



TITLE:

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## Revisiting the von Neumann–Wigner noncrossing rule and validity of a dynamic correlation diagram method

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The noncrossing rule for potential energy surfaces can be applied only, as originally postulated by von Neumann and Wigner, to slowly occurring changes; it has, however, over many years, been widely used to rationalize fast chemical reactions. Taking the conversion of Dewar benzene to benzene as an example, we demonstrate a reaction that has a timescale for which crossings are allowed. Since it is now established that elementary chemical reactions proceed over ca. 10–100 fs, as revealed experimentally by Zewail, the noncrossing rule cannot any longer be said to be valid for most chemical reactions. We further demonstrate that the mechanism of the chemiluminescent conversion of Dewar benzene to benzene is explained by an electronic state diagram derived using a dynamic correlation diagram method which allows crossings, whereas the reaction is not explained by a conventional approach, applying the noncrossing rule using a static correlation diagram method.

*Keywords:* Correlation diagram; Dewar benzene; femtosecond scale; noncrossing rule; uncertainty principle.

### 1. Introduction

In our previous study,<sup>1,2</sup> we demonstrated that Fukui's frontier orbital (FO) theory<sup>3,4</sup> and Woodward–Hoffmann's orbital symmetry conservation theory (W–H theory)<sup>5–7</sup> can be unified consistently by using the dynamic correlation diagram method which is not restricted by the noncrossing rule. Moreover, we showed that

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H. Nohira & T. Nohira

the intermediate state of an elementary reaction cannot be described accurately by a potential energy surface analysis based on the time-independent Schrödinger equation. For many researchers in the field of theoretical chemistry, however, it would be very difficult to accept that the noncrossing rule is invalid in the theory of quantum molecular dynamics. Nevertheless, although it is not widely known, von Neumann and Wigner provided a very important discussion on the applicability of the noncrossing rule in their paper; they clearly stated: “the wave function has no time to change in the case that the electron state changes very fast”.<sup>8</sup> In the present study, we discuss the applicability of the noncrossing rule for actual chemical reactions. As a typical example, we take the conversion from Dewar benzene to benzene, which is known for its chemiluminescence, and show clearly that the case is beyond the applicability of noncrossing rule. Finally, we demonstrate that the mechanism of this reaction including chemiluminescence is explained clearly using an electronic state diagram derived from the dynamic correlation diagram method; whereas, an explanation of the reaction is not possible by conventional approaches such as using potential energy surface analysis or via a static correlation diagram method in which the noncrossing rule is applied.

## 2. Theoretical Basis

For many years, it has been believed that, in principle, chemical reactions can be rigorously treated by quantum chemical reaction dynamics.<sup>9–11</sup> One of the most famous achievements in early quantum chemical reaction dynamics is the noncrossing rule, proposed by von Neumann and Wigner in 1929.<sup>8</sup> The noncrossing rule is exactly correct when dealing with steady states, and it is generally valid for approximately steady states. However, few researchers know that there is a short but extremely important description in the 1929 paper about the situations in which the rule is not valid.

### 2.1. *The von Neumann–Wigner’s criteria for the application of the noncrossing rule*

Since quantum chemical reaction dynamics deals with phenomena that vary with time, one must take into consideration the timescale of the reaction when applying this theory to it. As long as we are dealing with a quantum mechanical problem, the theory is restricted by the position–momentum and energy–time uncertainty principles. In fact, von Neumann and Wigner themselves included discussion on this subject in their 1929 paper.<sup>8</sup> Figure 1 shows the schematic of the avoided crossing, as it appeared in “Fig. 1” in the 1929 paper.

This figure was the original model of the electronic state diagram which often appeared in their later papers. Here,  $K$  is the reaction coordinate,  $\Delta k$  is the length of the coordinate near the crossing,  $E_1$  and  $E_2$  are the energy levels (eigenvalues) of two different states which interact with each other, and  $2\epsilon$  is the smallest energy difference between the energy levels.

