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Derivation of the phase factor and geometrical phase for an *N*-state degenerate system

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This work considers the case of degenerate vibronic coupling of N states all at one single point. For this case we first derived the extended single-state Born–Oppenheimer equation [M. Baer and R. Englman, Chem. Phys. Lett. **265**, 105 (1997)] and then showed that such a system, like the two-state system, can be described in terms of a single phase factor and is characterized by a well-defined geometrical phase. © *1998 American Institute of Physics.* [S0021-9606(98)01627-4]

I. INTRODUCTION

The Born–Oppenheimer (BO) treatment[1] is based on the fact that one may distinguish between the fast moving electrons and the much slower moving nuclei. Treating the electrons first leads to the adiabatic eigenfunctions and eigenvalues which are parametrically dependent on the nuclear coordinates. It may happen that these eigenvalues are degenerate at a point or along a line or even in a given region, features which were found to affect molecular spectra of isolated molecules.[2] This subject, known as degenerate vibronic coupling (DVC), was discussed in a series of publications, in particular by Renner,[3(a)] Teller,[3(b)] Jahn and Teller,[3(c)] and Longuet-Higgins and co-workers.[3(d)] More recently, Herzberg and Longuet-Higgins (LH)[4] found that such a degeneracy may cause the electronic eigenfunctions to be multivalued in configuration space which, if not carefully treated, may lead to a multivalued total wave function, an outcome which may lead to erroneous results.

The BO treatment when carried out for low enough energies (so that upper electronic states cannot be populated) leads to the well-known BO approximation. Within this approximation the (nonadiabatic) coupling terms to higher electronic states are ignored so that the Schrödinger equation which describes the motion of the heavy nuclei on the lowest electronic state becomes uncoupled. This approximation is valid as long as these coupling terms are nonsingular. It can be shown that when the electronic eigenfunctions are degenerate the nonadiabatic coupling terms become singular (the Hellman–Feynman theorem[5]) and so ignoring them may lead to inaccurate or even wrong numerical results.

Recently, Baer and Englman[6] (BE) derived a new single-state BO equation, which is an extension of the ordinary BO equation to include possible effects due to DVC. This extension was done for a two-state case where the total energy of the system is so low that the second state is much too high to be populated at any time. The relevance of this equation was verified numerically[7,8] as well as theoretically.[9,10]

Such an equation was not available a few years back, when the effect of conical intersection on the $D+H_2 \rightarrow HD+H$[11,12] and the $H+D_2 \rightarrow HD+D$[13] reaction processes were studied. *Ad hoc* treatments had to be developed to include such effects. The main idea behind them[11–13] was the explicit inclusion of the Longuet-Higgins (LH) phase factor[3(d),4,14] in the nuclear wave function to ensure that the full electronic-nuclear wave function of the whole system is unique in configuration space. In other words this modification was introduced to satisfy certain boundary conditions and it was done without affecting the ordinary (single-surface) Schrödinger equation (SE).[11–13]

We developed a different approach.[6,10] Employing the BO treatment[1] we kept, within the close coupling expansion, the two lowest coupled states thus assuming that the other, higher states, are decoupled from those two. Doing that we arrived at a new single-surface (state) BO equation which contains, explicitly, the nonadiabatic coupling terms. It is important to emphasize that this equation is relevant only for those instances where the total energy is well below the second state at any point in configuration space. It turned out that by incorporating these terms we managed to include, in the equation itself, features of the electronic wave functions which otherwise had to be imposed in an *ad hoc* way as boundary conditions. It is obvious that having a general equation for these purposes will not only facilitate the numerical treatment, but will contribute significantly to the theoretical study of such effects. For instance, having this equation we proved[9] that the LH phase factor is identical to the adiabatic–diabatic transformation (ADT) angle introduced several years ago.[15–18] In this respect I would like also to mention realistic applications of this approach as worked out by Yarkony.[19] In his studies he obtained geometrical (Berry) phases[20,21] for the H_3,[19(a)] CH_2, and H_2S[19(b)] systems from the relevant ADT angles calculated along closed loops around the conical intersections.

