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# The geometric phase effect in chemical reactions: A quasiclassical trajectory study

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The hyperspherical formulation of the vector potential arising due to the presence of a conical intersection in the adiabatic potential energy hypersurface of an  $A+B_2$  type reactive system is considered. We wish to treat the operators in the Hamiltonian (with or without vector potential) as classical variables and have seen the same direction of the relative shift in the peak position of the rotational distribution as in the quantum mechanical (QM) calculations by Kuppermann and Wu [Chem. Phys. Lett. **205**, 577 (1993)]. Though the absolute peak position of the rotational distributions (with and without geometric phase) obtained by quasiclassical trajectory (QCT) calculations differ from this QM calculation, the physical effect nevertheless becomes transparent once again by our calculation which requires very little computational effort. © 1997 American Institute of Physics. [S0021-9606(97)02140-5]

## I. INTRODUCTION

The complication due to the Born–Oppenheimer adiabatic separation of electronic and nuclear motion was addressed<sup>1–12</sup> in molecular systems where the presence of conical intersections of the adiabatic potential energy surfaces (PES) is considered to play a significant role. Nevertheless very impressive quasiclassical,<sup>13–18</sup> semiclassical,<sup>19,20</sup> and quantum mechanical<sup>21–46</sup> calculations have been performed for the  $H_3$  and its isotopic analogue systems ignoring the conical intersections. The persistent differences between theory<sup>13–46</sup> and experiment<sup>47–59</sup> gave motivation for an understanding of the above-mentioned complication. The nature of the complication in the Born–Oppenheimer separation when a conical intersection occurs, has been demonstrated by Herzberg and Longuet-Higgins.<sup>10</sup> If the phase of the electronic and nuclear wave functions are chosen in the usual way to make the first derivative term in the nuclear Schrödinger equation vanish, the adiabatic electronic wave function changes sign during a pseudorotation in nuclear configuration space around the conical intersection. To ensure the total wave function of the system to be single valued and continuous, there must be a compensating sign change in the nuclear wave function.<sup>60</sup> Thus one can make the electronic wave function continuous and single valued by another choice of phase factor or at the cost of introducing a vector potential in the effective nuclear Hamiltonian. The geometric properties of a Möbius strip has similarities with the above-mentioned sign change properties of the electronic wave function and this phenomenon is related to Berry's geometric phase<sup>61</sup> and the molecular Aharonov–Bohm effect.<sup>62</sup>

Kuppermann and Wu<sup>63–65</sup> made the electronic wave function continuous and single valued by multiplying it with a phase factor. They reported the effect of the geometric phase on the product rotational state distributions and integral cross sections for the reactions  $H+H_2$  and  $D+H_2$  by three-dimensional QM study. They have shown that for total energies higher than 1.8 eV (above the bottom of the ground-

state  $H_2$  potential energy well) and below 2.7 eV (the minimum of the conical intersection energy) the differential and integral cross sections are significantly influenced by the geometric phase effect.

Mead and Truhlar<sup>60</sup> formulated the effective nuclear Hamiltonian in Jacobi coordinates by introducing a vector potential to compensate the sign change in the electronic wave function. We have formulated a vector potential in hyperspherical coordinates for the  $A+B_2$  reactive system and have replaced the quantum operators in the Hamiltonian by the corresponding classical variables. The influence of geometric phase on the integral cross section of  $D+H_2$  has been studied at the collisional energy 1.8 eV by quasiclassical trajectory (QCT) calculation. The relative shift of the rotational distribution in presence of a vector potential, is qualitatively the same as indicated by Kuppermann and Wu.<sup>65</sup>

