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## On the perception of the geometric phase effects in the diabatic representation: A new perspective

Ang-Yang Yu\*

Chinese Academy of Sciences, Dalian, Liaoning province, (CHINA)

E-mail: xintongyang2011@163.com

### ABSTRACT

Conical intersection could influence nuclear motion through geometric phase effects. The nuclear Schrodinger equation acquires a vector potential term in the adiabatic representation when the geometric phase effects are considered. After combining the nuclear Schrodinger equation in the adiabatic representation with the theoretical treatment in the diabatic representation, a new equation is derived for the nuclear motion. The traditional nuclear motion equation has ignored the geometric phase in the diabatic representation whereas the new equation incorporates both the geometric phase effects and other nonadiabatic factors in the diabatic representation. © 2015 Trade Science Inc. - INDIA

### KEYWORDS

Conical intersection;  
Geometric phase effect;  
Schrodinger equation;  
Adiabatic representation.

### INTRODUCTION

Von Neumann and Wigner firstly introduced the concept of conical intersection in their pioneering work<sup>[1]</sup>. Conical intersections was subsequently published in ref<sup>[2]</sup>. In the so-called non-adiabatic dynamics, the nuclei could move on two Born-Oppenheimer potential energy surfaces, of which the local topology is the shape of a double cone. When the energies of these potential energy surfaces depend linearly on the nuclear coordinates, the confluence will be regarded as a conical intersection. The conical topology is responsible for some important effects induced by conical intersection. In the excited state, the molecule is usually funneled into the region of the conical intersection, facilitating radiationless decay. On the ground state potential energy surface, a conical intersection can pro-

duce the geometric phase effect, which will be discussed in this article. Based on the theory of electronically non-adiabatic processes.<sup>[3]</sup> Herzberg and Longuet-Higgins firstly discovered the geometric phase effect in molecular systems and described its potential use.<sup>[4]</sup> Wherever there is a conical intersection point in the configuration space, the real ground state adiabatic electronic wave function becomes double-valued for a closed path that encircles the conical intersection point. The significant change in the electronic wave-function has profound implications for the associated nuclear Schrodinger equation<sup>[5,6]</sup>. It is also known that a wave function  $\psi_{m+1/2}(\theta) = \exp[i \times (m + 1/2) \times \theta]$  (where  $m$  is an integer) is the origin of the half-integer quantization in the dynamic Jahn-Teller effect<sup>[4]</sup>. Mead and Truhlar pointed out that the dynamical consequences

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of this phenomenon are equivalent to the geometric phase effect<sup>[7]</sup>. The electronic wave-function was often altered to remove the sign change in the theoretical treatment. It is multiplied by a phase factor so that it returns to itself after traversing a closed loop around the conical intersection. The effect of this modification is to introduce a vector potential into the nuclear Schrodinger equation as shown in Refs.<sup>[7-9]</sup>.

In the realm of molecular reaction dynamics, the geometric phase effect often refers to the Berry phase effect or the molecular Aharonov-Bohm effect. The geometric phase effects on reaction dynamics proved to be a great amounts of progresses in the last decades<sup>[10]</sup>. Earlier theoretical work is performed for the reaction  $D+H_2(V=1, j=1) \rightarrow HD(V=1, j')+H$  and the product rotational state distribution is in good agreement with the experimental results. The general vector potential approach for including geometric phase effects in three-dimensional quantum scattering calculation was applied to the  $H+D_2(v, j) \rightarrow HD(v', j')+D$  reaction at 126 values of total energy in the collisional energy range 0.4-2.4eV<sup>[11]</sup>. These time-independent quantum dynamical results are not only consistent with recent experimental results, but also with calculations that used a time dependent quantum dynamical theory by Althorpe<sup>[12]</sup>. Both the time-dependent and time-independent methods reach the same conclusion that no overall geometric phase effect could be found in the observed quantities, however, these studies are in the framework of the adiabatic representation which separates the motion of nuclei with the electrons<sup>[13]</sup>.

