the bond lengths are optimized, that is, $\partial E/\partial R_i = 0$ ($i = 1, 2, \dots, n$) for a given value of Θ , the PVT is written again in its simplest form as Eq. (2) even though the system is not at equilibrium points.

$$E(\mathbf{R}_{\text{opt}}, \Theta) = -T(\mathbf{R}_{\text{opt}}, \Theta). \quad (2)$$

The choice of a set of internal coordinates is arbitrary provided that one bond length is at least included. In studying some types of chemical reactions, it is effective to choose one bond angle, which describe the reaction path most adequately, as the reaction coordinate. The selected bond angle is either one of the m bond angles or the angle defined newly by the linear combination of the m bond angles. The remaining internal coordinates, that is, $(m - 1)$ bond angles and n bond lengths, are optimized at each point on the path. Nalewajski [16, 17] called this path as the zero virial path (ZVP) and showed by model calculations that TS could be attained by tracing the ZVP starting from a stable point.

The ZVP approach suggests a possibility of a simple and clear analysis of reaction processes from the following reasons. At every point on the ZVP, the PVT is reduced to Eq. (2) and the total energy (E) is equal to the negative kinetic energy ($-T$) which can be decomposed into the MO contributions within the independent particle approximation or into the AO-AO pair contributions within the framework of the LCAO approximation [3]. For the latter decomposition, $-T$ (therefore E) consists only of the one- and two-center terms. This energy partitioning scheme is apparently similar to the E_{AB} partitioning scheme in the CNDO method. However, the present scheme is applicable in the *ab initio* method, and gives a simple and exact partition of the total energy. To our knowledge, other methods hitherto known are not capable to partition the total energy exactly into only the one- and two-center terms because of the three- and four-center atomic integrals. Using the full advantage of the simplified PVT, we carry out this energy partitioning along the ZVP, and investigate the modes of bond formation and fission during the reaction processes.

3. Calculation method

The Gaussian 80 program package is used throughout the calculation [18]. Basis sets are the split valence 3-21G type (i.e. 33-21G for Si and Mg, 3-21G for F, and 21G for H) [19, 20]. All the reaction processes are investigated on the singlet energy surface. To fulfill the condition of Eq. (2), it is essentially required to optimize all the bond lengths and at the same time to make the virial theorem be satisfied. The virial theorem does not generally hold for approximate wave functions, but it can be made to hold by the scaling procedure [21]. In the present study, the optimization of the bond lengths by the energy gradient method and the optimization of the scaling factor by the uniform scaling technique are simultaneously carried out for each value of the bond angle. The ZVP is obtained as the trajectory of these points.

4. Results and discussion

4.1. Reaction processes

The reaction processes of XAB systems ($X = \text{Si}$ or Mg and $\text{AB} = \text{H}_2$ or HF) are shown in Fig. 1, where the X atom is fixed to the origin of the coordinate system and the AB molecule is depicted by a segment. The bond angle A-X-B (Θ) is adopted as the reaction coordinate. The bond lengths (R_{XA} and R_{XB}) are optimized for each value of Θ (which is labeled on the segment AB). The y-axis is taken to the direction of the bisector of Θ . The reaction $\text{Si} + \text{H}_2 \rightarrow \text{SiH}_2$ proceeds under the C_{2v} symmetry. In the SiHF system, the reactant configuration is colinear like Si-F-H. However, the product has a bent configuration, where R_{SiH} is