Revisiting the von Neumann–Wigner noncrossing rule

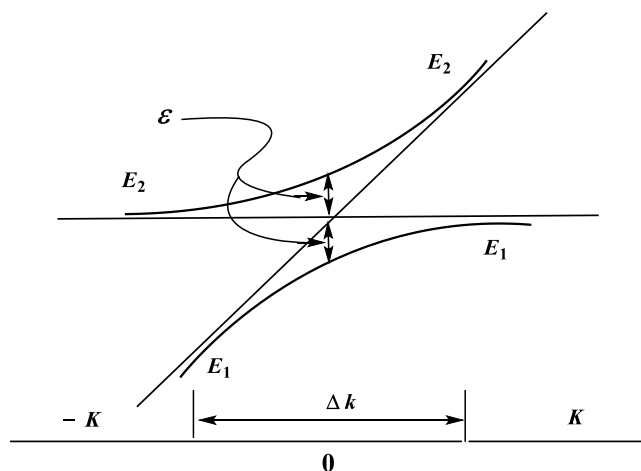


Fig. 1. Main features of the electronic state diagram presented as “Fig. 1” in the 1929 paper by von Neumann and Wigner.  $K$  is the value of reaction coordinate,  $\Delta k$  is the length of the coordinate near the crossing,  $E_1$  and  $E_2$  are the energy levels (eigenvalues) of two different states, and  $\varepsilon$  is half of the smallest distance between the energy levels.

According to the paper by von Neumann and Wigner,<sup>8</sup> under the condition in which

$$\Delta k \gg \frac{\hbar}{2\varepsilon} \frac{dk}{dt}, \quad (1)$$

the energy curves change adiabatically to become  $E_1$  and  $E_2$  (a noncrossing case). Whereas, if the condition

$$\Delta k \ll \frac{\hbar}{2\varepsilon} \frac{dk}{dt} \quad (2)$$

applies, von Neumann and Wigner stated, “in this case, the wave function has no time to change”, i.e. the crossing is allowed. However, their many papers, including the 1929 paper, mainly dealt with the cases in which Eq. (1) is assumed. Few people, therefore, know that they also referred to the case to which Eq. (2) applies. Presumably, since there was no experimental evidence available at that time concerning elementary chemical reactions occurring on short timescales, the conditions defined by Eq. (1) were believed to be reasonable by most scientists. Even currently, many researchers seem to have no doubts about the assumption of the conditions defined in Eq. (1) for chemical reactions.

Concerning the uncertainty principle in quantum chemical reaction dynamics, Levine pointed out in his famous textbook<sup>11</sup>: “The Heisenberg uncertainty principle puts a limit on our inherent ability to measure simultaneously momentum and position in the same direction.” He also wrote: “This is not quite as detrimental as it might seem because the value of Planck’s constant is moderate on the scale of interest to us.” However, is this true?

H. Nohira & T. Nohira

## 2.2. Verification of the criteria: A case of reaction from Dewar benzene to benzene

Zewail, the 1999s Nobel Laureate in chemistry, revealed that elementary chemical reactions proceed within the period of a molecular vibration, that is, the order of 10 fs to 100 fs ( $1 \text{ fs} = 10^{-15} \text{ s}$ ).<sup>12</sup> Prior to this, Karplus *et al.* studied simple chemical exchange reactions and reported that the reactions are best represented by a direct interaction model with an interaction time,  $\sim 50 \text{ fs}$ , on the order of that required for the atom to pass unimpeded by the molecule.<sup>13</sup> Levine also described the idea of a direct reaction, one that is over in a vibrational period, in his textbook.<sup>14</sup> We assumed the same timescale when developing the dynamic correlation diagram method.<sup>1,2</sup> Here, we discuss this issue, comparing a theoretical model with reported values for the actual reaction of Dewar benzene to benzene (Fig. 2).

