PHYSICAL REVIEW A, VOLUME 62, 032506

Extended approximated Born-Oppenheimer equation. I. Theory

Michael Baer,[1,2,*] Sheng H. Lin,[1] Alexander Alijah,[3] Satrajit Adhikari,[4] and Gert D. Billing[4]
[1]*Institute of Atomic and Molecular Science, 10764 Taipei, Taiwan Republic of China*
[2]*Department of Physics and Applied Mathematics, Soreq NRC, Yavne 81800, Israel*
[3]*Fakultät für Chemie, Universität Bielefeld, 33501 Bielefeld, Germany*
[4]*Department of Chemistry, H.C. Ørsted Institute, University of Copenhagen, DK-2100 Ø Copenhagen, Denmark*

(Received 10 December 1999; revised manuscript received 2 May 2000; published 15 August 2000)

In this study we consider Born-Oppenheimer coupled equations with the aim of deriving a single approximated Born-Oppenheimer-type equation which contains the effect of the nonadiabatic coupling terms. The derivation is done for a situation where N ($\geqslant 2$) adiabatic surfaces, including the ground-state surface, have a degeneracy along a single line (e.g., conical intersection). The new equation can be considered as an extended version of the Born-Oppenheimer approximation. Although derived for a nongeneral case, the extension to a general case is also discussed. As special cases we treat, in the present paper, the two-state system and, in the following paper, the three-state system.

PACS number(s): 31.30.−i, 31.15.−p, 03.65.−w

I. INTRODUCTION

One of the more interesting observations in molecular dynamics was made by Herzberg and Longuet-Higgins (HLH) [1] when they studied the Jahn-Teller conical intersection (CI) model. These authors found that assuming the existence of CI the corresponding electronic eigenfunctions have to be double-valued. HLH corrected for this deficiency in an *ad hoc* way. Irrespective of whether this correction is justified, the importance of the HLH observation is in pointing out that something *may* go wrong if the whole system of electrons and nuclei is not treated with care. This is particularly essential if, once the electronic eigenvalue problem is resolved, the resulting *nuclear* Schrödinger equation (SE) is solved, employing the Born-Oppenheimer (BO) approximation [2].

The starting point of the theory of molecular dynamics is usually the BO treatment, which is based on the fact that within molecular systems fast-moving electrons can be distinguished from slow-moving nuclei. This distinction also applies to the BO approximation, which is based on the assumption that nonadiabatic coupling terms are negligibly small, and that therefore the upper electronic surfaces do not affect the nuclear wave function on the lower surface. The relevance of this assumption is not considered to be dependent on the energy of the system. However, the ordinary BO approximation was also employed for cases where these coupling terms are not necessarily small, assuming that the energy can be made as low as required. The justification for applying the approximation in such a case is that for a low enough energy the upper adiabatic surfaces are classically forbidden, implying that the components of the total wave function related to these states are negligibly small. As a result the terms that contain the product of these components with the nonadiabatic coupling terms are also small, and will have a minor effect on the dynamical process. This assumption, which underlies many of the single-state dynamical calculations performed during the last three decades, becomes questionable when some of the nonadiabatic coupling terms are *infinitely* large. The reason for this is that, although the components of the total wave function may be negligibly small, their product with the large nonadiabatic coupling terms will result in non-negligible values, sometimes in even indefinitely large values. In that case this aspect of the BO approximation will break down for any energy no matter how low.

As is well known (and as follows from their definition), nonadiabatic coupling terms appear in the off-diagonal positions in the SE [3]. In order to form a single approximated BO equation that contains nonadiabatic coupling terms, these terms must first be shifted from their original off-diagonal positions to the diagonal. In a first publication on this subject Baer and Englman [4] showed that such a possibility may exist, and derived, for the two-state case, an approximated version of the BO equation which indeed contains the nonadiabatic coupling term. Subsequently one of the present authors [5] derived, from first principles and rigorously (i.e. without approximations), a new set of coupled BO-SE's for the two-dimensional Hilbert space, in which all nonadiabatic coupling terms were shifted from the off-diagonal to the diagonal position. The *two* equations, which now, among other functions, also contain the lower adiabatic potential energy surface in their diagonal, remain coupled, but the coupling term becomes a potential coupling. It was shown that this coupling term is multiplied by the original *adiabatic* nuclear wave function associated with the *upper* electronic state. Assuming again that, for a low enough energy, this wave function is small, the BO approximation can be imposed on this new set of equations by deleting this product. This procedure yields two (decoupled) BO equations, one of which is identical to the above-mentioned Baer-Englman (BE) equation.