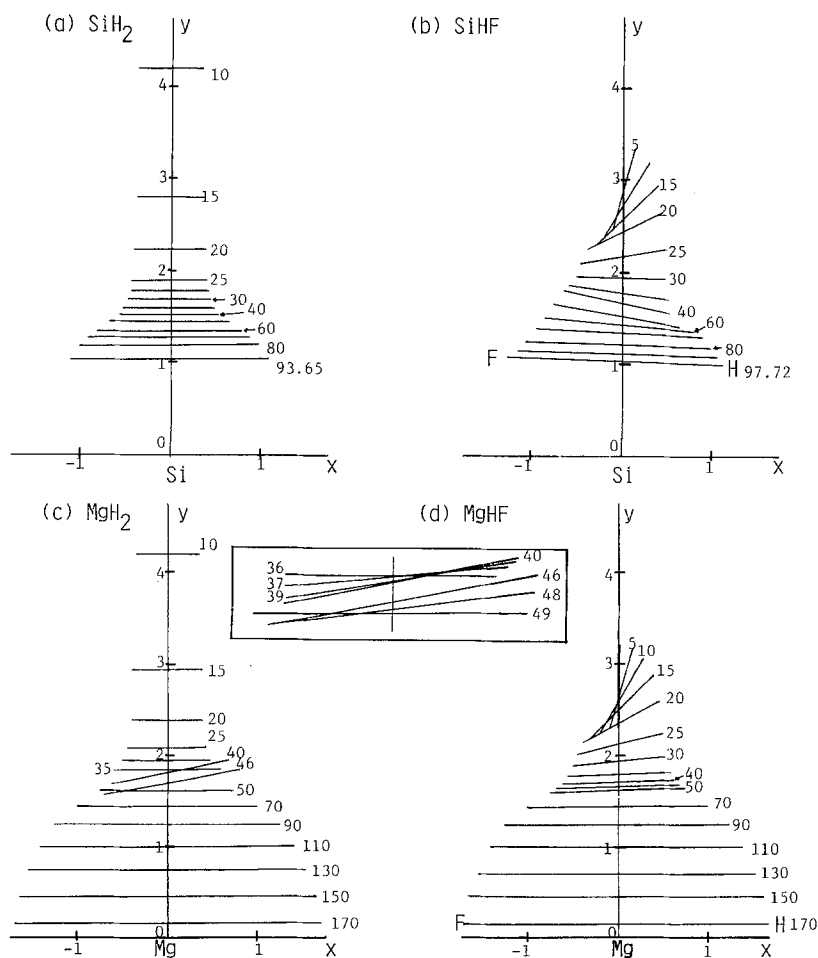


Fig. 1. Paths for the four reactions: $X + \text{AB} \rightarrow \text{XAB}$. X atom is fixed to the origin, and AB molecule is shown by a segment. The y-axis is taken to the direction of the bisector of the bond angle Θ . The number attached to the segment shows the value of Θ . The inserted diagram shows an enlargement around TS for the MgH_2 system

Table 1. Geometrical parameters for SiH₂ and SiHF molecules^a

		present	[22]	[23]	[24]	expt. [27, 28]
SiH ₂	Θ	93.65	91.30	93.44	93.9	92.1
	R_{SiH}	1.531	1.566	1.516	1.505	1.516
SiHF	Θ	97.72	—	—	97.6	—
	R_{SiH}	1.535	—	—	1.510	—
	R_{SiF}	1.637	—	—	1.596	—

^a Bond angles are in degree and bond lengths are in Å

shorter than R_{SiF} as shown in Table 1. For the structure of these molecules, more accurate *ab initio* calculations have been reported [22–24], which are also included in Table 1. In spite of the smallness of our basis sets, agreements are considerably good.

As easily recognized in Fig. 1, the structures of the MgH₂ and MgHF systems are similar to those of the SiH₂ and SiHF systems, respectively, in the reactant regions (i.e. $\Theta < \Theta_{\text{TS}}$). Contrary to the SiH₂ system, however, the exchange of HOMO and LUMO occurs during the reaction $\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2$. Then, the C_s symmetry is assumed for this reaction. Fig. 1c shows that the reaction path deviates from the C_{2v} path only around $\Theta = 36\text{--}49^\circ$ where TS is also located. The MgHF system resembles the SiHF system except for the colinear product. The bond angles at TS (Θ_{TS}) are compared with each other for the four systems in Table 2. Θ_{TS} for the MgAB system is much larger than Θ_{TS} for the SiAB system. Θ_{TS} for the XHF system is slightly larger than Θ_{TS} for the XH₂ system.

