On phase factors and geometric phases in isotopes of $\text{H}_3$: A line integral study

ZongRong Xu
Departamento de Química, Universidade de Coimbra, P-3049 Coimbra, Portugal

Michael Baer$^{(a)}$
Departamento Química, Universidade de Coimbra, P-3049 Coimbra, Portugal and Department of Physics and Applied Mathematics, SOREQ NRC, Yavne 81800, Israel

António J. C. Varandas
Departamento de Química, Universidade de Coimbra, P-3049 Coimbra, Portugal

(Received 4 March 1999; accepted 10 November 1999)

In this work we apply the line-integral technique to study possible geometric phase effects in the $2 \times 2$ diabatic double many-body expansion (DMBE) potential energy surface of three hydrogenic systems, namely, $\text{H}_3$, $\text{D}_2\text{H}$, and $\text{HD}_2$. First, we show that the phase obtained by employing the line-integral method is identical (up to a constant) to the ordinary diabatic angle of the orthogonal transformation that diagonalizes the diabatic potential matrix. Next this angle is studied numerically along the line formed by fixing the two hyperspherical coordinates $\rho$ and $\theta$ and letting $\phi$ change along the interval $[0, 2\pi]$. We find that in the $\text{H}_3$ system, where this line always encircles the seam, the corresponding line integral always produces the value $\pi$ for the geometric (Berry) phase. In the cases of the two isotopic systems we usually find the same results, but we also verify that for substantial regions in configuration space these lines do not encircle the seam and that, therefore, the line integrals produce the value of zero for the geometric phase. Analyzing the results, we establish that the Longuet-Higgins phase, which is usually assumed to be equal to $\phi/2$, is in general significantly different from this value for all studied mass combinations. © 2000 American Institute of Physics. [S0021-9606(00)00606-1]

I. INTRODUCTION

Following the Born–Oppenheimer treatment$^1$ it is believed that the adiabatic representation is the more suitable one for numerical and theoretical treatments of processes characterized by electronic transitions. The adiabatic framework, however, has one major disadvantage namely the fact that nonadiabatic coupling terms which are responsible for such transitions attain sometimes infinite values at some regions of configuration space causing the numerical treatment to be unstable.$^2,3$ It is therefore now accepted that in order to avoid these infinities one should transform to the diabatic representation where the coupling terms are ordinary potential couplings and the instabilities are in this way eliminated.$^4,5$ To reach the diabatic representation, one of two ways can be chosen: either produce the adiabatic potential energy surfaces (PESs) and the corresponding nonadiabatic coupling terms and then transform to the diabatic framework employing the adiabatic–diabatic transformation (ADT) matrix (which has first to be derived)$^6,7$ or form the diabatic potential matrix (DPM) directly.$^8,9,10,11,12,13$ Choosing this way one usually ascertains that once the DPM is obtained, diagonalizing it yields the correct adiabatic PESs which are the physical magnitudes of interest. In this process, which now gains more and more attention, the effect of electronic degenerate states is usually overlooked. It is well known now that degenerate states are responsible for geometric phase effects,$^{14–20}$ and the question may arise whether the particular DPM yields not only the correct adiabatic PESs but also the relevant geometric phase effects. Although these effects are determined by the behavior of the potentials in the vicinity of the degeneracy,$^{15–19}$ they are felt over large (and even infinite) regions of configuration space.$^4,5$ Therefore, numerical tools have to be developed to permit classifying these effects efficiently and correctly in both, the adiabatic and diabatic frameworks. In this work we discuss such a tool and apply it to three hydrogenic systems, $\text{H}_3$, $\text{D}_2\text{H}$, and $\text{HD}_2$. The $2 \times 2$ diabatic double many-body expansion (DMBE) PES$^8$ is used to carry out the numerical part.

The present study is motivated by recent instructive studies performed by Yarkony and co-workers.$^{21–24}$ They have shown, employing the line integral technique,$^3,7,25–28$ how efficient this approach can be in detecting the electronic degeneracy but so far their studies have been concerned with a region close to the locus of the crossing seam (denoted heretofore simply as seam); for an alternative approach which consists of monitoring the sign of the electronic wavefunction along the closed loop, see Ref. 29. Our study extends the scope to all configuration space.

