Adiabatic-diabatic transformations for molecular systems: a model study of two interacting conical intersections

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(Received 15 April 1999; revised version accepted 28 July 1999)

A model is presented for studying the interaction between two conical intersections (e.g. a dimer of two bound molecules each characterized by a conical intersection). The model is an extension of a previous model for a single conical intersection formed by an electron housed in a vibrating molecule (Baer, M. and Englman, R., 1992, Molec. Phys., 75, 293). We distinguish between two situations: when the coupling is weak (for instance when it takes place in the asymptotic region) and when it is strong. The study is accomplished by calculating the adiabatic-diabatic transformation (ADT) matrix. Whereas the features of the ADT matrix for weak coupling seem reasonable (and to a certain extent expected), we find some unexpected features in the case of strong interaction. In particular, the two characteristic ADT angles of the uncoupled systems namely \(\varphi_1/2\) and \(\varphi_2/2\) are replaced by two new ADT angles, namely, \((\varphi_1 + \varphi_2)/2\) and \((\varphi_1 - \varphi_2)/2\). This implies that the corresponding nuclear wavefunctions, which originally were multi-valued, become single-valued in cases of strong interaction.

1. Introduction

The study of effects of doubly degenerate electronic states on molecular processes is becoming a major subject in molecular physics [1–11]. In this context, Baer and Englman [7] suggested examining these effects by employing a model consisting of a molecular electron coupled to the vibrational motion of the molecule, i.e., a conical intersection [1, 2]. The electron–molecule coupling was studied within the framework of a two-state model (namely, a 2-dimensional Hilbert space), and it was shown [7–9] that the geometrical features of this system were determined solely by the adiabatic–diabatic transformation (ADT) angle \(\alpha\) [12]. It was shown also that the ADT angle, once calculated along a closed path around the point of degeneracy [7–9], yields the Berry phase \(\beta\) [3]. This was confirmed [9] both for the resulting Jahn–Teller-type degeneracy (in this case \(\beta\) was found to be equal to \(\pi\)) and when the Jahn–Teller degeneracy was removed by a perturbation \(\mu\) (in that case \(\beta\) was found to be equal to \(2\pi\) (or zero)). Recently [13] the model was extended to involve two such electrons, each one attached to a (different) molecule, and the aim was to study a situation where two systems, each governed by a conical intersection, interact with each other. This extended system was treated within a 4-dimensional Hilbert space and therefore it yielded some new geometrical features. However, this treatment was carried out assuming the interaction between the molecules to be weak. In the present article, the model is extended to include the case where the interaction is relatively strong, and the results are rather different.

2. The model

Our model contains two electrons, each housed in a separate molecule and with its motion coupled to the vibrational motion of the corresponding molecule. In addition, the two electrons interact with each other by a Coulomb force. Such a model can represent a weakly bound dimer of the form \(A_3 \cdots A_4\) [11b] or simply a scattering process between two molecules, both having conical intersections. The aim of the present study is to analyze the effect of this type of external electron–electron interaction on the degeneracy of the global system and the resulting multivaluedness of the nuclear wavefunctions: in other words, to obtain the ADT angles connected with this situation.

As in our previous study [13] the motion of each of the electrons will be described in terms of one (periodic) coordinate \(\theta_i, \ i = 1, 2\), and the vibrational motion of each of the two mother molecules will be described in terms of two coordinates: a polar periodic coordinate \(\varphi_1\) (\(\varphi_2\)) (defined along the interval \((0, 2\pi)\)) and a radial (dis-
The equation we are interested in solving is the following (electronic) eigenvalue equation:

\[ H = H_1 + H_2 + H_{12}, \]

where

\[ H_i = -\frac{1}{2}E_{el} \frac{\partial^2}{\partial \theta_i^2} + G_i \cos (2\theta_i - \varphi_i) \quad i = 1, 2, \]

and

\[ H_{12} = G \cos [2(\theta_1 + \varphi_1) - (\varphi_1 + \varphi_2)]. \]

In these equations, \( E_{el}, i = 1, 2 \), are characteristic electronic magnitudes and \( G_i, i = 1, 2 \), are the (inter-) electronic–nuclear coupling coefficients usually assumed to be equal to \( k_i q_i \), where \( k_i \) is a force constant of the \( i \)th molecule. The third term in equation (1), namely \( H_{12} \), describes a Coulomb-type interaction between the two electrons, each attached to one molecule, and therefore the coefficient \( G \) depends on the distance between the two molecules (and eventually on other physical magnitudes). Electronic Hamiltonians of two interacting molecules were discussed in a series of papers by Dexter et al. [11c–e].