The BE equation was later used first by Baer, Charutz, Kosloff, and Baer (BCKB) [6] and subsequently by Adhikari and Billing (AB) [7] to calculate *reactive* transition probabilities for a two-arrangement-channel model. It was found that whereas the total reactive probabilities obtained using the two types of the single BO equations (namely, the ordinary BO equation and the BE equation) were the same, the

---

[*] Guest professor at the Institute of Atomic and Molecular Science, Taipei, Taiwan.

state-to-state transition probabilities were significantly different. Repeating the calculations employing the two coupled diabatic equations (which can rigorously be derived from the two coupled adiabatic BO equations [3,8–11]) showed, without ambiguity, that the BE equation, in contrast to the ordinary BO equation, was the one to yield correct results. It could be of importance to point out that the calculations were done in two different frameworks: the BCKB calculations were done within the time-independent framework, and the AB ones within the time-dependent framework; still the findings were the same. AB also showed that their results are identical to those obtained by employing a third approach, due to Kuppermann and co-workers [12,13].

As mentioned earlier, the rigorously derived new set of BO equations leads to *two* approximate uncoupled BO equations, one of which is identified as the BE equation. It turns out that the two equations are needed in order to show that the decoupling yields outcomes that are consistent with the original assumptions. In this paper the decoupling process will be extended to an N-state case where $N \geqslant 2$. However it has to be emphasized that this extension will be done for a model and not for the general case. The main idea, at this stage, is to show that such an extension is viable, and that it is consistent with original imposed assumptions. In other words, the purpose is to form an ‘‘existence theorem’’ for the extended BO approximation to be applied for an N-state system. A tristate model will then be treated, in the following paper, to show that, indeed, the new extended BO approximation is capable of yielding the correct results as obtained by solving the full system of three BO coupled equations.

II. EXTENDED BORN-OPPENHEIMER APPROXIMATION

Our starting point is the BO system of coupled equations written in the form [3]

$$-\frac{1}{2m}\nabla^2\psi_j+(u_j(n)-E)\psi_j-\frac{1}{2m}\sum_{i=1}^{N}(2\tau_{ji}^{(1)}\cdot\nabla\psi_i+\tau_{ji}^{(2)}\psi_i)=0, \qquad (1)$$

where the $\psi_j(n)$ and $u_j(n)$, $n=j,\ldots,N$ are the nuclear wave functions and the (adiabatic) potential-energy surfaces, respectively, ∇ is the gradient (vector) operator, m is the mass of the system, $\tau^{(1)}$ is the nonadiabatic (vector) matrix of the first kind, and $\tau^{(2)}$ is non-adiabatic (scalar) matrix of the second kind, both defined as

$$\tau_{ji}^{(1)}=\langle\zeta_j|\nabla\zeta_i\rangle \quad \text{and} \quad \tau_{ji}^{(2)}=\langle\zeta_j|\nabla^2\zeta_i\rangle. \qquad (2)$$

Here $\zeta_j(e|n)$, $j=1,\ldots,N$ are the electronic eigenfunctions. Recalling that for a given Hilbert space the relation between $\tau^{(1)}$ and $\tau^{(2)}$ is

$$\tau^{(2)}=(\tau^{(1)})^2+\nabla\tau^{(1)}, \qquad (3)$$

Eq. (1) becomes (in a matrix notation):

$$-\frac{1}{2m}\nabla^2\Psi+\left(u-\frac{1}{2m}\tau^2-E\right)\Psi-\frac{1}{2m}(2\tau\cdot\nabla+\nabla\tau)\Psi=0. \qquad (4)$$

Here Ψ is a column matrix which contains the nuclear (ψ_j) wave functions, u is a diagonal matrix which contains the adiabatic potentials, the dot designates scalar product, and τ replaces $\tau^{(1)}$ (to simplify the notation).

As stated in Sec. I, we intend to derive an extended BO approximate equation for a Hilbert space of arbitrary dimensions, for a situation where all surfaces, including the ground-state surface, have a degeneracy along a single line (e.g., [9] conical intersection). A derivation of this kind, for an arbitrary τ matrix, can be done only in the two-state case. In order to derive such an equation for an $N(>2)$-dimensional case we have to limit somewhat the arbitrary form of the τ-matrix elements. In this sense the present derivation is not general. However, some of these limitations are not as severe as they may look, and it is hoped that with additional assumptions this procedure will be applicable also for a more general case.

The τ-matrix is an antisymmetric *vector* matrix with the components τ_p, $p=x,y,z\ldots$. In what follows each τ_p is assumed to be a product of a scalar *function* t_p and a *constant* antisymmetric matrix g (which does not depend on p). Thus

$$\tau_p=t_p g, \qquad (5)$$

or, recalling Eq. (2),

$$\tau_{pjk}=t_p g_{jk}=\langle\zeta_j|\nabla_p\zeta_k\rangle. \qquad (6)$$

If G is the unitary transformation matrix that diagonalizes g, and $i\omega$ is the resulting (imaginary) diagonal matrix with $i\omega_j$; $j=1,\ldots,N$ as the corresponding eigenvalues, it can be shown that, following the unitary transformation performed by G, Eq. (4) becomes