## II. THE HYPERSPHERICAL FORMULATION OF A KINETIC ENERGY OPERATOR IN THE PRESENCE OF VECTOR POTENTIAL

The presence of a phase factor means that the momentum operator ( $\hat{P}$ ) in hyperspherical coordinates form the effective nuclear Hamiltonian and consequently  $\hat{P}$  should be replaced<sup>60</sup> by  $(\hat{P} - \hbar \nabla \phi)$  where  $\nabla \phi$  is the vector potential of the Appendix. Note that the angle entering the vector potential is strictly only identical to the hyperangle  $\phi$  for an  $A_3$  system. The general expression given in Ref. 66 is a function of both  $\phi$ ,  $\theta$ , and the position  $\theta_0$  of the intersection. Thus for an  $A_3$  system we have  $\theta_0=0$  and for  $D+H_2$   $\theta_0$  is about  $11.5^\circ$ . However, since Kuppermann and Wu introduced the approximation  $\theta_0=0$  we shall also use this approximation here. With this approximation the nuclear kinetic energy operator ( $\hat{T}$ ) can be written as is

$$\hat{T} = \frac{1}{2\mu} (\hat{P} - \hbar \nabla \phi)^2 = \frac{1}{2\mu} (\hat{P}^2 - \hbar^2 \nabla^2 \phi - 2\hbar \nabla \phi \hat{P} + \hbar^2 \nabla \phi \nabla \phi). \quad (1)$$

As mentioned earlier, we wish to replace the QM operators with the corresponding classical variables. Thus the well-known expression for the  $P^2/2\mu$  is in hyperspherical coordinates<sup>67</sup>

$$\begin{aligned} \frac{P^2}{2\mu} = & \frac{1}{2\mu} \left[ P_\rho^2 + \frac{4}{\rho^2} \left( P_\theta^2 + \frac{1}{\sin^2 \theta} P_\phi^2 \right) \right] \\ & + \frac{P_\gamma [P_\gamma - 4 \cos \theta P_\phi]}{2\mu \rho^2 \sin^2 \theta} \\ & + \frac{(P_\alpha^2 - P_\gamma^2)(1 + \sin \theta \cos 2\gamma)}{\mu \rho^2 \cos^2 \theta}. \end{aligned} \quad (2)$$

The explicit expressions of the other terms in Eq. (1) can be evaluated in terms of hyperspherical coordinates using the Appendix

$$\begin{aligned} -\frac{\hbar^2}{2\mu} \nabla^2 \phi = & -\frac{\hbar^2}{2\mu} \sum_i \frac{\partial^2 \phi}{\partial X_i^2}, \\ \{ \text{where } X_i \equiv & (r_x, r_y, r_z, R_x, R_y, R_z) \} \\ = & 0, \end{aligned} \quad (3)$$

$$\begin{aligned} \frac{\hbar^2}{2\mu} \nabla \phi \nabla \phi = & \frac{\hbar^2}{2\mu} \sum_i \frac{\partial g f}{\partial X_i} \frac{\partial \phi}{\partial X_i}, \\ \{ \text{where } X_i & \\ \equiv & (r_x, r_y, r_z, R_x, R_y, R_z) \} \\ = & \frac{2\hbar^2}{\mu \rho^2 \sin^2 \theta}, \end{aligned} \quad (4)$$

and

$$\begin{aligned} -\frac{\hbar}{\mu} \nabla \phi P = & -\frac{\hbar}{\mu} \sum_i \frac{\partial \phi}{\partial X_i} P_{X_i}, \\ \{ \text{where } X_i \equiv & (r_x, r_y, r_z, R_x, R_y, R_z) \}, \end{aligned} \quad (5)$$

where the general form of  $P_{X_i}^*$  (the star indicates without coriolis term) in hyperspherical coordinates can be written as

$$P_{X_i}^* = P_\rho \frac{\partial \rho}{\partial X_i} + P_\theta \frac{\partial \theta}{\partial X_i} + P_\phi \frac{\partial \phi}{\partial X_i}.$$