This paper is arranged in the following way. In the next section is discussed the ADT angle formed by using the line integral approach and its relation to the ordinary diabatic transformation angle in the case of a two-dimensional Hilbert space. The $2 \times 2$ DMBE PES employed in this study is

$^a$Visiting Professor, Universidade de Coimbra.
presented briefly in the third section. In the fourth the diabatic transformation angle is calculated along closed paths for three hydrogenic systems, i.e., \( \text{H}_3 \), \( \text{DH}_2 \), and \( \text{HD}_2 \). The results are analyzed and conclusions drawn in the fifth section.

II. THE ADIABATIC–DIABATIC-TRANSFORMATION ANGLE

The ADT angle \( \alpha(s)^{3-7,27} \) is characteristic of a two-state system. In its most general form, it is defined as

\[
\alpha(s) = \alpha(s_0) + \int_{\Gamma} ds' \cdot \tau(s'),
\]

where \( s \) and \( s_0 \) are two points in an \( N \)-dimensional configuration space, \( \Gamma \) is a path within this space that combines these two points, \( ds \) is a differential vector along that path, \( \alpha(s_0) \) is some initial value usually assumed to be zero, the dot stands for scalar product, and \( \tau(s) \) is a vector which contains the components of the nonadiabatic coupling term between the two states defined as

\[
\tau(s) = \langle \chi_1(s) | \nabla \chi_2(s) \rangle.
\]

Here \( \chi_1(s) \) and \( \chi_2(s) \) are the two adiabatic electronic wave functions belonging to states 1 and 2, and \( \nabla \) is the gradient operator which is expressed in terms of the \( N \) coordinates. It is noticed that the ADT angle can be obtained once the adiabatic electronic eigenfunctions are given, and therefore it is a characteristic magnitude of the adiabatic representation.

A slightly different way of expressing \( \alpha \), which is more appropriate for our present purposes, is

\[
\alpha(s) = \alpha(s_0) + \int_{\Gamma} ds' \cdot \tau_s(s'),
\]

where \( \tau_s(s) \), the \( s \)-component of \( \tau \) along the path, is defined as

\[
\tau_s(s) = \left( \chi_1(s) \left| \frac{\partial}{\partial s} \chi_2(s) \right. \right).
\]

Next we consider the diabatic framework. Like the above described adiabatic one, the two-dimensional diabatic framework is characterized by an angle \( \gamma(s) \), associated with the orthogonal transformation which diagonalizes the diabatic potential matrix. Thus, if \( \mathbf{W} \) is the DPM and \( \mathbf{V} \) is the adiabatic one, the two are related by the orthogonal transformation matrix \( \mathbf{T} \), i.e.,

\[
\mathbf{V} = \mathbf{T}^{\dagger} \mathbf{W} \mathbf{T},
\]

where \( \mathbf{T}^{\dagger} \) is the conjugate-transposed of the \( \mathbf{T} \) matrix. For the two-state case, \( \mathbf{T} \) can be written in the form

\[
\mathbf{T} = \begin{pmatrix} \cos \gamma(s) & -\sin \gamma(s) \\ \sin \gamma(s) & \cos \gamma(s) \end{pmatrix},
\]

where \( \gamma(s) \) is given by

\[
\gamma(s) = \frac{1}{2} \tan^{-1} \frac{2W_{12}}{W_{11} - W_{22}}.
\]

Recalling \( \alpha(s) \), it is expected that the two angles are related. The connection is formed by the Hellmann–Feynman theorem\(^{11,30} \) which yields the relation between the \( s \) component of \( \tau(s) \), namely \( \tau_s(s) \), and the characteristic diabatic magnitudes

\[
\tau_s(s) = -\sin[2\gamma(s)] \mathbf{T}_i^{\dagger} \frac{\partial \mathbf{W}}{\partial s} \mathbf{T}_i,
\]

where \( \mathbf{T}_i, i = 1,2 \) are two columns of the \( \mathbf{T} \) matrix. Indeed, it has been shown\(^{31} \) (for an extended discussion on this topic, see also Ref. 27) by employing the Hellmann–Feynmann theorem that \( \tau_s(s) \) and the angle \( \gamma(s) \) which diagonalizes the diabatic potential matrix fulfill the following equation:

\[
\tau_s(s) = \frac{\partial \gamma(s)}{\partial s},
\]

and, therefore, by employing Eq. (3), one gets

\[
\Delta \alpha(s) = \Delta \gamma(s).
\]