In contrast to the previous study, here we intend to study also a strong interaction case. Usually this implies the study of the close proximity region. However, we do not mean this region (on the contrary this region is outside our interest because the molecules and their attached electrons lose (within it) their identity) but a different one, as will be defined later. This region, which still can be treated within our model, will be shown to be of physical importance although being far from the close proximity region.

3. The solution of the eigenvalue problem

The equation we are interested in solving is the following (electronic) eigenvalue equation:

\[ (H - \eta(\varphi_1, \varphi_2)) \Psi(\theta_1, \theta_2 \mid \varphi_1, \varphi_2) = 0, \]

where \( \eta(\varphi_1, \varphi_2) \) is an eigenvalue and \( \Psi(\theta_1, \theta_2 \mid \varphi_1, \varphi_2) \) is the corresponding eigenvector; the bar specifies the parametric dependence of \( \Psi \) on the nuclear coordinates \( \varphi_1 \) and \( \varphi_2 \). The solutions for this equation will be constructed from products of solutions of the following single-electronic eigenvalue equations [9]

\[ (H_i - u_{ij}) \psi_{ij} = 0 \quad i = 1, 2, j = 1, 2, \]

where the \( \psi_{ij} \) and the \( u_{ij} \) are the corresponding eigenvectors and eigenvalues. As for the indices, the first index designates the molecule and the second refers to one of the two lowest eigenvalues (we assume throughout this composition a 2-dimensional Hilbert space for each electronic molecule). Since in this way, for the global system, a 4-dimensional Hilbert space is formed, the function \( \Psi \) will be presented as a linear combination of products of the type \( \psi_{ij} \psi_{2k} \) where \( j, k = 1, 2 \). Thus:

\[ \Psi = \sum_{j,k=1}^{2} a_{jk} \psi_{ij} \psi_{2k}. \]

In [9] we showed that the two general adiabatic independent solutions of equation (5), relevant for our purpose, have the form

\[ \psi_1(\varphi) = a_n \cos^n (\varphi/2) \]

and

\[ \psi_2(\varphi) = b_n \sin^n (\varphi/2), \]

where the summation index \( n \) runs over the odd integers starting with \( n = 1 \). As in [9], we shall assume that each of the parameters \( G_i, i = 1, 2 \), is much smaller than the corresponding \( E_{el}, i = 1 \). This simplifies significantly the derivation of the functions \( \psi_1 \) and the corresponding \( u_{ij} \) values. Thus, following [9] we have for the eigenfunctions:

\[ \psi_{12} = C_i (c_i + \lambda_i c_i^3) \]

where

\[ C_i = \frac{1}{\sqrt{\pi}} (1 + \lambda_i), \]

and \( \lambda_i = (1/2)(E_{el})^{-1} G_i \); for the corresponding eigenvalues:

\[ u_{11} = \frac{1}{2} (E_{el} - G_i); \quad u_{12} = \frac{1}{2} (E_{el} + G_i) \quad i = 1, 2. \]
Substituting $\psi$ given in equation (6) in equation (4), multiplying the resulting expression by each of the (product) functions $\psi_{1j}\psi_{2k}$, where $j = 1,2$ and $k = 1,2$, integrating over the two electronic coordinates $\theta_i$, $i = 1,2$, and recalling equation (5) we obtain the $4 \times 4$ eigenvalue problem

$$
\begin{vmatrix}
H_{11,11} - \eta & 0 & 0 & -\frac{1}{2}G \\
0 & H_{11,22} - \eta & -\frac{1}{2}G & 0 \\
0 & -\frac{1}{2}G & H_{22,11} - \eta & 0 \\
-\frac{1}{2}G & 0 & 0 & H_{22,22} - \eta
\end{vmatrix} = 0
$$

(10)