Table 2. Geometrical parameters for product and TS in reactions $\text{X} + \text{AB} \rightarrow \text{XAB}$ ^a

XAB		product	TS
SiH ₂	Θ	93.65	30.10
	R_{SiH}	1.531	1.751
	R_{HH}	2.234	0.909
SiHF	Θ	97.72	36.00
	R_{SiH}	1.535	1.748
	R_{SiF}	1.637	1.940
	R_{HF}	2.390	1.154
MgH ₂	Θ	180	46.16
	R_{MgH}	1.726	1.715/2.026 ^b
	R_{HH}	3.452	1.494
MgHF	Θ	180	49.74
	R_{MgH}	1.712	1.815
	R_{MgF}	1.726	1.782
	R_{HH}	3.438	1.513

^a Bond angles are in degree and bond lengths are in Å.

^b Two Mg–H bonds are not equivalent at TS

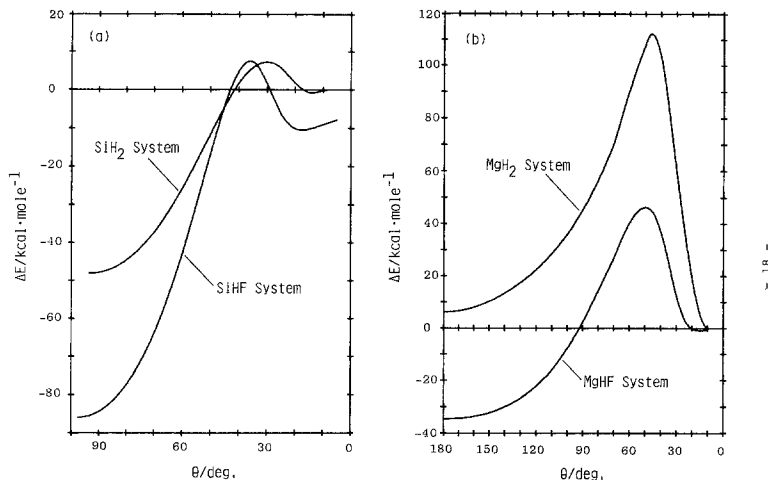


Fig. 2. Total energy changes (ΔE) along the ZVP for the four reactions. The sum of energies of the isolated atom and diatomic molecule is taken to be zero

4.2. Total energy curves

Fig. 2 shows the changes of the total energy (ΔE) along the ZVP for the four reactions. In the present calculation for the SiAB systems, the singlet state of the Si atom is adopted for the reactant in order to consider the overall reaction on a single energy surface. So absolute magnitude of the activation energy is not discussed but we will focus on the qualitative differences among the four energy curves. However, the product region ($\theta > \theta_{TS}$) seems to be reliable semiquantitatively. The results for the SiH₂ and SiHF systems (Fig. 2a) show that both reactions proceed easily. In other words, the H₂ and HF molecules dissociate. The stabilization of the product is larger for the SiHF system. Though it is a considerable simplification to regard these reactions as the chemisorption, we find following correspondence between the present calculation and the experimental data: (1) HCl and HBr molecules easily dissociate on the Si single crystalline surfaces [12]. (Experimental data have not been reported for HF molecule.) (2) The dissociation of H₂ to H atoms is slow on the flat surface [6], but the molecule dissociates at the active sites such as the step and kink [4]. The CNDO cluster calculation concerning the adsorption of H₂ and HF on the amorphous silicon also suggests the larger stabilization for the HF molecule [9].

Contrary to the Si atom, the Mg atom is singlet in its ground state. Fig. 2b shows that no stabilization occurs throughout the reaction process for the MgH₂ system. We may conclude that this reaction does not proceed. Similar result has been obtained by the *ab initio* calculation including more than two Mg atoms [25]. For the MgHF system, the activation energy is below half that of MgH₂ system. Furthermore the energy of the product system is considerably lower than that of the reactant. This reaction may be possible, though more accurate calculations, which is expected to lower the activation energy, are desired to draw the final conclusion.

4.3. Atom-bond partitioning of total energy

The total energy is partitioned into the one- and two-center AO-AO terms without approximation as mentioned in Sect. 2, and one- and two-center terms are summed up to the atomic and bond contributions, respectively. In the present analysis, the process of bond fission and formation is discussed by the use of these contributions as a bond index.