It is easy to evaluate  $\partial \rho / \partial X_i$ ,  $\partial \theta / \partial X_i$ , and  $\partial \phi / \partial X_i$  [for  $X_i \equiv (r_x, r_y, r_z, R_x, R_y, R_z)$ ] using equation (A1) of the Appendix and after introducing the coriolis term,<sup>67</sup> the  $P_{X_i}$ 's become

$$\begin{aligned} P_{r_x} = & \left( \frac{r_x}{\rho} P_\rho - \frac{2R_y}{\rho^2} P_\theta + \frac{2R_x}{\rho^2 \sin \theta} P_\phi - \omega_z r_y \right), \\ P_{r_y} = & \left( \frac{r_y}{\rho} P_\rho - \frac{2R_x}{\rho^2} P_\theta - \frac{2R_y}{\rho^2 \sin \theta} P_\phi + \omega_z r_x \right), \\ P_{r_z} = & (\omega_x r_y - \omega_y r_x), \\ P_{R_x} = & \left( \frac{R_x}{\rho} P_\rho + \frac{2r_y}{\rho^2} P_\theta - \frac{2r_x}{\rho^2 \sin \theta} P_\phi - \omega_z R_y \right), \\ P_{R_y} = & \left( \frac{R_y}{\rho} P_\rho + \frac{2r_x}{\rho^2} P_\theta + \frac{2r_y}{\rho^2 \sin \theta} P_\phi + \omega_z R_x \right), \\ P_{R_z} = & (\omega_x R_y - \omega_y R_x), \end{aligned} \quad (6)$$

where  $\omega_x$ ,  $\omega_y$ , and  $\omega_z$  are the components of instantaneous angular velocity of the rotating axes  $XYZ$  with respect to the stationary axes  $X'Y'Z'$ .

Substituting  $\partial \phi / \partial X_i$  and  $P_{X_i}$  in Eq. (5) we get after some simplification,

$$-\frac{\hbar}{\mu} \nabla \phi P = -\frac{4\hbar P_\phi}{\mu \rho^2 \sin^2 \theta}. \quad (7)$$

It is important to note that Eq. (7) becomes independent of the Coriolis term because the symmetrical components of  $P$  and  $\nabla \phi$  (at least for  $A+B_2$  system) cancel it identically.

Thus the total Hamiltonian ( $H$ ) in presence of a vector potential is

$$\begin{aligned} H = & \frac{1}{2\mu} \left[ P_\rho^2 + \frac{4}{\rho^2} \left( P_\theta^2 + \frac{1}{\sin^2 \theta} P_\phi^2 \right) \right] \\ & + \frac{P_\gamma [P_\gamma - 4 \cos \theta P_\phi]}{2\mu \rho^2 \sin^2 \theta} \\ & + \frac{(P_\alpha^2 - P_\gamma^2)(1 + \sin \theta \cos 2\gamma)}{\mu \rho^2 \cos^2 \theta} + \frac{2\hbar^2}{\mu \rho^2 \sin^2 \theta} \\ & - \frac{4\hbar P_\phi}{\mu \rho^2 \sin^2 \theta} + V(\rho, \theta, \phi). \end{aligned} \quad (8)$$

The coupled first-order Hamilton equations of motion for all the coordinates are derived from the above Hamiltonian by the usual prescription.<sup>68</sup>

$$\begin{aligned} \dot{q}_i = & \frac{\partial H}{\partial p_i}, \\ \dot{p}_i = & -\frac{\partial H}{\partial q_i}. \end{aligned} \quad (9)$$

### III. RESULTS AND DISCUSSION

During initialization and final analysis of the QCT calculations, the numerical values of the Morse potential parameters which we have used are  $D_e = 4.580$  eV,  $r_e = 0.7416$  Å, and  $\beta = 1.974$  Å<sup>-1</sup>. It is important to note that the potential energy as a function of internuclear distance

obtained from the analytical expression (with the above parameters) and the LSTH<sup>69</sup> surface asymptotically agreed very well.