Here $H_{jk,k'}$ are defined as follows:

$$
H_{11,11} = E_{el} - \frac{1}{2}(G_{01} + G_{02} - G), \\
H_{11,22} = E_{el} - \frac{1}{2}(-G_{01} + G_{02} + G), \\
H_{22,11} = E_{el} - \frac{1}{2}(G_{01} - G_{02} + G), \\
H_{11,22} = E_{el} - \frac{1}{2}(-G_{01} - G_{02} - G)
$$

(11)

where

$$
G_{0i} = G_{i} - G_{i} \frac{G_{i}}{4E_{el}} \quad \text{and} \quad E_{el} = \frac{1}{2}(E_{1el} + E_{2el}).
$$

(12)

It is noted that in this treatment we obtained the $H$ matrix elements to first-order accuracy. In what follows we assume that $G_i \ll E_{el}$ and so that $G_i$’s will replace $G_{0i}$’s.

To obtain the eigenfunctions we must first obtain the eigenvalues which, in this case, can be derived readily because the determinant of $4 \times 4$ breaks up into a product of two determinants of $2 \times 2$. The four corresponding eigenvalues are

$$
\eta_1^\pm = E_{el} \pm \frac{1}{2}[ (G_1 + G_2)^2 + G^2 ]^{1/2} + \frac{1}{2}G \\
\eta_2^\pm = E_{el} \pm \frac{1}{2}[ (G_1 - G_2)^2 + G^2 ]^{1/2} - \frac{1}{2}G
$$

(13)

In what follows we consider two extreme situations.

(1) In this situation $G \gg G_i, i = 1,2$. Usually this is encountered when the interatomic displacements are small. In other words since $G_i = k_i q_i, i = 1,2$, it is noted that $G_i$ is small whenever $q_i$ approaches zero. In contrast to the values of the $G_i$’s the value of $G$ is determined essentially by the distance between the two molecules and hardly by their $q_i$ values. Therefore, as long as this distance is not too large we assume that $G$ will fulfill the above condition. As a result we obtain the following eigenvalues,

$$
\eta_1^+ = E_{el} + \frac{1}{2}(G_1 + G_2 + G), \\
\eta_1^- = E_{el}, \\
\eta_2^+ = E_{el} + \frac{1}{2}(G_1 - G_2 + G), \\
\eta_2^- = E_{el} + \frac{1}{2}(G_1 + G_2 - G)
$$

(14)

and the corresponding eigenvectors,

$$
\Psi_1^+ = \frac{1}{2}(\psi_{11}^0 \psi_{22} + \psi_{12} \psi_{21}), \\
\Psi_1^- = \frac{1}{2}(\psi_{11} \psi_{21} + \psi_{12} \psi_{22}).
$$

(15)

From equation (1) it is seen that ignoring the coupling $H_{12}$ all four surfaces become degenerate when both $q_1$ and $q_2$ are equal to zero. Incorporating the coupling removes part of the degeneracy leaving only two surfaces degenerate.

At this stage it is important to emphasize that assuming $G$ to be large enough to fulfill the condition $G \gg G_i, i = 1,2$ does not necessarily imply that the two molecules have to be in close proximity. For instance in the vicinity of each of the molecules’ equilibrium distance, i.e., $q_i \sim 0; i = 1,2$, the corresponding $G_i = k_i q_i, i = 1,2$ are relatively small and $G$ does not have to be particularly large to fulfill the above requirement. In this study, purposely, we excluded the close proximity region (where $G$ is expected always to fulfill the above-mentioned condition) because within it the molecules and their attached electrons lose their identity. It is obvious that our treatment is meaningful as long as the two interacting molecules more or less keep their identity.

(2) This is the situation when $G_i \gg G_i, i = 1,2$ (in what follows we assume that $G_2 > G_1$). This case was treated by us before [13] but is considered here again to show that our present more general formulation yields the same results. Usually this is encountered when the atomic displacements ($q_1$ and $q_2$) are not small and the distance between the two molecules is large. Again since $G_i = k_i q_i, i = 1,2$, the value of $G_i$ increases when $q_i$ increases. As for $G$, since it is determined primarily by the distance between the two molecules (and only vaguely by the $q_i$ values) it is expected to decrease as this distance increases. Therefore, as long as this distance is large enough the above condition is fulfilled. As a result we obtain the eigenvalues

$$
\eta_1^+ = E_{el} + \frac{1}{2}(G_1 + G_2 + G), \\
\eta_1^- = E_{el}, \\
\eta_2^+ = E_{el} + \frac{1}{2}(G_1 - G_2 + G), \\
\eta_2^- = E_{el} + \frac{1}{2}(G_1 + G_2 - G).
$$