Manolopoulos and Child used a model Hamiltonian to study the sets of possible sign changes when  $N$  real quantum states are transported adiabatically around the  $N$ -fold degeneracy in Ref.<sup>[14]</sup>. Baer and his collaborators focused on the topological features and formulated an extended Born-Oppenheimer equation for two and three coupled electronic states in Refs.<sup>[15,16]</sup>. The location of conical intersections and the continuous representation of the local topography of seams of conical intersection of three or more electronic states has been investigated either<sup>[17-19]</sup>. Opalka and Domcke have modeled a PES for a threefold degeneracy in  $CH_4^+$  system<sup>[20]</sup>. Addi-

tionally, the rovibrational structure and the GP effect have been studied by Wörner et al<sup>[21]</sup>. Sarkar et al introduced an approach to deduce a generalized BO equation in Ref.<sup>[22]</sup> with the inclusion of GP effect by extension of the LH theorem<sup>[23]</sup> to four-fold Jahn-Teller systems<sup>[24,25]</sup>. What is more, Das et al returned to an issue related to the BO treatment to yield reliable diabatic potentials in Ref.<sup>[26]</sup>. To the best of our knowledge, no theoretical treatment of the geometric phase effect has been reported in the diabatic representation although there are some advances listed above. In this paper, the emphasis is the form of the Schrodinger equation which incorporates the geometric phase effects and some other non-adiabatic factors in the diabatic representation.

## THEORY AND RESULTS

In the quantum dynamics theory shown in Refs.<sup>[27-29]</sup>, there are two ways of incorporating the geometric phase effects theoretically. The first approach expands the nuclear wave functions in terms of a double-valued basis set. The basis set changes sign around the conical intersection point. The geometric phase is put into the basis set at the beginning and the resulting nuclear wave functions are double-valued functions around the conical intersection point. The approach has some disadvantages because it is difficult to implement in many cases.

The second approach is to multiply the real double-valued electronic wave function by a complex phase factor such that the new electronic wave is a complex single-valued function around the conical intersection point. The nuclear wave functions are then single-valued around the conical intersection. As a result, the nuclear Schrodinger equation acquires a vector potential term and takes the following form:

$$\left[ \frac{1}{2m} (-i\nabla - \mathbf{A}(\bar{r}))^2 + V(\bar{r}) \right] \psi(\bar{r}) = E\psi(\bar{r}) \quad (1)$$

Where  $V(\bar{r})$  is the ground electronic state potential energy surface (PES) for the molecule of interest and  $\mathbf{A}(\bar{r})$  is the relevant vector potential. Both  $V(\bar{r})$  and  $\mathbf{A}(\bar{r})$  are functions of the internuclear distances and  $m$  is the reduced mass of the investigated sys-

tem. The advantage of this approach is that the nuclear wave functions can be expanded in terms of a single-valued basis set. The inconvenience results from the more complicated form of nuclear Schrodinger equation than before. However, once numerical methods could solve this generalized Born-Oppenheimer equation, the situation can be treated simply by using the appropriate functional form for  $A(\bar{r})$  in equation(1), that is to say, this approach can be extended to the more general conical intersection problem. Kendrick's time independent quantum dynamical calculations in Ref.<sup>[11]</sup> use this type of method. In the current theoretical work described below, the vector potential approach is utilized to treat the geometric phase effects in the diabatic representation.