In the final analysis of the QCT calculations,  $j'$  (the angular momentum) is uniquely defined. Using the final coordinate ( $r'$ ) and momentum ( $p'$ ), the rotational angular momentum ( $L = r' \times p'$ ) and  $j'$  [setting  $L^2 = j'(j' + 1)\hbar^2$ ] can be obtained. Once the rotational angular momentum ( $L$ ) is determined, we can find the vibrational energy ( $E_{\text{vib}} = E_{\text{int}} - E_{\text{rot}}$ ). From the vibrational energy the final vibrational quantum number ( $v'$ ) is obtained using the expression for the energy levels of a Morse oscillator (scheme A). But, at higher values of  $v'$  this expression is not accurate and the following semiclassical formula, based on the Bohr–Sommerfeld quantization,

$$v' = -\frac{1}{2} + \frac{1}{h} \oint p_r dr \quad (10)$$

was used instead (scheme B).

The energy dependence of the integral cross section for  $D + H_2(v=1, j=0) \rightarrow HD(v') + H$  reaction (without introducing the vector potential in the Hamiltonian) are shown in Figs. 1(a) and 1(b) where the resolution of the final vibrational states ( $v'$ ) of  $HD$  are performed by scheme A and scheme B, respectively. We have also compared Figs. 1(a) and 1(b) with the QCT calculations of Aoiz *et al.*<sup>18</sup> and accurate QM calculations of Zhang and Miller<sup>39</sup> on the same potential energy surface (LSTH)<sup>69</sup> for values of the collision energy from threshold to 0.3 eV. For each energy we have calculated  $5 \times 10^4$  QCT's so as to ensure convergence. Though the overall trend of our results [in both Figs. 1(a) and 1(b)] the energy dependence of the integral cross sections to the specific  $v'$  state are very similar to other results,<sup>18,39</sup> Fig. 1(b) shows better agreement with the QM results. So, we have used scheme B (based on Bohr–Sommerfeld quantization) for the final state analysis of  $v'$  in all the following calculations.

We have performed QCT calculations of integral cross sections for the  $D + H_2(v=1, j) \rightarrow DH(v', j') + H$  reaction at the total energy of 1.8 eV (translational energy 1.0 eV) with the LSTH<sup>70</sup> potential energy parameters. These studies have been done with or without inclusion of geometric phase starting from three different initial states [ $(v=1, j=1)$ ,  $(v=1, j=2)$ , and  $(v=1, j=3)$ ] and for each case  $1.2 \times 10^5$  QCT's are taken where convergence was obtained with about  $5 \times 10^4$  QCT's. Starting from any of these particular initial states, the distribution of integral cross sections versus  $j'(v'=1)$  has been shown in Figs. 2(a)–2(c) with and without inclusion of the geometric phase effect and compared with each other. We have also compared our QCT result with the available experimental distribution ( $v'=1, j'$ ) obtained by Zare and co-workers<sup>52,54,55</sup> in Fig. 2(a).

In Figs. 2(a)–2(c), one can see that there are relative shifts of the peak of the rotational distributions towards the left from  $j'=12$  to  $j'=8$  to 10 in the presence of the geometric phase effect and the effect become prominent as the initial rotational state varies from  $j=1$  and 2, whereas for  $j=3$  the effect is small. For the  $D + H_2(v=1, j=1)$