(16)
and the corresponding eigenvectors
\[
\begin{align*}
\Psi_1^+ &= \psi_{12} \psi_{22}, \\
\Psi_1^- &= \psi_{11} \psi_{21}, \\
\Psi_2^+ &= \psi_{12} \psi_{21}, \\
\Psi_2^- &= \psi_{11} \psi_{22}.
\end{align*}
\] (17)

From equation (16) it is seen that the coupling removes the degeneracy of the system. The reason is that a degeneracy is formed only when \( G_1 < G_2 \) is equal to zero, but in this case the degeneracy is removed by the perturbation even though it is small.

This completes the derivation of the eigenvalues and the eigenfunctions for the two limiting cases. In the next section we shall use these eigenfunctions to calculate the ADT matrix.

4. The derivation of the non-adiabatic coupling terms and the adiabatic–diabatic transformation matrices

Next we derive the ADT matrix [12]. It turns out that the only way to guarantee that a nuclear wavefunction possesses the correct geometrical features is to employ the ADT matrix [12](if it exists) which transforms a set of single-valued functions to a set of functions with the required geometry. In other words, the ADT matrix contains the geometrical properties of the system enforced by the electronic eigenfunctions. This fact was demonstrated in a series of studies, all of which (except for a recent preliminary study on the same system [13]) were performed for a 2-dimensional Hilbert space [7–9]. The present study will be applied to the more extended 4-dimensional Hilbert space.

To derive the ADT matrix we must first obtain the non-adiabatic coupling matrices \( \tau \). Having the eigenfunctions we derive the non-adiabatic coupling matrices \( \tau_{\varphi_1} \) and \( \tau_{\varphi_2} \). These are \( 4 \times 4 \) anti-symmetrical matrices with elements [12a]

\[
(\tau_{\varphi_i})_{mn} = q_i^{-1} \left\langle \Psi_m \left| \frac{\partial}{\partial \varphi_i} \Psi_n \right. \right\rangle, \quad i = 1, 2, \quad (18)
\]

where the \( \Psi_m, m = 1, \ldots, 4 \), designate the \( \Psi \)‘s defined in equations (15) and (17). As in the previous section, we distinguish between the two situations (in each of these we obtain different ADT matrices), the first of which is when the two molecules interact strongly and the other is when they do so weakly. Employing equation (15) we obtain the \( \tau_{\varphi_1} \) and \( \tau_{\varphi_2} \) for the first case, namely,

\[
\begin{align*}
\tau_{\varphi_1} &= \frac{1}{2q_1} \left( \begin{array}{cccc} 0 & 0 & 1 & 0 \\
-1 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 \\
-1 & 0 & 0 & 0 \\
\end{array} \right), \\
\tau_{\varphi_2} &= \frac{1}{2q_2} \left( \begin{array}{cccc} 0 & 0 & -1 & 0 \\
-1 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 \\
-1 & 0 & 0 & 0 \\
\end{array} \right).
\end{align*}
\] (19)

and employing equation (17) we obtain them for the second case,

\[
\begin{align*}
\tau_{\varphi_1} &= \frac{1}{2q_1} \left( \begin{array}{cccc} 0 & 0 & 1 & 0 \\
1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 \\
1 & 0 & 0 & 0 \\
\end{array} \right), \\
\tau_{\varphi_2} &= \frac{1}{2q_2} \left( \begin{array}{cccc} 0 & 0 & 1 & 0 \\
-1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
-1 & 0 & 0 & 0 \\
\end{array} \right).
\end{align*}
\] (20)