The bond length between the carbon atoms at positions 1 and 4 in Dewar benzene is  $1.6 \text{ \AA}$ , while the distance between the 1 and 4 carbons in benzene is  $2.8 \text{ \AA}$ .<sup>15,16</sup> When the 1–4 bond of Dewar benzene is broken to form benzene, the distance between the carbon atoms changes by  $1.2 \text{ \AA}$ . Here, the displacement of atomic distance that is of interest to our examination of the state crossing is supposed to be one tenth of  $1.2 \text{ \AA}$ , that is,  $\Delta k = 1.2/10 \times 10^{-8} \text{ cm} = 1.2 \times 10^{-11} \text{ m}$ . To the best of our knowledge, there are no reports of studies of the energy gap of the Dewar benzene/benzene transformation over such intervals, i.e. of the order of  $1 \times 10^{-11} \text{ m}$ . However, a gap of the energy levels between  $\text{Na-I}$  and  $\text{Na}^+ \cdot \text{I}^-$  of  $2\varepsilon \approx 0.025 \text{ eV} = 0.57 \text{ kcal mol}^{-1}$  has been reported (see p. 379 of Ref. 11). In the case of the conversion of hexatrienes to cyclohexadienes,  $0.1 \text{ kcal mol}^{-1}$  has been reported as the energy gap between  $S_1$  and  $S_2$  in a model system.<sup>17</sup> Whereas, there are influential opinions that the energy gap is regarded as substantially zero from the theoretical perspective of conical intersections.<sup>18–22</sup> Together, these reported results imply that it is reasonable to assume that the energy gap of the Dewar benzene/benzene reaction is smaller than  $1 \text{ kcal mol}^{-1}$ ; that is, we can assume  $2\varepsilon = 1.0 \text{ kcal mol}^{-1} = 6.9 \times 10^{-21} \text{ J molecule}^{-1}$ , and therefore,  $h/(2\varepsilon) = (6.63 \times 10^{-34} \text{ J s})/(6.9 \times 10^{-21} \text{ J}) = 9.6 \times 10^{-14} \text{ s}$ .

Incidentally, the period  $T$  of the characteristic vibration of the C–C bond can be calculated from the wavenumber of the vibration ( $1050 \text{ cm}^{-1}$ ) as  $3.2 \times 10^{-14} \text{ s}$ . Thus,

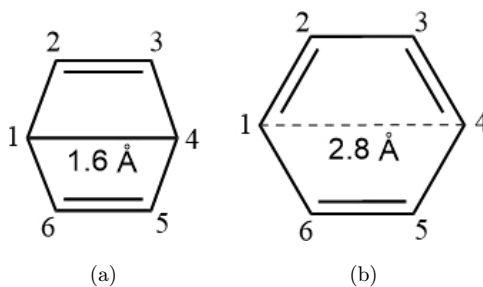


Fig. 2. Structures of Dewar benzene (a) and benzene (b). In the interconversion reaction between (a) and (b), the 1–4 carbon bond is broken and the distance between these atoms increases from  $1.6 \text{ \AA}$  to  $2.8 \text{ \AA}$ .

*Revisiting the von Neumann–Wigner noncrossing rule*

we can estimate the changing velocity,  $dk/dt$ , from the change of distance ( $\Delta x = 1.2 \text{ \AA}$ ) and the half of the periodic time ( $\Delta t = T/2$ ),  $dk/dt = \Delta k/\Delta x = (1.2 \text{ \AA})/(1.6 \times 10^{-14} \text{ s}) = 7.5 \times 10^3 \text{ m s}^{-1}$ . Then, the value of  $h/(2\varepsilon) \times (dk/dt)$  is calculated to be  $(9.6 \times 10^{-14} \text{ s}) \times (7.5 \times 10^3 \text{ m s}^{-1}) = 7.2 \times 10^{-10} \text{ m}$ . When this value is compared with  $\Delta k = 1.2 \times 10^{-11} \text{ m}$ , it is obvious that  $\Delta k \ll h/(2\varepsilon) \times (dk/dt)$ . Therefore, we can conclude that according to the von Neuman–Wigner criteria, the intermediate state of this elementary chemical reaction does not correspond to the so-called the noncrossing case but to the case where crossing occurs, i.e. when “the wave function has no time to change”.<sup>8</sup> What did von Neumann and Wigner think about the velocity of bond breaking in chemical reactions?