Then, if we assume that \( \alpha(s_0) = 0 \), one has

\[
\alpha(s) = \gamma(s) - \gamma(s_0).
\]

This relation will be used in the present work to study geometric phase effects within the diabatic framework for the \( \text{H}_3 \) system and its two isotopic analogs. It is important to emphasize that Eq. (9) holds for any angle \( \gamma(s) \) that diagonalizes a diabatic potential matrix because the components of the nonadiabatic coupling vector \( \tau(s) \), as calculated from the Hellmann–Feynman theorem, always fulfills the requirement \( \mathbf{V} \times \tau(s) = 0 \).

III. THE POTENTIAL ENERGY SURFACE

The systems considered in this study for illustrative purposes concerns the two lowest doublet states of \( \text{H}_3 \). To treat them we employ the lowest reported adiabatic PESs\(^{32} \) which have been obtained using the double many-body expansion (DMBE)\(^{33,34} \) method. The lower of the two has been extensively applied in numerous dynamics calculations and found to yield reliable results (e.g., Refs. 35 and 36, and references therein). Moreover, it has recently been employed for three-dimensional (\( J = 0 \)) wave packet calculations within the diabatic framework,\(^8 \) for which it was necessary to employ the full DPM. This \( 2 \times 2 \) matrix is defined by\(^{37} \)

\[
W_{11} = \sum_{i=1}^{3} Q_i + X_{\text{EHF}}^{(3)} + \frac{1}{2}(2J'_{1} - J'_{2} - J'_{3}) + V_{\text{dc}},
\]

\[
W_{22} = \sum_{i=1}^{3} Q_i + X_{\text{EHF}}^{(3)} - \frac{1}{2}(2J'_{1} - J'_{2} - J'_{3}) + V_{\text{dc}},
\]

\[
W_{12} = W_{21} = \frac{1}{2}(J'_{2} - J'_{3}),
\]

where the \( Q \)'s and \( J' \)'s are the well known Coulomb and exchange integrals which can be obtained semiempirically from the diatomic singlet and triplet eigenstates. \( X_{\text{EHF}}^{(3)} \) a three-body extended Hartree–Fock type energy, and \( V_{\text{dc}} \) the total dynamical correlation energy. Note that the prime in the \( Q \)'s and \( J' \)'s expresses the fact that such quantities are calculated from the extended Hartree–Fock diatomic curves alone.
In what follows we shall be interested in the location of the seam defined by the conditions \( r_{AB} = r_{BC} = r_{AC} \) where \( r_{AB} \), \( r_{BC} \), and \( r_{AC} \) are the interatomic distances. Since we intend to study the geometric properties produced by this seam we follow a suggestion by Kuppermann and co-workers\(^{38,39}\) and employ the hyperspherical coordinates \((\rho, \theta, \varphi)\) which are most suitable for this purpose.\(^{40-45}\) Consequently, following previous authors,\(^{41,45}\) we express the three above-mentioned distances in terms of these coordinates, i.e.,

\[
\begin{align*}
    r_{AB}^2 &= \frac{1}{2} d_A^2 \rho^2 \left[ 1 + \sin \frac{\theta}{2} \cos (\varphi + \chi_{AC}) \right], \\
    r_{BC}^2 &= \frac{1}{2} d_B^2 \rho^2 \left[ 1 + \sin \frac{\theta}{2} \cos (\varphi) \right], \\
    r_{AC}^2 &= \frac{1}{2} d_C^2 \rho^2 \left[ 1 + \sin \frac{\theta}{2} \cos (\varphi - \chi_{AB}) \right],
\end{align*}
\]

where

\[
\begin{align*}
    d_A^2 &= \frac{m_X}{\mu} \left( 1 - \frac{m_X}{M} \right), & \chi_{XY} &= 2 \tan^{-1} \left( \frac{m_Y}{\mu} \right), \\
    \mu &= \sqrt{\frac{m_A m_B m_C}{M}}, & M &= m_A + m_B + m_C.
\end{align*}
\]