While considering more general systems we found that the two-state treatment can be extended, under certain conditions, to a DVC situation where $N(>2)$ states are all degenerate at the same point. It is not clear whether general N-state systems have single characteristic phase factors or geometrical phases and even so the derivation of those might be too complicated if one tries to study the general case. We found that by introducing a few simplifying assumptions one is able to obtain the relevant extended single-state (surface) BO-SE. Moreover, it will be shown that in this particular situation the relevant LH phase factor and the geometrical phase can also be obtained.

II. DERIVATION OF THE *N*-STATE SINGLE-SURFACE BO EQUATION

I shall consider a system of N coupled electronic states which result from the application of the BO close coupling expansion.[1] In what follows only the lowest state (or parts of it) are classically accessible by the heavy particles whereas the other $(N-1)$ adiabatic states are classically forbidden. The relevant equation to be considered is[15–18]

$$-\frac{1}{2m}(\mathbf{I}\nabla^2+2\boldsymbol{\tau}\cdot\nabla+\nabla\boldsymbol{\tau}+\boldsymbol{\tau}\cdot\boldsymbol{\tau})\boldsymbol{\chi}+(\mathbf{u}-E\mathbf{I})\boldsymbol{\chi}=0, \tag{1}$$

where $\mathbf{u}$ is the (diagonal) potential matrix which contains the adiabatic potential energy surfaces, $\mathbf{I}$ is the unity matrix, $\boldsymbol{\chi}$ is a column matrix which contains the adiabatic nuclear wave functions related to the various potential energy surfaces, ∇ is defined as the gradient for any number of (mass-scaled) coordinates, and $\boldsymbol{\tau}$ is an antisymmetric matrix which contains the nonadiabatic coupling terms:

$$\tau_{\mathbf{ij}}=\langle\phi_{\mathbf{i}}|\nabla\phi_{\mathbf{j}}\rangle. \tag{2}$$

Here $|\phi_{\mathbf{i}}\rangle$ and $|\phi_{\mathbf{j}}\rangle$ are the (real) adiabatic electronic eigenfunctions. Before going into the derivation a few assumptions must be made and a few things clarified.

(a) I shall discuss a case where all the N surfaces are degenerate at one single point. It is important to realize that if, let us say, the third and the first adiabatic states are degenerate at a given point, then this is also a point of degeneracy for the first and the second states. The reason is that all states are adiabatic and therefore are arranged so that the second state is always between the first and the third.

(b) To simplify the derivation I shall discuss the case where all N states are coupled only to the ground surface and not to each other. Also I will assume that the various coupling terms are all equal. Thus

$$\tau_{ij}=\begin{cases}0, & i=2,...,N, \quad j=2,...,N\\ 0, & i=j\\ \tau, & i=1, \quad j=2...N\\ -\tau, & i=2...N, \quad j=1.\end{cases} \tag{3}$$

Equation (1) will now be written in an explicit form (namely, term-by-term), incorporating the assumptions just made:

$$-\frac{1}{2m}[\nabla^2-(N-1)\tau^2]\chi_1+(u_1-E)\chi_1-\frac{1}{m}\tau\cdot\sum_{j=2}\nabla\chi_j-\frac{1}{2m}\nabla\tau\sum_{j=2}\chi_j=0, \tag{4a}$$

$$\begin{aligned}&-\frac{1}{2m}\nabla^2\chi_2+(u_2-E)\chi_2+\frac{1}{m}\tau\cdot\nabla\chi_1+\frac{1}{2m}\nabla\tau\chi_1+\frac{1}{2m}\tau^2\sum_{j=2}\chi_j=0,\\ &\qquad\vdots\\ &-\frac{1}{2m}\nabla^2\chi_N+(u_N-E)\chi_N+\frac{1}{m}\tau\cdot\nabla\chi_1+\frac{1}{2m}\nabla\tau\chi_1+\frac{1}{2m}\tau^2\sum_{j=2}\chi_j=0,\end{aligned} \tag{4b}$$

where we used the fact that the elements of $\boldsymbol{\tau}\cdot\boldsymbol{\tau}$ are:

$$(\boldsymbol{\tau}\cdot\boldsymbol{\tau})_{ij}=\begin{cases}-(N-1)\tau^2, & i=j=1\\ 0, & i=1,j=2...N \quad \text{or} \quad i=2...N,j=1\\ -\tau^2, & i=2...N \quad \text{and} \quad j=2...N.\end{cases} \tag{5}$$