Next the \( 4 \times 4 \) ADT matrices will be obtained. If \( A \) is such a matrix it follows from the solution of the vector equation [12a]

\[
\nabla A + \tau A = 0
\]

where \( \nabla \) is the gradient operator and \( \tau \) is a vector of matrices where each component refers to one coordinate. In our present case we encounter four coordinates \( \varphi_1, \varphi_2, q_1 \) and \( q_2 \) but in [9] we showed that within a first-order approximation the radial non-adiabatic coupling terms are zero. Therefore \( \tau \) and also \( \nabla \) are two-component vectors: one component with respect to \( \varphi_1 \), and the other with respect to \( \varphi_2 \):

\[
\begin{align*}
&\frac{1}{q_1} \frac{\partial}{\partial \varphi_1} A + \tau_{\varphi_1} A = 0, \quad (22a) \\
&\frac{1}{q_2} \frac{\partial}{\partial \varphi_2} A + \tau_{\varphi_2} A = 0. \quad (22b)
\end{align*}
\]

The necessary condition for equation (22) to have a unique solution is that [12]

\[
\text{curl } \tau = [\tau \times \tau]
\]

Again as was shown in [13] this condition is fulfilled by the present \( \tau \) matrices and so the uniqueness is guaranteed.
To solve equation (22) we use the fact that $\sigma$ is a constant vector matrix. Because of that the solution can be presented as a product of two matrices, one dependent on $\varphi_1$ and the other on $\varphi_2$:

$$A = A_1(\varphi_1)A_2(\varphi_2).$$  \hspace{1cm} (24)

Since $A$ has to be orthogonal, $A_1$ and $A_2$ must be orthogonal as well. The matrices $A$ will be solved subject to the boundary condition that $A(\varphi_1 = 0, \varphi_2 = 0) = I$. The way we shall solve equation (22) is to substitute equation (24) in (22a) and multiply it, from the right hand side by $(A)^{-1}$, so that we obtain an equation for $A_1$ only:

$$\frac{1}{q_1} \frac{d}{d\varphi_1} A_1 + \tau_{\varphi_1} A_1 = 0.$$  \hspace{1cm} (22a')

A solution will be found for the boundary condition $A_1(\varphi_1 = 0) = I$. The appendix shows how a general solution for such an equation can be derived. Once $A_1(\varphi_1)$ is obtained we consider equation (22b) where, again, equation (24) is employed to replace $A$. To obtain an equation for $A_2$ the matrix $A_1$ has to commute with $\tau_{\varphi_2}$ which indeed it does. Thus, multiplying the newly formed equation (22b) by $(A_1)^{-1}$ from the left hand side finally yields the equation for $A_2$:

$$\frac{1}{q_2} \frac{d}{d\varphi_2} A_2 + \tau_{\varphi_2} A_2 = 0.$$  \hspace{1cm} (22b')

Equation (22b') is solved in the same way as (22a'). As a result of these treatments we obtain the following solutions.

For the strong coupling case the matrices $\tau$ in equation (19) are used and we obtain the following $A_i$, $i = 1, 2$:

$$A_1(\varphi_1) = \begin{pmatrix} \cos \alpha_1 & 0 & 0 & \sin \alpha_1 \\ 0 & \cos \alpha_1 & -\sin \alpha_1 & 0 \\ 0 & \sin \alpha_1 & \cos \alpha_1 & 0 \\ -\sin \alpha_1 & 0 & 0 & \cos \alpha_1 \end{pmatrix},$$

where $\alpha_1$ is equal $$(\varphi_1/2),$$

and

$$A_2(\varphi_2) = \begin{pmatrix} \cos \alpha_2 & 0 & 0 & \sin \alpha_2 \\ 0 & \cos \alpha_2 & \sin \alpha_2 & 0 \\ 0 & -\sin \alpha_2 & \cos \alpha_2 & 0 \\ -\sin \alpha_2 & 0 & 0 & \cos \alpha_2 \end{pmatrix},$$

where $\alpha_2$ is equal $$(\varphi_2/2).$$

For the weakly coupled case we use the matrices $\tau$ in equation (20) and we obtain for $A_i$, $i = 1, 2$:

$$A_1(\varphi_1) = \begin{pmatrix} \cos \alpha_1 & 0 & 0 & -\sin \alpha_1 \\ 0 & \cos \alpha_1 & 0 & -\sin \alpha_1 \\ 0 & \sin \alpha_1 & \cos \alpha_1 & 0 \\ 0 & 0 & \sin \alpha_1 & \cos \alpha_1 \end{pmatrix},$$