### The Schrodinger equation in the diabatic representation

Since the electrons move much faster than the nuclear atom, which is the origin of the Born-Oppenheimer approximation. The total wave function of the investigated system can be expanded as:

$$\Psi(\bar{q}; \bar{r}) = \sum_{i=1}^N \psi_i(\bar{r}) \phi_i(\bar{q}; \bar{r}_0) \quad \text{where } \bar{r} = (r_a) \text{ are}$$

the coordinates of the nuclear in a space fixed frame,  $\bar{q} = (q_i)$  are the coordinates of the electrons.  $\psi_i(\bar{r})$  is the nuclear wave function and  $\phi_i(\bar{q}; \bar{r}_0)$  is the adiabatic electronic wave-function for the electron which satisfy the electron Schrodinger equation:

$$\hat{H}_e \phi_i(\bar{q}; \bar{r}_0) = E_e \phi_i(\bar{q}; \bar{r}_0) \quad (2)$$

Where  $E_e$  is the eigenvalue of electron Hamilton which depends on the nuclear coordinates. Here we define that it is the electronic adiabatic representation when  $\bar{r} \equiv \bar{r}_0$ , on the contrary, it is the diabatic representation when  $\bar{r} \neq \bar{r}_0$ .

In the adiabatic representation, the nuclear Schrodinger equation could be expressed as the following form:

$$-\frac{1}{2m} \nabla^2 \psi + (\hat{H}_e - E) \psi = 0 \quad (3)$$

In which the well-known Born-Oppenheimer

approximation is contained. As for the diabatic representation where  $\bar{r}$  is a variable and  $\bar{r}_0$  is a constant, the electronic Hamilton could be expressed as:

$$\hat{H}_e(\bar{q}; \bar{r}) = \hat{H}_e(\bar{q}; \bar{r}_0) + [\mathbf{V}(\bar{q}; \bar{r}) - \mathbf{V}(\bar{q}; \bar{r}_0)] \quad (4)$$

In which  $\mathbf{V}$  is the potential energy operator. After taking  $\langle \phi_i(\bar{q}; \bar{r}_0) |$  into the molecular Schrodinger equation calculations, the nuclear motion equation becomes:

$$\left[ -\frac{1}{2m} \nabla^2 - E \right] \psi_j(\bar{r}) + \sum_{i=1}^N v_{ji}(\bar{r}; \bar{r}_0) \psi_i(\bar{r}) = 0 \quad (5)$$

Where

$$v_{ji}(\bar{r}; \bar{r}_0) = \tilde{v}_{ji}(\bar{r}; \bar{r}_0) + u_i(\bar{r}_0) \delta_{ji}$$

and

$$\tilde{v}_{ji}(\bar{r}; \bar{r}_0) = \langle \phi_i(\bar{q}; \bar{r}_0) | \mathbf{V}(\bar{q}; \bar{r}) - \mathbf{V}(\bar{q}; \bar{r}_0) | \phi_i(\bar{q}; \bar{r}_0) \rangle$$

$v_{ji}(\bar{r}; \bar{r}_0)$  is the non-adiabatic coupling term which couples the different electronic states together.

### The geometric phase in the diabatic representation

As has been mentioned, the electronic wave function changes its sign when transported adiabatically around a closed path containing the conical intersection point. The phenomenon is recognized as the geometrical phase. Mead and Truhlar multiply the real double-valued electronic wave function by a complex phase factor so that the new electronic wave function is a complex single-valued function around the conical intersection<sup>[7]</sup>. The nuclear functions are then single-valued around the conical intersection. The resulting nuclear Schrodinger function acquires a vector potential term and takes the following form<sup>[7-10]</sup>:

$$\left[ -\frac{1}{2m} (-i\nabla - \mathbf{A}(\bar{r}))^2 \right] \psi + (\hat{H}_e - E) \psi = 0 \quad (6)$$

or the equivalent form:

$$\left[ -\frac{1}{2m} (-i\nabla - \mathbf{A}(\bar{r}))^2 + \mathbf{V}(\bar{r}) \right] \psi(\bar{r}) = E \psi(\bar{r}) \quad (7)$$

In which  $\mathbf{V}(\bar{r})$  is the ground state potential energy surface (PES) of the investigated system and  $\mathbf{A}(\bar{r})$  is the relevant vector potential term. Both  $\mathbf{V}(\bar{r})$  and  $\mathbf{A}(\bar{r})$  are functions of the internuclear distances  $\bar{r}$  and  $m$  is the reduced mass of the investigated sys-