Let us examine the case which fits Eq. (1), which has been widely accepted as an adiabatic change. That is:  $dk/dt \ll \Delta k \times (2\varepsilon/h) = (1.2 \times 10^{-11} \text{ m}) \times (1.0 \times 10^{13} \text{ s}^{-1}) = 1.2 \times 10^2 \text{ m s}^{-1}$ . Assuming  $dk/dt$  to be  $1.2 \text{ m s}^{-1}$ , one hundredth of  $1.2 \times 10^2 \text{ m s}^{-1}$ , the time necessary to change the bond length of  $1.2 \text{ \AA}$  is as follows:  $(1.2 \times 10^{-10} \text{ m})/(1.2 \text{ m s}^{-1}) = 1.0 \times 10^{-10} \text{ s}$ . This means that von Neumann and Wigner tacitly assumed that changes of chemical bonds (elementary chemical reactions) required longer durations than  $1.0 \times 10^{-10} \text{ s}$ .

### 3. Explanation of Chemiluminescent Reaction from Dewar Benzene to Benzene by Using a Dynamic Correlation Diagram Method

#### 3.1. Previous studies on the correlation diagrams

The conversion of Dewar benzene to benzene, which is accompanied by chemiluminescence, has aroused the interest of many researchers; many papers dealing with this reaction have been published so far.<sup>15,23–35</sup> Furthermore, many attempts have been made to explain the reaction, utilizing a conventional approach, by potential energy surface analysis or via conventional static correlation diagram method, applying the noncrossing rule.<sup>28–35</sup>

The framework of Dewar benzene contains cyclobutene. Woodward and Hoffmann first proposed fundamental correlation diagrams, which we call static correlation diagrams, for the disrotatory and conrotatory conversions from cyclobutenes to butadienes observing the noncrossing rule.<sup>7–9</sup> Then, Van der Lugt and Oosterhoff indicated more detailed correlation diagrams, which are also classified as static correlation diagrams, for the photochemical cyclization from butadiene to cyclobutene based on the potential energy surface analysis, in which the noncrossing rule was definitely observed.<sup>36,37</sup> While such arguments were going on, one of the present authors proposed a new correlation diagram, which we call a dynamic one, for the disrotatory conversion from butadiene to cyclobutene without considering the noncrossing rule.<sup>38</sup>

#### 3.2. Comparison between the static and dynamic correlation diagrams

According to the above-mentioned cases of cyclobutene to butadiene, we can immediately draw both the static and dynamic correlation diagrams for the reaction

H. Nohira & T. Nohira

from Dewar benzene to benzene. The results are shown in Figs. 3(a) and 4(a). The overlap values between the reactant and product orbitals are listed on the right side. The calculation method of the overlap is given in Supplementary Materials.

To create the electronic state diagram for the reaction, on one side one writes down the calculated approximate energy levels of the orbitals for Dewar benzene, and on the other side, those for benzene are written. Since high accuracy is not required for the energy levels, the simple Hückel method<sup>39</sup> has been used for the calculation here. In our previous paper, we assumed the energy level of the C–C single bond of cyclohexadiene was  $1.3\beta$  ( $\beta$  is the value of the overlap integral in simple Hückel theory); here, taking the ring strain of Dewar benzene into account, we estimate it as  $1.2\beta$ .