Here \( X, Y, \) and \( Z \) stand for \( A, B, \) and \( C \). Equating the three interatomic distances with each other we find that the seam is a straight line, for which \( \rho \) is arbitrary but \( \varphi \) and \( \theta \) have fixed values \( \varphi_s \) and \( \theta_s \), determined by the masses only, namely,

\[
\begin{align*}
    \varphi_s &= \tan^{-1} \left( \frac{\cos \chi_{AC} - t \cos \chi_{AB} - \left( \frac{d_A}{d_C} \right)^2 + t \left( \frac{d_A}{d_B} \right)^2}{\sin \chi_{AC} + t \sin \chi_{AB}} \right), \\
    \theta_s &= 2 \sin^{-1} \left( \frac{\left( \frac{d_A}{d_B} \right)^2 - 1}{\cos (\varphi_s - \chi_{AB}) - \left( \frac{d_A}{d_B} \right)^2 \cos \varphi_s} \right),
\end{align*}
\]

where \( t \) is given in the form

\[
    t = \left| \left( \frac{d_A}{d_C} \right)^2 - 1 \right| \left| \left( \frac{d_A}{d_B} \right)^2 - 1 \right|^{-1}.
\]

Equations (19) to (21) are valid when all three masses are different. In case two masses are equal, namely \( m_B = m_C \), we get for \( \theta_s \) the simplified expression

\[
    \theta_s = 2 \sin^{-1} \left( \frac{m_B - m_A}{m_B + 2 m_A} \right)
\]

and for \( \varphi_s \) the value \( \pi \) when \( m_A > m_B \), and the value zero when \( m_A < m_B \). In case all three masses are equal (then \( t = 1 \)), one has \( \theta_s = 0 \), and \( \varphi_s = 0 \) (or \( \pi \)).

In what follows we discuss the \( H_2 \) system and the two isotopic systems \( DH_2 \) and \( HD_2 \).

**IV. RESULTS**

The aim of this study is to use the above described 2 \( \times \) 2 DPM \( W \) to calculate the ADT angle \( \alpha \), given in Eq. (3), as a function of the hyperspherical coordinates \( \varphi \) for fixed values of \( \theta \) and \( \rho \). In Sec. II we have shown that \( \alpha(\varphi) \) and \( \gamma(\varphi) \), the diabatic transformation angle, are equal up to a constant \( \gamma_0 = \gamma(\varphi = 0) \) [see Eq. (11)]. Therefore, in the numerical treatment, we shall calculate \( \gamma(\varphi) \) employing Eq. (7), and then calculate \( \alpha(\varphi) = \gamma(\varphi) - \gamma(\varphi = 0) \). In what follows \( \alpha \) is labeled as \( \alpha(\varphi|\theta, \rho) \).

**A. The \( H_3 \) system**

The \( H_3 \) system is characterized by its seam being defined for the value \( \theta_s = 0 \), which therefore makes it independent of \( \varphi \) (or \( \varphi_s \)). This feature guarantees that each path formed by \( \varphi \) varying from 0 to \( 2\pi \), for fixed values of \( \theta \) and \( \rho \), encircles the seam. In Fig. 1. are presented \( \alpha(\varphi|\theta, \rho) \) functions as calculated for different values of \( \theta \) and \( \rho \). Specifically, Fig. 1(a) shows results for \( \rho = 6a_0 \) and four values of \( \theta \), namely \( \theta = 0.01, 0.1, 1, \) and 3 rad, and Fig. 1(b) for \( \theta = 1 \) rad and four values of \( \rho \), namely \( \rho = 1, 3, 6, \) and 12\( a_0 \). It is clear that in