$$-\frac{1}{2m}(\nabla+it\omega)^2\chi+(w-E)\chi=0, \qquad (7)$$

where χ is related to Ψ through the transformation

$$\Psi=G\chi, \qquad (8a)$$

and the nondiagonal diabatic potential matrix W is related to the adiabatic potential matrix u as

$$w=G^*uG. \qquad (8b)$$

Here G^* is the complex conjugate of G. Considering Eq. (7), it is seen that the first term in front of the (column) vector χ is a diagonal matrix, because t is a vector of functions (not of matrices), and ω is a diagonal matrix. However, due to the transformation a new nondiagonal potential matrix is formed which couples the various differential equations. It is important to emphasize that so far the derivation has been rigorous, and no approximations have been imposed. Thus the solution of Eq. (7) will be the same as the solution of Eq. (4). Having arrived at Eq. (7), we are now in a position to impose the BO approximation. As stated earlier, since for low enough energies all upper adiabatic states are energetically closed, each of the corresponding adiabatic functions ψ_j, $j=2,\ldots,N$ is expected to fulfill the condition

$$|\psi_1| \gg |\psi_j|, \quad j=2,\ldots,N \tag{9}$$

at those regions of configuration space (CS) where the lower surface is energetically allowed. This assumption has to be employed with great care, because so far it was proven, numerically, to hold for a two-state system $(N=2)$ only. Although some risk is involved by extending it to an arbitrary number of states, we shall make this assumption. In the following paper we show that this assumption is nicely fulfilled for a three-state case.

Our next step is to analyze the product $W\chi$ for the jth equation of Eq. (7). Recalling Eqs. (8a) and (8b), we have:

$$\begin{aligned}(w\chi)_j &= \{(G^*uG)(G^*\Psi)\}_j = (G^*u\Psi)_j = \sum_{k=1}^{N} G^*_{jk}u_k\psi_k\\ &= u_1\chi_j - u_1\sum_{k=1}^{N} G^*_{jk}\psi_k + \sum_{k=1}^{N} G^*_{jk}u_k\psi_k\end{aligned}$$

or (10)

$$(w\chi)_j \doteq u_1\chi_j + \sum_{k=2}^{N} G^*_{jk}(u_j-u_1)\psi_k, \quad j=1,\ldots,N.$$

It should be noted from Eq. (10) that, for each j $(=1,\ldots,N)$ this equation contains the product of the function χ_j and the lowest *adiabatic* potential surface u_1 and a summation of products of the negligibly small ψ_k's (namely, only those for $k\geq 2$) with potential terms. Substituting Eq. (10) into Eq. (7) and deleting, in each of the equations, these summations, yields the following system of equations:

$$-\frac{1}{2m}(\boldsymbol{\nabla}+it\omega_j)^2\chi_j+(u_1-E)\chi_j=0, \quad j=1,\ldots,N. \tag{11}$$

It should be noted that this system of N equations for the N χ functions is decoupled, and therefore each equation stands on its own and can be solved independently of all other equations. However, it is also to be noted that all these equations are solved for the same (adiabatic) potential-energy surface u_1 but for different ω_j's.

Once the χ functions are derived the final adiabatic vector Ψ_f is obtained from Eq. (8a) when applied to χ_f. In particular the final nuclear wave function ψ_{1f} follows from the explicit expression:

$$\psi_{1f}=\sum_{k=1}^{N} G_{1k}\chi_{kf}. \tag{12}$$

A potential difficulty associated with this approach is due to the fact that the calculated χ functions also yield, through the transformation in Eq. (8a), all other ψ_f functions, namely, ψ_{jf}, $j>1$. These functions, by definition, have to be identically zero at all asymptotes, because they belong to the upper adiabatic states which are classically forbidden at all these regions. At this stage nothing in the theory guarantees that the calculated χ functions will fulfill this demand.

There is, however, at least one case for which the calculated χ functions will produce ψ_{jf}'s, $j>1$, which are all identically zero, and that is the case when Eqs. (11) are gauge invariant [13–15] (we shall elaborate on the gauge invariance property in Sec. III). At this stage let us assume that the functions $(t\omega_j)$; $j=1,\ldots,N$ are such that these equations are gauge invariant, so that various χ's, if calculated for the same boundary conditions, are all identical. Thus our next step will be to determine the boundary conditions for the χ functions in order to solve Eq. (11). To find those we need to impose boundary conditions on the ψ functions. We assume that at the given (initial) asymptote all ψ's are zero except for the ground-state function ψ_{1in}. Thus

$$\psi_1=\psi_{1in}, \quad \psi_j=\psi_{jin}=0, \quad j=2,\ldots,N. \tag{13a}$$

Due to Eq. (8a), the boundary conditions for the χ functions are given in the form