Fig. 3a shows the Si and H atomic contributions and the H-H and Si-H bond contributions along the ZVP of the SiH_2 system. All the components show drastic changes around Θ_{TS} . This trend is common to the four reactions. At TS, H-H bond is cleaved by 82% while the Si-H bonds are formed only by 32%. The resultant destabilization is compensated by the stabilization of the H atomic contribution which is ascribed to the electronegative character of the H atom in the Si-H bond. The migration of electron density from the Si atomic region to the Si-H bond region is responsible for the destabilization of the Si atomic contribution. The electropositive character of the Si atom in the bond further promotes this trend.

The structures of the product and TS for the four reactions are shown in Table 2. At TS of the SiH_2 system, the bond length R_{HH} is longer by 24% than that in the H_2 molecule while R_{SiH} is elongated only by 14% from the value in the product. These geometrical consideration may lead that the formation of the Si-H bond occurs more early than the fission of the H-H bond. However, the atom-bond energy partitioning has shown the opposite results. Thus, the degree of bond formation and fission is not estimated only from the changes of bond lengths.

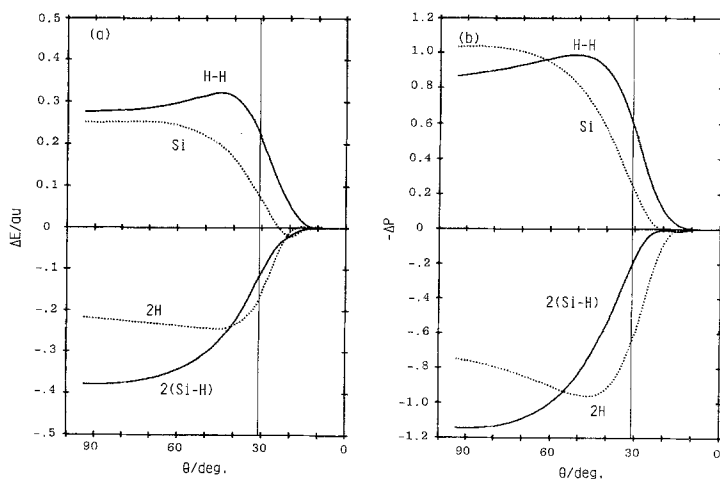


Fig. 3. (a) The changes in the atomic and bond contributions defined by the kinetic energy partitioning scheme for the SiH_2 system. Positive (negative) value shows the increase (decrease) in energy and the destabilization (stabilization) of the system. A thin vertical line shows Θ_{TS} . (b) The changes in the atomic and atomic bond populations (ΔP) for the SiH_2 system. Positive (negative) value in $-\Delta P$ shows the decrease (increase) in electron density in the corresponding part

The electron density in molecules is usually decomposed into the atomic and bond parts using the Mulliken population analysis [26]. Fig. 3b shows the changes of the atomic and atomic bond populations (ΔP) on the ZVP for the SiH_2 system. In Figs. 3a and 3b, the corresponding curves resemble each other though the details are different. The similarity is mainly ascribed to the common use of the MO coefficient within the LCAO framework, that is, an accumulation of electron density in a certain region brings increases in both population and kinetic energy of that region. However, the sum of all the changes in the population is always zero, while that in the kinetic energy is equal to the negative change in the total energy. The difference between the curves in Figs. 3a and 3b may be ascribed to this fact.

The results of the atom-bond energy partitioning for the SiHF system are shown in Fig. 4. The destabilization of the Si and H-F contributions and the stabilization of the H, F, Si-H, and Si-F contributions are understood from the similar reasons to the SiH_2 system. At TS, the H-F bond is broken by 73% while the Si-H and Si-F bonds are formed by 38 and 13%, respectively. Thus, the breaking of the old bond again precedes the formation of the new bonds. Especially, the destabilization due to the H-F bond breaking is compensated by the stabilization of the F atomic contribution. The latter shows a minimum around $\Theta = 50^\circ$. Since the Si-F bond is hardly formed in this region, the electronic state of the F atom is considered to be the F^- anionlike. In the region of $30^\circ < \Theta < 60^\circ$, the formation of the Si-H bond precedes that of the Si-F bond.