![Graphs showing ADT angle \( \alpha \) as a function of \( \varphi \) for different \( \theta \) and \( \rho \) values.](image-url)
all eight cases $\alpha(\varphi = 2\pi|\theta\rho) = \pi$ which according to our theory implies that the $2 \times 2$ DMBE diabatic potential correctly describes the symmetry properties of this system.\textsuperscript{15-19,29} It is also seen that as long as the circle around the seam has a small radius $d(= \rho \sin \theta)$, namely when either $\theta$ or $\rho$ are small enough the dependence of $\alpha$ on $\varphi$ is like that expected in the case of a conical intersection (i.e., $\alpha = \varphi/2$). However, once this radius increases, the dependence of $\alpha$ on $\varphi$ changes gradually to become an equally spaced increasing steplike function, halved by the straight line $\alpha = \varphi/2$. It is noticed that the larger the radius $d$ the larger are the sizes of the these steps and the more they become abrupt. The three steps that are encountered in each case can be rationalized from the adiabatic PES which is known to have a threefold symmetry with respect to $\varphi$ once the two other coordinates are held fixed.

In Fig. 2 are presented the adiabatic PESs as a function of $\varphi$ for fixed values of $\theta$ and $\rho$, namely $\theta = 2\text{ rad}$ and $\rho = 6a_0$. Specifically, Fig. 2(a) shows the adiabatic surfaces, and Fig. 2(b) the three terms of the DPM. The notable features are the expected threefold permutational symmetry, and (although not shown for brevity) the fact that peaks arise for large $\rho$ values due to the Coulomb repulsions which occur when the interatomic distances of the diatomic molecule in the triatomic system becomes small.

**B. The DH\textsubscript{2} and the HD\textsubscript{2} systems**

The equations for the (straight line) seams are as follows: $(\theta_s = 0.4023\text{ rad}, \varphi_s = \pi)$ for DH\textsubscript{2} and $(\theta_s = 0.5048\text{ rad}, \varphi_s = 0)$ for HD\textsubscript{2}. Although the tangents of the two lines differ slightly, all other results of interest are similar. The fact that $\theta_s$ is no longer zero implies that not all the circles with constant $\theta$ and $\rho$ encircle the seam; in fact the loops with $\theta < \theta_s$ will not encircle the seam.

In Fig. 3 are presented $\alpha(\varphi|\theta\rho)$ curves for DH\textsubscript{2}, all calculated for $\rho = 6a_0$. In Fig. 3(a) are shown two curves for the case where the line integral does not encircle the seam, namely, for $\theta = 0.2$ and $0.4$ rad, and in Fig. 3(b) for the case where the line integral encircles the seam, namely for $\theta = 0.405$ and $2$ rad. It is seen that the curves in Fig. 3(a) reach the value zero, and those in Fig. 3(b) the value $\pi$. In particular, two curves, those in Fig. 3(a) for $\theta = 0.400$ rad and in Fig. 3(b) for $\theta = 0.405$ rad, were calculated along loops very close to the crossing seam and indeed their shapes are
similar—they both yield an abrupt step—but one curve reaches the value of zero and the other the value \( \pi \). Both types of results justify the use of the line integral to uncover the locus of the seam.

Similar results but for HD\(_2\) are shown in Fig. 4, again calculated for \( \rho = 6a_0 \). In Fig. 4(a) we present the results when \( \theta < \theta_s ( = 0.5048 \text{ rad}) \), namely with \( \theta = 0.2 \) and 0.45 rad, and in Fig. 4(b) for \( \theta > \theta_s \), namely with \( \theta = 0.55 \) and 2 rad. Although the curves are somewhat flatter, they all behave similarly to the corresponding curves in Fig. 3 and therefore the same analysis (and conclusion) applies here, too.

The results for the isotopic system never exhibit the typical conical result, namely \( \alpha = \varphi/2 \) that was encountered in the \( \text{H}_2 \) case for paths which encircle the seam very closely. The main reason for this is that the plane formed by fixing \( \rho \) and \( \theta \), is perpendicular to the seam in case of the \( \text{H}_3 \) system but not for its isotopomers.