where $\alpha_1$ is equal to $$(\varphi_1/2),$$

and

$$A_2(\varphi_2) = \begin{pmatrix} \cos \alpha_2 & -\sin \alpha_2 & 0 & 0 \\ \sin \alpha_2 & \cos \alpha_2 & 0 & 0 \\ 0 & 0 & \sin \alpha_2 & \cos \alpha_2 \\ 0 & 0 & -\sin \alpha_2 & \cos \alpha_2 \end{pmatrix},$$

where $\alpha_2$ is equal to $$(\varphi_2/2).$$

From equations (25)–(28) it is seen that all four $A_i$ matrices fulfill the required boundary condition $A_i(\varphi_1 = 0) = I$. Since $A$ is equal to the product $A_1A_2$ (see equation (24)), $A$ changes sign whenever either $A_1$ or $A_2$ does, which happens when either $\varphi_1$ or $\varphi_2$, respectively, completes a full cycle $(\varphi_i \rightarrow \varphi_i + 2\pi)$. It is interesting to note that when both complete a cycle no change of sign follows.

5. Discussion and conclusion

In this work we concentrated on deriving the ADT matrix for a model system which consists of two interacting polyatomic molecules both of which have conical intersections. The main purpose of this study is to establish the way the interaction between the two molecules affects characteristic features of the two isolated molecules. To this end we considered two situations, one in which the interaction between the two molecules $G$ is weak, so that at least one of the $G_j$’s fulfills the condition $|G_j| \gg |G|$, and the other when the interaction is relatively strong, so that $G \gg G_j$, $j = 1, 2$. In both cases we assume the two interacting molecules to be far enough from each other so that their identity is not lost. In [13] we considered only the weak interaction situation. The results of that study were validated in the present study, which is, in two respects, more general. (i) In the previous study we employed zero-order electronic eigenfunctions and here we use first-order eigenfunctions. (ii) The basis set used to solve equation (4) was taken to be a single term of the type $\psi_1\psi_2\chi$, whereas here we assumed it to be a linear combination of all the four products as presented in equation (6). The novel part in the present work is the study of the stronger interaction case. The study concentrates on deriving the ADT matrix which is significant in two respects: (a) it yields the required topological features (symmetry and multi-valuedness) of the nuclear wave-
functions; and (b) it is required for further studies of the nuclear (or atomic) dynamics.

We refer first to the weak interaction situation. In this case we found that adding the coupling forms one single $4 \times 4$ ADT matrix $A$ out of the two ADT matrices (each characterized by a single ADT angle). We found that $A$ changes sign whenever one of the electronic basis functions changes sign (this happens when either $\varphi_1$ or $\varphi_2$ completes a cycle). This implies that the nuclear wavefunctions, like the electronic ones, have to be multi-valued. In the single molecular electron case we showed that change of sign of the ADT matrix, and therefore also the multivaluedness of the nuclear wavefunction, are closely connected with the fact that the electronic eigenvalues (namely, the nuclear potential energy surfaces) have a degeneracy [9]. From the present study it follows that this feature is doubled in case a second molecular electron is added to the system. However, we found also that coupling the two systems partly removes the degeneracy, reducing the two infinite seams formed in such a situation to a surface of degeneracy in the extended configuration space (see equation (16)). Moreover, we showed that although the coupling removes the degeneracy almost entirely, it hardly affects the multi-valuedness of the nuclear wavefunctions. This is because the $4 \times 4$ ADT matrix changes sign whenever one of the angles completes a cycle. A more extensive analysis is given in [13].

A new situation is encountered for the strong interaction case. To see this, we shall first form, employing equations (25) and (26), the relevant ADT matrix $A$.

$$A(\varphi_1, \varphi_2) = \begin{pmatrix} \cos \alpha & 0 & 0 & \sin \alpha \\ 0 & \cos \beta & -\sin \beta & 0 \\ 0 & \sin \beta & \cos \beta & 0 \\ -\sin \alpha & 0 & 0 & \cos \alpha \end{pmatrix},$$

where

$$\alpha = \alpha_1 + \alpha_2 = \frac{1}{2}(\varphi_1 + \varphi_2)$$

and

$$\beta = \alpha_1 - \alpha_2 = \frac{1}{2}(\varphi_1 - \varphi_2).$$

The following should be noted.