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tem. It should be noted that the nuclear Schrodinger equations (6) and (7) only incorporated the geometric phase effect in the adiabatic representation. The method described in Section 2.1 is used to deal with the geometric phase effect in the diabatic representation. To avoid the repetition of mathematical details in Refs.<sup>[8,9]</sup>, the derivation processes have been omitted and the deduced equation is given below:

$$[\frac{1}{2m}(-i\nabla - \mathbf{A}(\bar{\mathbf{r}}))^2 - \mathbf{E}] \psi_j(\bar{\mathbf{r}}) + \sum_{i=1}^N v_{ji}(\bar{\mathbf{r}}; \bar{\mathbf{r}}_0) \psi_i(\bar{\mathbf{r}}) = 0 \quad (8)$$

The equation has a new expression, in which  $v_{ji}(\bar{\mathbf{r}}; \bar{\mathbf{r}}_0)$  has the same physical meaning as the counterpart in the adiabatic representation. The new equation takes the geometric phase effect into consideration in the diabatic representation. It is the first Schrodinger equation that incorporates both the geometric phase effects and other non-adiabatic factors.

## DISCUSSIONS

The incorporation of geometric phase effects is independent of the treatment of electronic Hamiltonian in the diabatic representation, therefore, current theoretical deduction is reasonable and practical applications are feasible. In this part, we discuss the possible applications of the new equation. Let us take the research in molecular spectra as an example, an accurate theoretical prediction of the vibrational spectra for a pure nitrogen ring, say, cyclic- $\text{N}_3$  molecule, is obtained up to the energy of the  ${}^2\text{A}_2/{}^2\text{B}_1$  conical intersection in Ref.<sup>[30]</sup>. A coupled-channel approach using the hyperspherical coordinates and the recently published ab initio potential energy surface of Ref.<sup>[31]</sup> is employed including the geometric phase effects. All vibrational energies are analyzed and assigned in terms of the normal vibration mode quantum numbers. The magnitude of the geometric phase effect is determined for each state, compared with the one neglecting the geometric phase effects. One of the main results is that it is equal to  $100 \text{ cm}^{-1}$  for the lowest-lying vibrational state and exceeds  $600 \text{ cm}^{-1}$  for higher vibrational states, which confirms the existence of the geometric phase effects in the cyclic- $\text{N}_3$ . However, all the theoretical results are still obtained in the adiabatic

representation and different theoretical results will appear after incorporating the geometric phase effects (GPE) in the diabatic representation. The reason is that the traditional nuclear motion equation has ignored the geometric phase in the diabatic representation whereas the new equation incorporates both the geometric phase effects and other nonadiabatic factors in the diabatic representation. Therefore, someone who performs such calculations will demonstrate a valuable theoretical work and tell us a new story.

Another possible application direction is the investigation of geometric phase effects induced photodissociation dynamics. The geometric phase effects have been observed in the photodissociation of phenol.<sup>[32]</sup> The mode specific Phenoxy radicals formation is resulted from the geometric phase effect at the conical intersection between the ground and first excited state potential energy surfaces. The geometric phase effects on photodissociation dynamics at a two-dimensional symmetry-allowed conical intersection (CI) was also investigated recently.<sup>[33]</sup> If the newly derived equation(8) is put into use in those work effectively, there will be more fruitful results.

## CONCLUSION

In this work, the geometric phase is considered in the diabatic representation. A new equation is derived for the nuclear motion. Since the new equation incorporates both the geometric phase effects and other nonadiabatic factors, new algorithms or procedures could be developed in the near future. The particularity of the new nuclear motion equation lies in the nonadiabatic coupling terms and the geometric phase vector term. Therefore, it could be generalized to many problems in nonadiabatic chemistry containing the conical intersections. The new equation is also the first equation in the diabatic representation, which deals with the geometric phase effects. Overall, this new equation could bring out new results in molecular spectra, molecular reaction dynamics as well as photodissociation dynamics.

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