**V. DISCUSSION AND CONCLUSIONS**

In this work we applied the line integral technique to study features of diabatic PESs originated by the degeneracy of the adiabatic PESs. By applying the Hellmann–Feynman theorem we made a connection between the ADT angle \( \alpha \) and the diabatic transformation angle \( \gamma \), which is obtained following the diagonalization of the diabatic matrix. The two were proved to be identical up to an additive constant. The geometric phase features of \( \text{H}_3 \) and the two isotopic \( \text{DH}_2 \) and \( \text{HD}_2 \) systems were studied by applying this angle. The line along which the \( \gamma \) angle was calculated was defined in terms of the hyperspherical coordinates (\( \rho, \theta, \varphi \)) and was formed by holding \( \rho \) and \( \theta \) fixed and varying \( \varphi \) along the range \([0, 2\pi]\). Whereas in the case of \( \text{H}_3 \) we got for \( \alpha \) nice symmetrical shapes (for different \( \rho \) and \( \theta \) values), in the case of the two other systems we have obtained somewhat less symmetrical curves. In addition, it is important to mention that the assumption \( \alpha(\varphi, \theta \rho) = \varphi/2 \) was hardly fulfilled in all three systems, i.e., not in the \( \text{H}_3 \) system nor in its two isotopic variants.

Having the two adiabatic surfaces and \( \alpha(\varphi, \theta \rho) \), we were able to calculate the corresponding DPM \( W \). This we did twice: once using the actual \( \gamma \) which yields the original diabatic matrix \( W(\gamma) \) and once for \( \gamma = \varphi/2 + \gamma(\varphi = 0) \) which yields the ‘conical’ diabatic matrix \( W_\varphi(\varphi/2) \). Having the two DPMs we calculated \( \Delta W = W(\gamma) - W_\varphi(\varphi/2) \). Although not shown for brevity, the three elements of the \( \Delta W \) matrix have in most cases been found to be rather large, which implies that significant errors may arise if the ‘conical’ diabatic matrix \( W_\varphi(\varphi/2) \) is employed for studying polyatomic reactive (exchange) processes. The results presented so far indicate that some assumptions made in previous reactive scattering calculations may not be as accurate as one would wish. Indeed, in all calculations of this type it has been assumed (based on the Jahn–Teller model) that \( \alpha(s)[\text{or } \gamma(s)] = \eta/2 \) where \( \eta \) is an angle which encircles the conical intersection.\(^{38,39,42,46–48}\)

We have shown here that this assumption is in general not fulfilled for the \( \text{H} + \text{H}_2 \) reaction and its isotopic analogs, except in the case of the homonuclear \( \text{H} + \text{H}_2 \) reaction and very close to the seam. Of course, we by no means imply that those calculations are wrong or inaccurate but just that it would be appropriate to repeat them with the form of the \( \alpha(s)[\text{or } \gamma(s)] \) suggested in the current work. Moreover, in the early pioneering calculations\(^{38,39,42,45}\) \( \eta \) was assumed to be equal to the hyperspherical angle \( \varphi \). We have shown here that such an assumption is appropriate for \( \text{H} + \text{H}_2 \) but not always for its isotopic analogs. Again, we do not mean to criticize such calculations (since, indeed, most of them\(^{38,39,42,45}\) refer to the homonuclear hydrogen trimer) but just to point out that it would be interesting to carry out further calculations on systems such as \( \text{D} + \text{H}_2 \)\(^{49}\) using the method proposed in the present work.

In a recent paper Yarkony\(^{46}\) suggested to trace locations of degenerate states by encircling the locus of the seam with an angle that can be derived by ‘diagonalizing virtually any symmetric (real-valued Hermitian) electronic property operator.’ As an example, Yarkony considered a dipole moment operator suggested for similar purposes several years ago by Werner and Meyer.\(^{50}\) Yarkony showed\(^{46}\) that, for the system \( \text{CH}_2 \), he could expose the locus of the seam. The main limitation of his procedure is that it must be carried out relatively...
close to the locus of the (conical) intersection. In other words, while searching for the locus of the intersection, only small parts of configuration space can be inspected whereas in realistic cases such inspections have to be made on large portions of configuration space. Such successful large-scale inspections are guaranteed by the line integral approach.

ACKNOWLEDGMENT

This work has been supported by the Fundação para a Ciência e Tecnologia, Portugal, under program PRAXIS XXI.