For the MgH_2 system, we omit the discussion of the atom-bond partitioning, since the reaction was not realistic considering the calculated value of the activation energy. Fig. 5 shows the results of the atom-bond energy partitioning for the MgHF system. The degree of breaking of the H-F bond at TS is larger than that for the SiHF system, which is consistent with the larger value of Θ_{TS} for the MgHF system. The destabilization in the H-F and Mg contributions is larger than the stabilization in the F and Mg-F contributions. This difference is

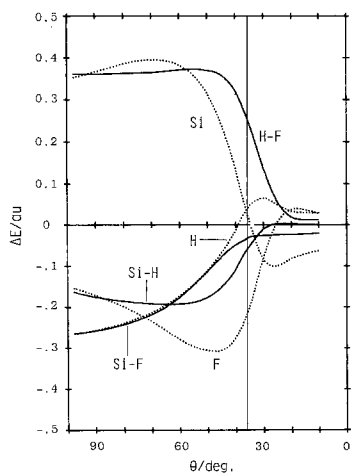


Fig. 4. The changes in the atomic and bond contributions for the SiHF systems. See captions to Fig. 3(a)

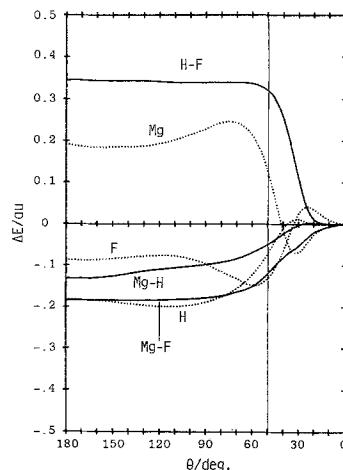


Fig. 5. The changes in the atomic and bond contributions for the MgHF system. See captions to Fig. 3(a)

mainly responsible for the activation energy. The bond lengths R_{MgH} and R_{MgF} at TS is almost the same as those in the product. (R_{MgH} and R_{MgF} are larger only by 6 and 3% than those in the product, respectively.) However, the energy partitioning shows that the stabilization of the Mg-H bond at TS is only 37% of that in the product. For the Mg-F bond, the stabilization at TS is 68% of that in the product. Contrary to the SiHF system, the formation of the Mg-F bond precedes that of the Mg-H bond. The stabilization of the F atomic contribution around $\Theta = 55^\circ$ is not as remarkable as that in the SiHF system. The difference may be ascribed to the difference in the structure at TS; R_{SiF} is 1.94 Å while R_{MgF} is 1.78 Å. This shorter Mg-F distance explains the weak ionicity of the F atom.

5. Conclusion

In this paper, the ZVP method has been applied to the comparative investigation of the four reactions: $\text{Si} + \text{H}_2 \rightarrow \text{SiH}_2$, $\text{Si} + \text{HF} \rightarrow \text{SiHF}$, $\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2$, and $\text{Mg} + \text{HF} \rightarrow \text{MgHF}$. The structures of the product and TS, and the activation energy of the reactions have been obtained. In this method, TS is attained by tracing the ZVP starting from the stable point. At every point on the ZVP, the total energy is partitioned into the atomic and bond contributions without approximations. Using these energy contributions as the bond index, the processes of bond formation and fission have been discussed in detail.

Only the reaction $\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2$ was found unrealistic judging from the large activation energy. A common feature in the other three reactions is the preceding cleavage of the H-H or H-F bond prior to the formation of the X-H and X-F bonds. Part of the destabilization due to this bond fission is compensated by the stabilization in the atomic contributions and the rest results in the activation energy. This energy partitioning scheme also shows that the degree of bond formation and fission is not proportional to the changes in the bond lengths

between the reactant and TS and between the TS and product. The simple and clear nature of the ZVP approach is expected to be useful in the study of reaction processes especially for large and complicated systems.

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