$$\chi_{jin}=G^*_{1j}\psi_{1in}, \quad j=1,\ldots,N. \tag{13b}$$

It is seen that the boundary conditions for the χ functions are all identical, up to a constant $[=(G_{1j})^*]$, and therefore the same applies to the χ functions at every point in CS. Thus if at a given asymptotic region we define χ_f as the χ function calculated for a χ_{in} which is identical to ψ_{in} (not proportional to it), then it can be shown [see Eq. (12)] that the ψ functions at this particular asymptote, namely ψ_{jf}, $j=1,\ldots,N$ become

$$\psi_{1f}=\chi_f, \quad \psi_{jf}=0, \quad j=2,\ldots,N. \tag{12$'$}$$

Thus, for the particular case of a gauge invariant set of uncoupled equations, we indeed obtain a solution which is compatible with the assumptions.

We now summarize what has been achieved so far. It was found that in order to construct a BO approximation for an N-state BO system that takes into account the nonadiabatic coupling terms, we have to solve N uncoupled differential equations all related to the electronic *ground* (or lowest) state but with different eigenvalues of the nonadiabatic matrix as presented in Eq. (11). In order for these equations to yield a meaningful physical solution, the eigenvalues of the *g* matrix cannot be arbitrary functions but have to fulfill certain requirements. It was shown that if, for instance, these eigenvalues produce gauge invariant equations the solution will be compatible with the assumption concerning the BO approximation. In Sec. III we shall show that the necessary condition for an arbitrary nonadiabatic τ matrix to be relevant is that its eigenvalues have to be such that Eqs. (11) are gauge invariant.

III. ''QUANTIZATION'' OF THE EIGENVALUES OF THE NONADIABATIC COUPLING MATRIX ALONG A CLOSED PATH

In a previous publication [16] it was proved that the eigenvalues of the nonadiabatic matrices have to be *quantized* (similar to the Bohr-Sommerfeld quantization of the angular momentum) in order to yield a continuous, uniquely defined, *diabatic* potential matrix $W(s)$. As a result we assume that the extended BO approximation, as presented in Sec. II, will be applied only to those cases that fulfill these quantization rules. Next we briefly summarize the main points of the derivation for the quantization, and present the final outcome. This will be done in two steps: first we derive the features required from the adiabatic-diabatic transformation (ADT) matrix [8–10] to yield continuous diabatic potentials, and then, in the second step, we refer to the nonadiabatic coupling matrix (the ADT matrix is obtained once the nonadiabatic matrix is given).

We start by assuming the existence of an ADT matrix $A(s,s_0)$, which transforms a given *adiabatic* potential matrix $u(s)$ to a diabatic potential matrix $W(s,s_0)$ [3,8–10]:

$$W(s,s_0)=A^*(s,s_0)u(s)A(s,s_0). \tag{14}$$

Here $A^*(s,s_0)$ is the complex conjugate matrix of $A(s,s_0)$, s_0 is a given initial point in CS, and s is some other point. Next it is assumed that $W(s,s_0)$ is uniquely defined throughout CS, and our aim is to derive the features to be fulfilled by $A(s,s_0)$ in order to ensure the uniqueness of $W(s,s_0)$. In this respect it is important to mention that $u(s)$ is uniquely defined throughout CS.

To reveal the features of $A(s,s_0)$, we introduce a closed path Γ defined in terms of a continuous parameter λ, so that the starting point s_0 of the path is at $\lambda=0$. Next we define β as the value attained by λ, once the path completes a full cycle, and reaches its starting point. Thus, for instance, in the case of a circle $\beta=2\pi$.

Having introduced these definitions, we can now express our assumption regarding the uniqueness of $W(s,s_0)$ in the following way: at *each point* s_0 in CS the diabatic potential matrix $W(\lambda)\,[\equiv W(s,s_0)]$ fulfills the relation

$$W(\lambda=0)=W(\lambda=\beta)\,. \tag{15}$$

Following Eq. (14) this requirement implies that for every point s_0 we have

$$A^*(0)u(0)A(0)=A^*(\beta)u(\beta)A(\beta). \tag{16}$$

To continue, we introduce another transformation matrix D, defined as

$$D=A(\beta)A^*(0), \tag{17}$$

which for every s_0 makes a connection between $u(\beta)$ and $u(0)$:

$$u(\beta)=Du(0)D^*. \tag{18}$$

The D matrix is, by definition, a unitary matrix (because it is a product of two unitary matrices), and, at this stage, except for being dependent on the path Γ (and, eventually, on the initial point s_0), is rather arbitrary. In what follows we shall derive the features of D.