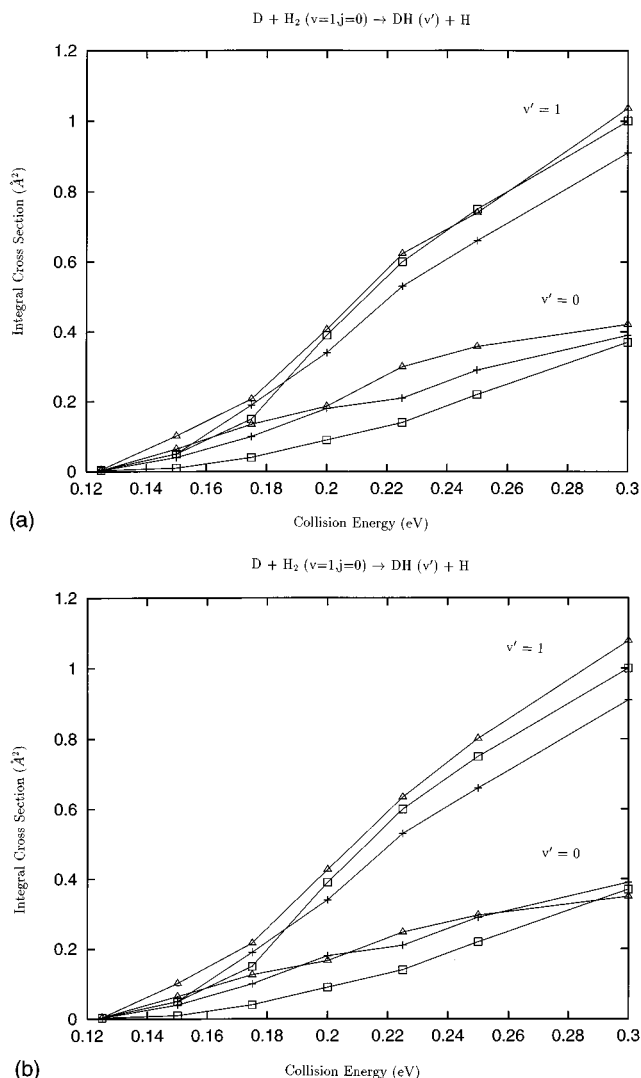


FIG. 1. Vibrationally resolved reaction cross sections (in  $\text{\AA}^2$ ) as a function of translational energy for the  $D + H_2(v=1, j=0) \rightarrow DH(v') + H$  reaction (shown by solid lines with open triangles) using (a) scheme A and (b) scheme B, respectively. In both of these figures, the QCT (Ref. 18) and QM (Ref. 39) results are presented by solid lines with plus signs and open squares, respectively.

$\rightarrow DH(v', j') + H$  reaction with the same total energy 1.8 eV. Kuppermann and Wu<sup>65</sup> have shown that the peak of the rotational state distribution moves towards the left in presence of a geometric phase. Although the absolute position of the peak (from  $j'=10$  to  $j'=8$ ) of this calculation and the experiment are different from our calculations, it is worthwhile to see that the peak position of the rotational distribution without geometric phase effect using classical hyperspherical calculation comes at  $j'=12$  (the overestimation is due to the use of classical mechanics) which is different from the quantum calculation having the peak at  $j'=10$ .

The relative shift of the peak position of the rotational distribution in the presence of a vector potential thus confirms the effect of the geometric phase of the  $D + H_2$  system displaying conical intersections. The most important aspect of our calculation is that one can see this effect using classical mechanics also and with respect to QM calculation the