Figure 3(b) shows the corresponding electronic state diagram based on Fig. 3(a). If the reaction proceeds along the potential energy surface of Fig. 3(b), the ground state of Dewar benzene directly corresponds to the ground state of benzene. This picture, however, is inconsistent with the actual observed phenomenon in which thermal isomerization of Dewar benzene to benzene proceeds via the formation of an excited state of benzene, accompanied by chemiluminescence. It is sometimes explained that the chemiluminescence occurs via the triplet state of benzene because the potential energy surface of the triplet state crosses that of singlet state.<sup>29,30</sup> However, a comparatively low yield of triplet state has been measured experimentally.<sup>40</sup> Consequently, we cannot explain this characteristic chemiluminescence by a conventional static electronic state diagram in which the lowest singlet potential surface does not cross any other singlet surfaces.

As mentioned above, considering the timescale of this reaction, we are not limited by the noncrossing rule in drawing its correlation diagram. Instead, we can make use of a new approach, applying the dynamic correlation diagram method, to obtain the diagrams shown in Figs. 4(a) and 4(b).

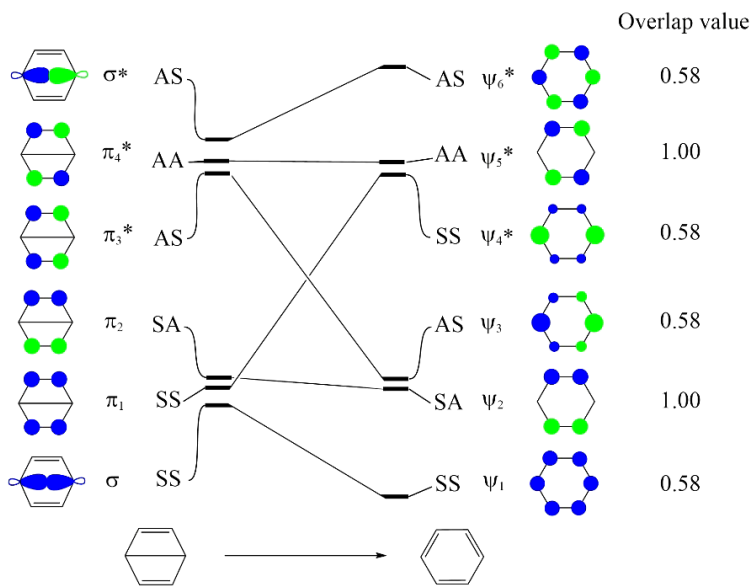
When the 1,4  $\sigma$ -bond of Dewar benzene is broken in a disrotatory manner, the orbital has to transform into the  $\Psi_4^*$  orbital of benzene, and the  $\sigma^*$  orbital forms the  $\Psi_3$  orbital, with minimal changes to the shapes of the molecular orbitals. The overlap values are calculated to be 0.82 for both transformations and are larger than the corresponding values of 0.58 in Fig. 3(a). In the same way, when we select the largest overlap, we can connect as follows:

$$\pi_1 \rightarrow \Psi_1, \quad \pi_2 \rightarrow \Psi_2, \quad \pi_3^* \rightarrow \Psi_6^*, \quad \pi_4^* \rightarrow \Psi_5^*$$

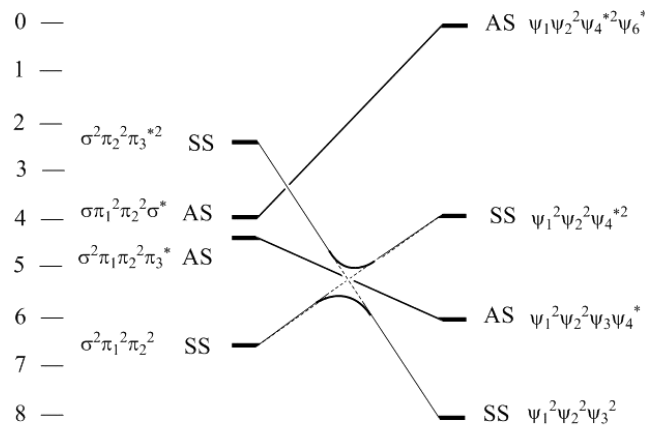
Based on the correlation diagram shown in Fig. 4(a), we can draw the electronic state diagram as shown in Fig. 4(b). In this diagram, the electron configuration of the ground state of Dewar benzene,  $\sigma^2\pi_1^2\pi_2^2$ , is related to that of the second excited state of benzene,  $\Psi_1^2\Psi_2^2\Psi_4^{*2}$ . The sums of the bonding energies of these orbitals in units of  $\beta$  are calculated as follows:

$$\begin{aligned} \sigma^2\pi_1^2\pi_2^2 &= (1.2 \times 2) + (1.0 \times 2) + (1.0 \times 2) = 6.4\beta, \\ \Psi_1^2\Psi_2^2\Psi_4^{*2} &= (2.0 \times 2) + (1.0 \times 2) + (-1.0 \times 2) = 4.0\beta. \end{aligned}$$

Revisiting the von Neumann–Wigner noncrossing rule



(a)



(b)

(b)

Fig. 3. (Color online) (a) Conventional static orbital correlation diagram, and (b) corresponding electronic state diagram for the conversion of Dewar benzene to benzene. Phases of wave functions and energy levels are based on the simple Hückel method. The phases are color-coded, with blue indicating positive and green indicating negative, or *vice versa*. The molecular symmetry is denoted as follows: S indicates a symmetric wavefunction, A indicates an antisymmetric wavefunction, and the label gives the vertical symmetry first and then the horizontal.



H. Nohira & T. Nohira

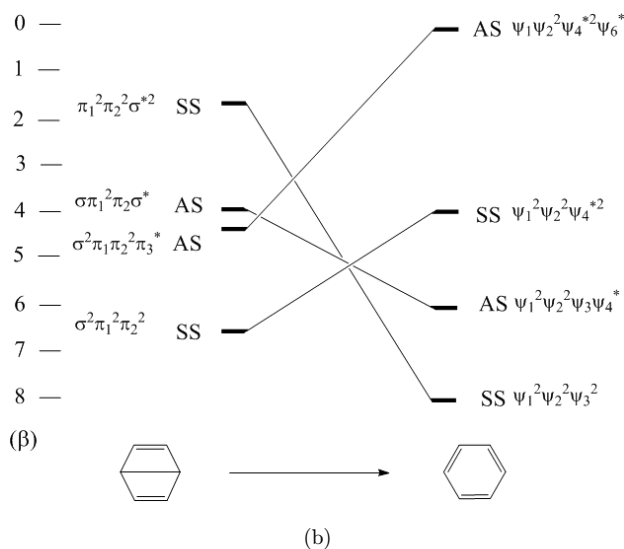
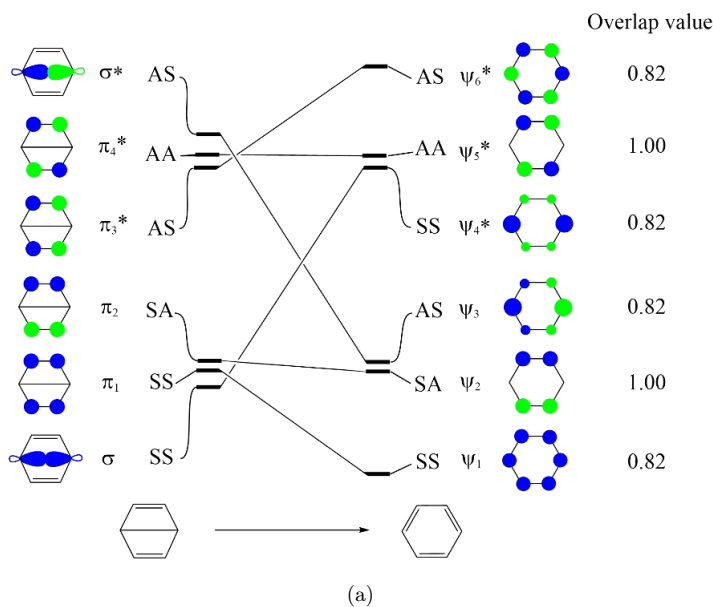


Fig. 4. (a) Dynamic orbital correlation diagram, and (b) corresponding electronic state diagram for the conversion of Dewar benzene to benzene.