Since the adiabatic eigenvalues are uniquely defined at each point in CS we have: $u(0)\equiv u(\beta)$, and therefore Eq. (18) can also be written as

$$u(0)=Du(0)D^*. \tag{18$'$}$$

Performing the multiplication, it can be shown that it yields the following system of relations between the adiabatic eigenvalues $u_j(0)$ and the D-matrix elements:

$$\sum_{j=1} (D^*_{kj}D_{kj}-\delta_{kj})u_j(0)=0, \quad k=1,\dots,N. \tag{19}$$

Equation (19) is reminiscent of a homogeneous set of algebraic equations, with the $u_j(0)$ as ''unknowns.'' It has to hold for every arbitrary point $s_0(\equiv\lambda=0)$ and for an, essential, arbitrary set of nonzero (adiabatic eigenvalues) $u_j(0)$; $j=1,\dots,N$. Due to the arbitrariness of the $u_j(0)$'s, Eqs. (19) can be satisfied if and only if the ''coefficients'' become identically zero, namely, the D matrix elements have to fulfill the conditions

$$(D_{jk})^*D_{jk}=\delta_{jk}, \quad j,k=1,\dots,N \tag{20}$$

or

$$D_{jk}=\delta_{jk}\exp(i\chi_k). \tag{21}$$

Thus D is a diagonal matrix which contains in its diagonal complex numbers whose norm is 1. In what follows the D matrix is termed as ''topological matrix.''

Recalling Eq. (17), we obtain that:

$$A(\beta)=DA(0). \tag{22}$$

It is noted that $A(\beta)$ does not have to be identical $A(0)$, that is, it does not have to be uniquely defined at every point in CS, in order to be able to produce physical meaningful diabatic potentials; however, upon tracing a closed path, it has to fulfill the conditions as specified in Eqs. (21) and (22).

Our next step will be to derive $A(\beta)$, and this we do by applying the first-order differential vector equations [8]

$$\nabla A+\tau A=0, \tag{23}$$

where τ, as mentioned earlier, is the nonadiabatic coupling matrix. In considering Eq. (23) we are facing two problems: (a) Does Eq. (23) have a solution? (b) Is the solution unique? The conditions for Eq. (23) to have a solution are discussed in Appendix A. Solutions exist for any complete Hilbert space or a sub-Hilbert space of dimension $M(<N)$, which is made up of eigenfunctions all satisfying the conditions

$$\tau_{ij}=\langle\zeta_i|\nabla\zeta_j\rangle=0 \quad \text{for} \quad i\leqslant M, \quad j>M. \tag{24}$$

Equation (23) does not necessarily yield a uniquely defined A matrix. These are guaranteed if and only if the τ-matrix elements are all regular functions defined at *every* point in CS. However we have seen that in order to obtain uniquely defined diabatic potentials it is *not necessary* for the A matrix to be uniquely defined throughout CS, and therefore we shall ignore this fact and just go ahead and derive A (for the above-defined sub-Hilbert space) by a direct integration of Eq. (23). Formally the solution of Eq. (23) can be written as an ordered integral [10]

$$A(s)=\exp\left(-\int_{s_0}^{s}\mathbf{ds}\cdot\tau\right)A(s_0), \tag{25}$$

where the integration is performed along a path Γ that combines s and s_0, $\mathbf{ds}$ is a differential (vector) length element along this path, and the dot stands for a scalar product (we recall that τ is a vector). More general cases are treated in Refs. [16], [17]. Here we just carry out the derivation for the τ-matrix elements defined in Eq. (5), so that the expression for the A-matrix can be obtained without any difficulty:

$$A(s)=G\exp\left(-i\omega\int_{s_0}^{s}\mathbf{ds}\cdot\mathbf{t}(s)\right)G^{*}A(s_0), \tag{25$'$}$$

where, as we recall, the (constant) matrix G is the unitary transformation matrix that diagonalizes g, and $i\omega$ is a diagonal matrix with $i\omega_j$, $j=1,\ldots,N$ being the eigenvalues of the g matrix. We also recall that $\mathbf{t}$ is the vector with the components t_p as defined in Eq. (5). Next we consider Eq. (17), where we introduced the D matrix, for which, following Eq. (25), we obtain an explicit expression:

$$D=\exp(\oint_{\Gamma}\mathbf{ds}\cdot\tau(s)) \tag{26}$$

or [10]

$$D=G\exp(-i\omega\oint_{\Gamma}\mathbf{ds}\cdot\mathbf{t}(s))G^{*}. \tag{26$'$}$$

Since the matrix D has to be a diagonal matrix with numbers of norm 1 [namely, $(+1)$'s and (-1)'s in the diagonal], this fact imposes strong limitations on the allowed values of the τ-matrix elements. In the special cases that will be discussed in this paper, these limitations lead to a kind of quantization of the eigenvalues $(\omega_j t)$ of the τ matrix, very much reminiscent of the Bohr-Sommerfeld quantization law of the angular momentum [16–18]. To see this more explicitly we consider the two simplest cases for the D matrix. For the case that D is the unit matrix [namely, only $(+1)$'s in the diagonal], we obtain that each of the eigenvalues of the τ matrix has to fulfill the quantization rule

$$\frac{1}{2\pi}\omega_j\oint_{\Gamma}\mathbf{ds}\cdot\mathbf{t}(s)=n_j,\quad j=1,\ldots,N, \tag{27}$$

where n_j is *an integer* (this, in fact, is the case of the ordinary BO equation). In the same way, if the D matrix is the unit matrix multiplied by (-1) [namely, only (-1)'s in the diagonal], the values of all n_j have to be *half of an odd integer*. In this and the following paper, we shall discuss to some extent the two- and three-state cases. The general M-state case, where the τ-matrix elements are functions of the coordinates, are discussed in Refs. [17] and [18].