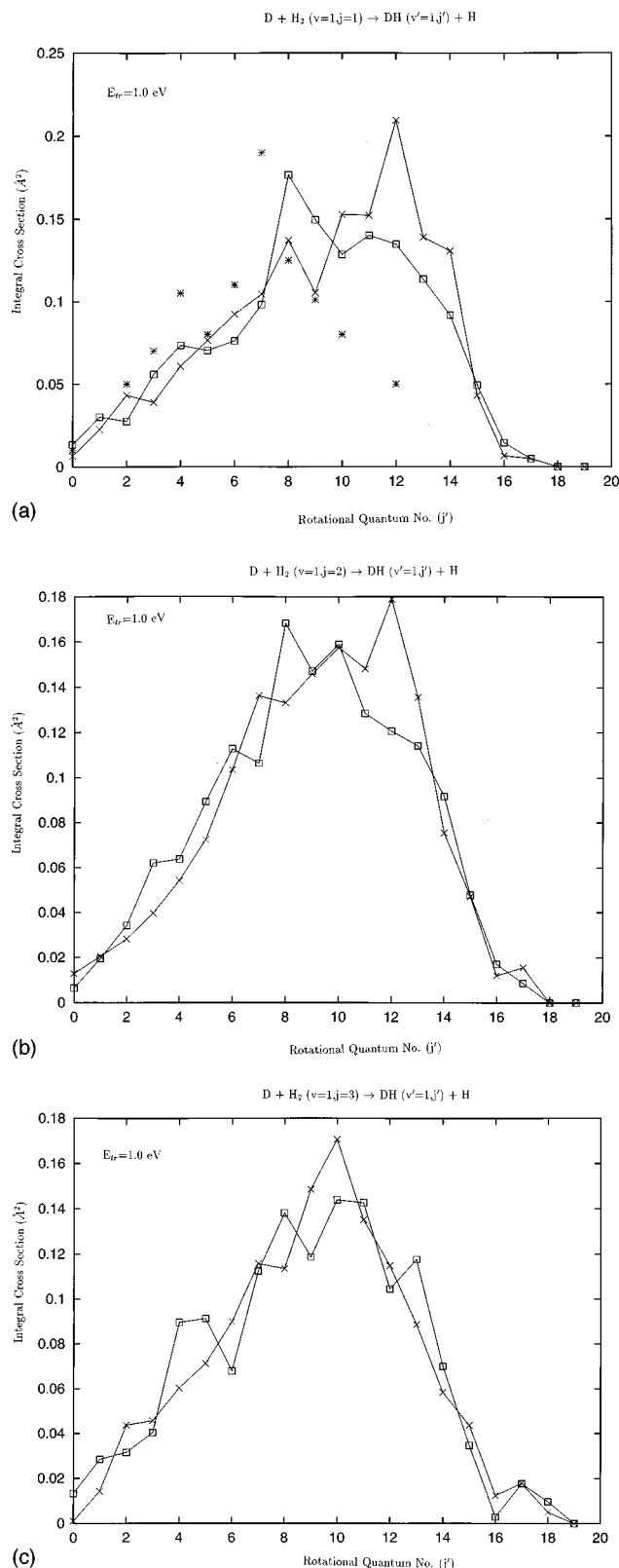


FIG. 2. Integral cross sections in ( $\text{\AA}^2$ ) at  $E = 1.8$  eV for the  $D + H_2(v = 1, j) \rightarrow DH(v' = 1, j') + H$  reaction as a function of the  $DH$  rotational state quantum number  $j'$ . The results are shown for the initial rotational state  $j = (a) 1$ , (b) 2, and (c) 3, respectively. In (a), the solid lines with open squares and crosses present results with and without the geometric phase, respectively. In the same figure, the experimental results (Ref. 54) are represented by stars. Similarly, in both (b) and (c), the solid lines with crosses and open squares indicate results without and with the geometric phase, respectively.

computer CPU time is in our calculation almost negligible. This might be of importance for heavier systems, where the quantum calculations are even more troublesome and where also the use of classical mechanics is more justified.

The impressive form of vector potential in the Appendix for the  $A + B_2$  system motivates us to generalize further the formulation of the vector potential for any  $A + BC$  system. In our next communication we shall present this generalization.

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## APPENDIX: EVALUATION OF THE VECTOR POTENTIAL

The connection between Jacobi and the hyperspherical coordinates is given by<sup>70</sup>

$$r_x = -\frac{\rho}{\sqrt{2}} \left( \cos \frac{\theta}{2} + \sin \frac{\theta}{2} \right) \cos \frac{\phi}{2},$$

$$r_y = \frac{\rho}{\sqrt{2}} \left( \cos \frac{\theta}{2} - \sin \frac{\theta}{2} \right) \sin \frac{\phi}{2},$$

$$r_z = 0,$$

$$R_x = \frac{\rho}{\sqrt{2}} \left( \cos \frac{\theta}{2} + \sin \frac{\theta}{2} \right) \sin \frac{\phi}{2},$$

$$R_y = \frac{\rho}{\sqrt{2}} \left( \cos \frac{\theta}{2} - \sin \frac{\theta}{2} \right) \cos \frac{\phi}{2},$$

$$R_z = 0, \quad (A1)$$

and the interatomic distances of the triangle  $ABC$  due to any  $A + BC$  (here, we have taken the case  $B = C$ ) type reactive system are given by<sup>19</sup>