### 3.3. Potential energy profile

On the basis of Fig. 4(b), we can draw the potential energy profile of this reaction by connecting the most probable transformation of each orbital, as shown in Fig. 5. This figure clearly indicates that the vibrational excited state of Dewar benzene (N) is transformed to the electronically and vibrational excited state of benzene (P) in half

Revisiting the von Neumann–Wigner noncrossing rule

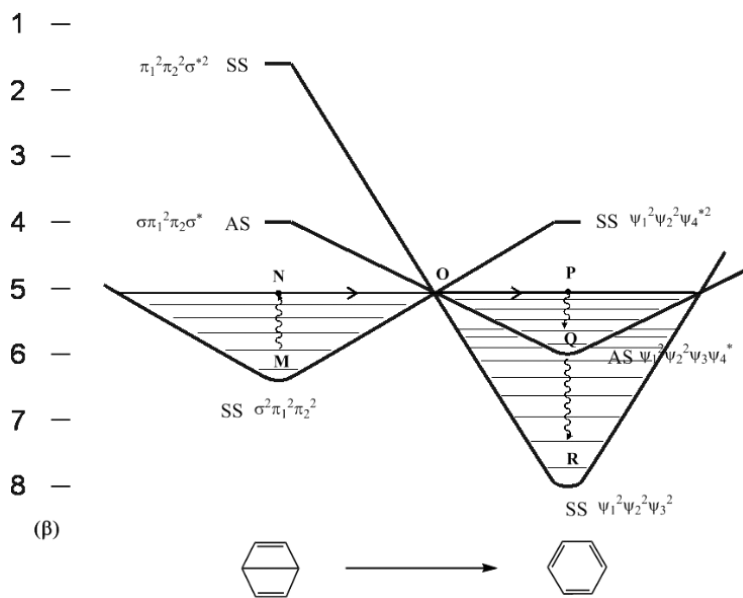


Fig. 5. Schematic representation of the potential energy profile for the conversion of Dewar benzene to benzene based on the electronic state diagram shown in Fig. 4(b).

of the time period of the vibration via the crossing point (O). The state (P), which is above the electronically excited state of benzene (Q), goes to the ground state of benzene (R) with the emission of light. In this way, we are able to logically explain the physical phenomenon that is the thermal isomerization of Dewar benzene to benzene proceeding via the formation of an excited state of benzene, accompanied by chemiluminescence.

#### 4. Conclusion

It has been long unheeded that von Neumann and Wigner themselves pointed out that the noncrossing rule is not applicable for changes occurring within very short times. We have demonstrated, taking the conversion of Dewar benzene to benzene as an example, that the timescale for this reaction exactly corresponds to the case in which the crossing is allowed. Considering the fact that elementary chemical reactions proceed within the period of a molecular vibration, that is, they completed within  $\sim 10\text{--}100$  fs, as revealed by Zewail, the noncrossing rule can no longer be said to be valid for most chemical reactions. According to conventional static correlation diagram methods, in which the noncrossing rule is applied, it is not possible to properly describe the chemical change of Dewar benzene to benzene accompanied by chemiluminescence. By contrast, we can describe this reaction effectively by our newly proposed electronic state diagram method, based on the dynamic correlation diagram method, without use of the noncrossing rule. Thus, the dynamic correlation

H. Nohira & T. Nohira

diagram method, where a correlation diagram is drawn based on the concept that the shapes of the molecular orbitals of reactants transform into those of the products with minimal changes, is very effective for understanding the nature of chemical reactions. Finally, we note that in studying quantum chemical dynamics, it is necessary to discuss the features of reactions while taking into consideration the accuracy of timescales and energies, in order to avoid wasting effort on subjects that cannot be solved due to intrinsic uncertainty.

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*Revisiting the von Neumann–Wigner noncrossing rule*

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H. Nohira & T. Nohira

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