We are now in a position to make a connection between the quantization of the eigenvalues of the τ matrix and the gauge invariant requirement of Eqs. (11) in order to yield an extended BO approximation. It is known that Eqs. (27), with n_j being either a series of integers or a series of half of odd integers, are in fact necessary conditions for Eqs. (11) to become gauge invariant. In other words the quantization requirement, which is a necessary condition for having *uniquely defined diabatic potentials*, also guarantees the existence of the extended BO equation. The fact that all the equations in Eq. (11) are gauge invariant means that they all yield, for the same set of initial conditions, identical solutions. Since this is the case it is, in fact, sufficient to consider only one of these equations. Thus, like the ordinary BO approximation, the inclusion of the effect of the nonadiabatic coupling terms leads to a single (extended) BO approximation.

In Sec. IV we explicitly discuss the two-state model. The following paper is devoted to the tristate case.

IV. STUDY OF THE TWO-STATE SYSTEM

In the two-state case the τ matrix has only one nonzero element, and therefore it can always be written as required in Eq. (5), where the g matrix is given in the form

$$g=\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}, \tag{28}$$

and the resulting eigenvalues are $\pm i\omega$, where $\omega=1$. For this g matrix we obtain the following unitary G matrix:

$$G=\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ i & -i\end{pmatrix}, \tag{29}$$

which, in turn, yields the following diabatic potential matrix W [see Eq. (8b)]:

$$w=\frac{1}{2}\begin{pmatrix}u_1+u_2 & u_1-u_2\\ -(u_1-u_2) & u_1+u_2\end{pmatrix}. \tag{30}$$

The corresponding two uncoupled (extended) BO equations are then

$$\left[-\frac{1}{2m}(\boldsymbol{\nabla}\pm it)^2+u_1-E\right]\chi=0, \tag{31}$$

and the topological matrix D is given in the form [see Eq. (26$'$)]

$$D=G\exp\left(\pm i\oint_{\Gamma}\mathbf{ds}\cdot\mathbf{t}(s)\right)G^{*}, \tag{26$''$}$$

where we recall $\omega_{1,2}=\pm 1$. If D is chosen to be the unit matrix the quantization of the $t(s)$ function yields the condition

$$\frac{1}{2\pi}\oint_{\Gamma}\mathbf{ds}\cdot\mathbf{t}(s)=n \quad n=0,1,\ldots, \tag{27$'$}$$

which is the case of no topological effects, and in fact yields, for $n=0$ (as well as for $n=1$), the *ordinary* BO approximation [see Eq. 31]. On the other hand, choosing D to be a negative unit matrix yields the condition

$$\frac{1}{2\pi}\oint_{\Gamma}\mathbf{ds}\cdot\mathbf{t}(s)=(2n+1)/2 \quad n=0,1,\ldots, \tag{27$''$}$$

which is the usual condition for an (extended) conical intersection. In this case the extended BO equation in Eq. (31) becomes identical to the BE equation [4] which, as mentioned in Sec. I was successful in yielding the correct state-to-state transition probability for a model that contains a conical intersection.

V. CONCLUSIONS

In this study we considered BO coupled equations with the aim of deriving an approximated set of uncoupled equations which, in contrast to the original BO approximated equation, will also contain effects of the nonadiabatic coupling terms. It is important to extend the BO approximation in this way because, in case electronic states are degenerate, some of the nonadiabatic coupling terms may become infinite, thus affecting the dynamics of the nuclei, irrespective of how far it takes place from the location of the degeneracy. The ordinary procedure to treat these infinities is to eliminate them by transforming to the diabatic (or quasidiabatic) framework, [3,8–10]. However the main drawback of this transformation is that once done, the BO *approximation* can no longer be activated, and one is forced to treat the system of equations in its full dimensionality. An alternative way to overcome this difficulty, while still maintaining the possibility of imposing the BO approximation, is to perform a transformation (or a series of transformations) that will not eliminate the nonadiabatic coupling terms, but shift them from their off diagonal positions to the diagonal ones. Once such a procedure is completed the BO approximation can be introduced.