(a) The ADT matrix, which is of dimension $4 \times 4$, usually transforms a $4 \times 4$ adiabatic set of equations to a $4 \times 4$ diabatic set of equations. However, in this case it transforms the $4 \times 4$ adiabatic set of equations to two uncoupled $2 \times 2$ diabatic sets of equations: one set of coupled equations is related to the second and the third states in equation (14), which are seen to be degenerate, and the other set of equations is related to the first and the fourth states, in equation (14), which possess no degeneracy.

(b) Whereas the original two uncoupled systems are characterized by their respective ADT angles, namely $(\varphi_1/2)$ and $(\varphi_2/2)$, the newly, strongly coupled system is characterized by the two angles $\alpha$ and $\beta$ (see equation (30)) which have the range $(0, 2\pi)$. This implies that the newly formed nuclear functions will be, in each case, single-valued. This result may be unexpected but a deeper look reveals that indeed this is the correct result. We recall that the strong interaction case is formed when both $q_1$ and $q_2 \approx 0$. Due to the (relative) strong coupling at the extended origin $(q_1, q_2) = (0, 0)$ two different situations are encountered when a path surrounds this origin: a double degeneracy situation and a no-degeneracy situation. In both cases, of course the corresponding ADT angles will be defined in the range of $(0, 2\pi)$ and therefore the respective Berry phases are either zero or $2\pi$.

M.B. would like to thank Dr R. Baer for valuable discussions regarding the various aspects of this study.

**Appendix**

*Derivation of the matrix $A$ from equation (22*)

We shall consider the following equation which, although somewhat different from the one in the text, bears a straightforward relationship to it:

$$\frac{d}{d\varphi} A + A \tau \ = \ 0, \quad (A1)$$

where $\tau$ is an anti-symmetric matrix of dimension $N \times N$ with the property that each row contains one single nonzero element (being $1$ or $-1$).

Differentiating equation (A1) with respect to $\varphi$ we obtain

$$\frac{d^2 A}{d\varphi^2} + \tau \frac{dA}{d\varphi} = 0. \quad (A2)$$

Replacing $(dA/d\varphi)$ by equation (A1) and recalling the fact that $\tau^2 = -I$ where $I$ is the unity matrix, we obtain for equation (A2) the result

$$\frac{d^2 A}{d\varphi^2} + A = 0. \quad (A3)$$

Equation (A3) implies that each element in $A$ can be written as a linear combination of $\cos \varphi$ and $\sin \varphi$:

$$A_{ij} = a_{ij} \cos \varphi + b_{ij} \sin \varphi. \quad (A4)$$

The coefficient matrices $a$ and $b$ are determined by initial conditions and by the fact that $A$ must fulfil equation (A1). Since $A$, for $\varphi = 0$, is required to be the unity matrix, this implies that $a_{ij} = \delta_{ij}$ where $\delta_{ij}$ is the
Kronecker $\delta$-function. Next we return to equation (A 1) and consider the $k$th row. Let us assume that the $m$th element of $\tau$ in this row, $\tau_{km} = \pm 1$ (then the rest are zero). The multiplication of the $k$th row of $\tau$ and the matrix $A$ will produce the $m$th row of $A$ and therefore from equation (A 1),

$$\frac{dA_k}{d\varphi} + A_m = 0,$$  \hspace{1cm} (A 5)

where $A_k$ and $A_m$ are the $k$th and the $m$th rows of $A$. Considering now each element in equation (A 5) we obtain

$$b_{kj} \cos \varphi - \delta_{kj} \sin \varphi = \pm (b_{mj} \sin \varphi + \delta_{mj} \cos \varphi)$$  \hspace{1cm} (j = 1, \ldots, N).  \hspace{1cm} (A 6)

Since these equalities must hold for every $\varphi$, we find the following relations ($k \neq m$):

$$b_{km} = -b_{mk} = \pm 1; \quad b_{kj} = 0 \quad j \neq m;$$

$$b_{jm} = 0 \quad j \neq k.$$  \hspace{1cm} (A 7)

Thus, the matrix $A$ has elements different from zero at the diagonal (where they are equal to $\cos \varphi$) and at those locations where the matrix $\tau$ has the elements $\pm 1$ (at these locations the values of the $A$ elements are equal to $\pm \sin \varphi$).

This completes the derivation.

References