$$\frac{R_{AB}^2}{d_1^2} = \frac{\rho^2}{2} (1 + \sin \theta \cos \phi),$$

$$\frac{R_{BC}^2}{d_2^2} = \frac{\rho^2}{2} (1 + \sin \theta \cos(\phi - \xi)),$$

$$\frac{R_{CA}^2}{d_2^2} = \frac{\rho^2}{2} (1 + \sin \theta \cos(\phi + \xi)), \quad (A2)$$

where  $d_k^2 = (m_k/\mu) (1 - m_k/M)$ ,  $m_1 m_2$ , and  $m_2$  are the masses of the atom  $A$ ,  $B$ , and  $C$ , respectively, in the corners of the triangle  $ABC$ .  $M = m_1 + m_2 + m_2$  and  $\mu = \sqrt{m_1 m_2 m_2 / M}$  and the angle  $\xi = 2 \arctan(m_2/\mu)$ .

From Eq. (2) one can write

$$\tan \phi = \frac{(\cos \xi - 1)[(R_{BC}^2/d_2^2) - (R_{CA}^2/d_2^2)]}{\sin \xi[(R_{BC}^2/d_2^2) + (R_{CA}^2/d_2^2) - (2R_{AB}^2/d_1^2)]}. \quad (A3)$$

Considering the geometry of the triangle  $ABC$ , the interatomic distances can be expressed in terms of Jacobi coordinate as

$$\begin{aligned} R_{AB}^2 &= (r_x^2 + r_y^2) d_1^2, \\ R_{BC}^2 &= \frac{R_x^2 + R_y^2}{d_1^2} + \frac{(r_x^2 + r_y^2) d_1^2}{4} - r_x R_x - r_y R_y, \\ R_{CA}^2 &= \frac{R_x^2 + R_y^2}{d_1^2} + \frac{(r_x^2 + r_y^2) d_1^2}{4} + r_x R_x + r_y R_y. \end{aligned} \quad (\text{A4})$$

It would be convenient for obtaining the expressions of the gradient of hyperangle  $\phi$  with respect to Jacobi coordinates to introduce the physical region of the conical intersection in the following manner:

$$\begin{aligned} \frac{\partial \phi}{\partial r_i} &= \frac{\partial \phi}{\partial R_{AB}} \frac{\partial R_{AB}}{\partial r_i} + \frac{\partial \phi}{\partial R_{BC}} \frac{\partial R_{BC}}{\partial r_i} + \frac{\partial \phi}{\partial R_{CA}} \frac{\partial R_{CA}}{\partial r_i}, \\ \frac{\partial \phi}{\partial R_i} &= \frac{\partial \phi}{\partial R_{AB}} \frac{\partial R_{AB}}{\partial R_i} + \frac{\partial \phi}{\partial R_{BC}} \frac{\partial R_{BC}}{\partial R_i} + \frac{\partial \phi}{\partial R_{CA}} \frac{\partial R_{CA}}{\partial R_i}, \end{aligned} \quad (\text{A5})$$

where  $i \equiv x, y, z$ .

To obtain an explicit expression for  $\nabla \phi$ , we have used Eqs. (1)–(5) and after a little algebra it is interesting to note that  $\nabla \phi$  becomes independent of  $d_k$  and  $\xi$  at least for any arbitrary  $A + B_2$  type reactive system.

$$\begin{aligned} \frac{\partial \phi}{\partial r_i} &= \frac{-2}{\rho^2 \sin \theta} (r_i \sin \phi + R_i \cos \phi), \\ \frac{\partial \phi}{\partial R_i} &= \frac{2}{\rho^2 \sin \theta} (-r_i \cos \phi + R_i \sin \phi), \\ \frac{\partial \phi}{\partial r_z} &= 0, \\ \frac{\partial \phi}{\partial R_z} &= 0, \end{aligned} \quad (\text{A6})$$

where  $i \equiv x, y$ .

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