The *shift* transformation in the present study was done with respect to a certain class of nonadiabatic coupling matrices, mainly with the aim of proving an ‘‘existence theorem’’ for an extended BO approximation for an $N(\geqslant 2)$ system. However, although not carried out for the most general case, the present treatment reveals some interesting results. It was found that the suggested procedure is compatible with the requirement that the nonadiabatic matrix has to yield a *uniquely* defined diabatic potential matrix. This, as discussed in previous publications, implies Bohr-Sommerfeld-type quantized eigenvalues of the nonadiabatic coupling matrix. The quantization, as shown, also guarantees that *all N* decoupled equations, that follow as a result of deleting the (potential) coupling terms, are invariant under gauge transformation, and therefore yield, for a similar set of boundary conditions, identical result. In other words, it is enough to solve one equation only because all the others will yield the same solution.

Having successful results for the nongeneral case brings us to the next subject, namely, how to extend this procedure to a more general case? Assuming we have a nonadiabatic matrix which yields continuous diabatic potentials, then the recipe we are suggesting is as follows: One has to derive, for each point in CS, the eigenvalues of the nonadiabatic matrix, and then insert one continuous set of these in Eqs. (11) for $j=1$, and solve it for given boundary conditions. The method how to solve such an equation was described in Ref. [4].

Finally we would like to refer the subject of whether the $\boldsymbol{\tau}$ matrix is a pure longitudinal-type vector or not because it is only these kinds of vectors that fulfill the Curl condition as expressed in Eq. (A3) in the Appendix (or its extensive version for a general dimension M (>2)). This question was and still is frequently raised by referees and others. The answer is only partly given here, and more extensively in Ref. [18]. It goes as follows: $\boldsymbol{\tau}$ matrices formed for a sub-Hilbert space as defined in Eq. (24) [or in Eq. (A7) in the Appendix) can be shown to fulfil the extensive version of Eq. (A3), and therefore by definition have only the longitudinal component (and completely lack the transverse component). The present paper, as well as the next one, deal only with this kind of situation.

ACKNOWLEDGMENTS

One of the authors (M.B.) would like to thank Professor Y. T. Lee and Professor S. H. Lin for their warm hospitality at the IAMS, and the Academia Sinica for supporting this research.

APPENDIX: ON THE SOLUTION OF THE FIRST-ORDER DIFFERENTIAL VECTOR EQUATION $\boldsymbol{\nabla}A+\boldsymbol{\tau}A=\mathbf{0}$

The equation mentioned in the title is Eq. (23). The solution of this equation, namely, the adiabatic-to-diabatic transformation (ADT) matrix A, is frequently questioned by referees and others, and so we decided to discuss it to some extent in this appendix. However, in order to simplify the discussion we shall refer to a two-coordinate–two-state case for which the ADT matrix can be presented in terms of an angle γ which has to fulfill the first-order differential equation [8]

$$\boldsymbol{\nabla}\gamma-\boldsymbol{\tau}=\mathbf{0}, \tag{A1}$$

where $\boldsymbol{\nabla}=(\partial/\partial r,\partial/\partial R)$. The solution of Eq. (A1) can be written in several ways, as already stated in Ref. [8]. One way of doing this is

$$\gamma(r,R)=\gamma(r_0,R_0)+\int_{r_0}^{r}\tau_r(r,R_0)dr+\int_{R_0}^{R}\tau_R(r,R)dR, \tag{A2}$$

where τ_r and τ_R are the two components of τ. Our task is now to show that the expression in Eq. (A2) is indeed a solution of Eq. (A1). A straightforward differentiation of Eq. (A2) with respect to R yields the R component of Eq. (A1) namely,

$$\frac{\partial\gamma(r,R)}{\partial R}=\tau_R(r,R). \tag{A1a}$$

To show that also the r component of Eq. (A1) is fulfilled, we have to assume that at the point (r,R) the following (curl) relation holds:

$$\mathrm{curl}\,\tau=\frac{\partial\tau_r}{\partial R}-\frac{\partial\tau_R}{\partial r}=0. \tag{A3}$$

In Ref. [8] it was shown that as long as the two electronic eigenfunctions are analytic functions with respect to the nuclear coordinates, at the point (r,R) and its close proximity this relation is indeed fulfilled. Assuming the existence of Eq. (A3) along the whole route Γ from (r_0,R_0) to (r,R), one can show that the solution given in Eq. (A2) also fulfills the second component of Eq. (A1), namely,

$$\frac{\partial\gamma(r,R)}{\partial r}=\tau_r(r,R). \tag{A1b}$$

We shall now generalize this result to any path Γ, and refer to the following presentation of the solution of Eq. (A1):

$$\gamma(s)=\gamma(s_0)+\int_{s_0}^{s}\tau\cdot\mathbf{ds}, \tag{A4}$$

where s and s_0 are two points in CS combined by the path Γ. It is important to realize that Eq. (A1) has a solution along the path Γ, and this solution is given in Eq. (A4), if along this path (and only along this path) the relevant functions are analytic, or in other words the curl relation in Eq. (A3) is fulfilled. The existence of the solution is not affected in any way by the existence of singular points in the region that contains the path Γ. These singular points may affect the *uniqueness* of the solution but not its existence.

The generalized solution of Eq. (A1) may also be written, in a more explicit way, as

$$\gamma(s)=\gamma(s_0)\exp\left(-\int_{s_0}^{s}\mathbf{ds}\cdot\tau\right). \tag{A5}$$

This expression can be extended to any N-state system by writing an explicit solution for the ADT matrix $A(s)$ in the following way [10]:

$$A(s)=\exp\left(-\int_{s_0}^{s}\mathbf{ds}\cdot\tau\right)A(s_0), \tag{A6}$$

where τ is now not a single matrix element but the full $N\times N$ matrix.

To prove the existence of the curl condition in Eq. (A3) or its extended version to any dimension N [8], we had to assume the resolution of the unity operator in terms of the electronic eigenstates of the relevant N-dimensional Hilbert space. Recently, however, we have shown that the extended version of Eq. (A3) also exists for a sub-Hilbert space of dimension M $(<N)$ if certain conditions are fulfilled [18]. These conditions can be summarized as follows: All the coupling terms formed by electronic eigenfunctions belonging to the sub-Hilbert space with electronic eigenfunctions belonging to other parts of this Hilbert space have to be identically zero. These conditions can be written in a more mathematical form as

$$\tau_{ij}=\tau_{ij}^{(1)}=\langle\zeta_i|\nabla\zeta_j\rangle=0\quad\text{for}\quad i\leqslant M,\quad j>M. \tag{A7}$$

As mentioned, the proof was given in Ref. [18], and will not be repeated here. It is important to mention that in general the complete Hilbert is expected to be composed of several sub-Hilbert spaces of this kind. Assuming that a situation like this, indeed, exists in molecular systems, we can refer to sub-Hilbert spaces and the discussion in the body of the paper is related for these situations.

The only open question to be considered is whether there is any evidence of the existence of sub-Hilbert spaces. In general, hardly any effort was made in this respect Yarkony was, until recently, the only one to look for such systems, but so far without success [19]. It seems however that Mebel, Baer, and Lin were somewhat more successful, and while studying the C_2H system found that the two lowest eigenstates of this system indeed form, for given fixed C-C distances, sub-Hilbert spaces [20].

---

[1] G. Herzberg and H. C. Longuet-Higgins, Discuss. Faraday Soc. **35**, 77 (1963).

[2] M. Born and J. R. Oppenheimer, Ann. Phys. (Leipzig) **84**, 457 (1927).

[3] M. Baer, in *Theory of Chemical Reaction Dynamics*, edited by M. Baer (CRC Press, Boca Raton, FL, 1985), Vol. II, Chap. 4.

[4] M. Baer and R. Englman, Chem. Phys. Lett. **265**, 105 (1996).

[5] M. Baer, J. Chem. Phys. **107**, 10662 (1997).

[6] R. Baer, D. Charutz, R. Kosloff, and M. Baer, J. Chem. Phys. **105**, 9141 (1996).

[7] S. Adhikari and G. D. Billing, J. Chem. Phys. **111**, 40 (1999).

[8] M. Baer, Chem. Phys. Lett. **35**, 112 (1975).

[9] Z. H. Top and M. Baer, J. Chem. Phys. **66**, 1363 (1977).

[10] M. Baer, Mol. Phys. **40**, 1011 (1980).

[11] M. Baer and R. Englman, Mol. Phys. **75**, 293 (1992).

[12] B. Lepetit and A. Kuppermann, Chem. Phys. Lett. **166**, 581 (1990); A. Kuppermann and Y.-S. M. Wu, *ibid.* **205**, 577 (1993).

[13] A. Kuppermann, in *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. H. Zhang (Dekker, New York, 1996), p. 411.

[14] T. Pacher, L. S. Cederbaum, and H. Koppel, Adv. Chem. Phys. **84**, 293 (1993).
[15] K. Huang, *Quarks, Leptons and Gauge Fields* (World Scientific, Singapore, 1982).
[16] M. Baer and A. Aljah, Chem. Phys. Lett. **319**, 489 (2000).
[17] M. Baer, J. Phys. Chem. A **104**, 3181 (2000).
[18] M. Baer, Chem. Phys. Lett. **322**, 520 (2000).
[19] D. R. Yarkony, J. Chem. Phys. **105**, 10456 (1996); R. G. Sadygov and D. R. Yarkony, *ibid.* **110**, 3639 (1999); **109**, 20 (1998); N. Matsunaga and D. R. Yarkony, *ibid.* **107**, 7825 (1997); G. Chaban, M. S. Gordon, and D. R. Yarkony, J. Phys. Chem. A **101**, 7953 (1997).
[20] A. Mebel, M. Baer, and S. H. Lin, J. Chem. Phys. **112**, 10703 (2000).