Next, I multiply the jth equation in Eq. (4b) by a constant Γ_j, add them all up and add the sum to Eq. (4a). This leads to the following expression:

$$\begin{aligned}&-\frac{1}{2m}\nabla^2\left(\chi_1+\sum_{j=2}\Gamma_j\chi_j\right)+(u_1-E)\left(\chi_1+\sum_{j=2}\Gamma_j\chi_j\right)\\ &\quad+\frac{1}{2m}(N-1)\tau^2\left\{\chi_1+\frac{1}{N-1}\left(\sum_{j=2}\chi_j\right)\left(\sum_{j=2}\Gamma_j\right)\right\}\\ &\quad-\left(\frac{1}{m}\tau\cdot\nabla+\frac{1}{2m}\nabla\tau\right)\left(\chi_1\sum_{j=2}\Gamma_j-\sum_{j=2}\chi_j\right)\\ &\quad+\sum_{j=2}(u_j-u_1)\Gamma_j\chi_j=0.\end{aligned} \tag{6}$$

Since I consider a case where the energy is low enough so that all upper states are classically forbidden (the adiabatic approximation) Eq. (6) can be simplified by neglecting the last summation term. This is justified because each term in the summation is relatively small. The reason is that whereas (u_j-u_1) have all finite values the functions χ_{ji} where $j>1$ are all relatively small at *all* points in configuration space. This argument does not apply to the terms that contain τ, or its derivative, because τ is assumed to be singular, at least, at one point [see (a) where I assumed that all N states degenerate at one point and at this point τ becomes singular]. Therefore the product of τ with $\nabla\chi_{ji}$ may not be negligibly small at every point and may affect the final results as for instance it does in case of a conical intersection.

To continue I shall introduce a new constant Γ defined as:

$$\Gamma=\sum_{\mathbf{j}=2}\Gamma_{\mathbf{j}} \tag{7}$$

and extract Γ from the parentheses in the fourth term. Due to the changes discussed above one gets

$$-\frac{1}{2m}\nabla^2\left(\chi_1+\sum_{j=2}\Gamma_j\chi_j\right)+(u_1-E)\left(\chi_1+\sum_{j=2}\Gamma_j\chi_j\right)$$
$$+\frac{1}{2m}(N-1)\tau^2\left(\chi_1+\frac{\Gamma}{N-1}\sum_{j=2}\chi_j\right)$$
$$-\Gamma\left(\frac{1}{m}\tau\cdot\nabla+\frac{1}{2m}\nabla\tau\right)\left(\chi_1-\sum_{j=2}\Gamma^{-1}\chi_j\right)=0. \tag{8}$$

The values of Γ_j, $j=2,...,N$ are not determined as yet. It can be seen that if they are chosen to fulfill the relation:

$$\Gamma_j=\lambda=i\frac{1}{\sqrt{\mathbf{N}-1}}\Rightarrow\Gamma=i\sqrt{\mathbf{N}-1} \tag{9}$$

then one can define a function:

$$\chi=\chi_1+\frac{i}{\sqrt{N-1}}\sum_{j=2}\chi_j \tag{10}$$

and the equation for χ [which follows from Eq. (8)] is:

$$-\frac{1}{2m}(\nabla^2-(\mathbf{N}-1)\tau^2)\chi+(u_1-E)\chi$$
$$-\frac{i}{2m}\sqrt{\mathbf{N}-1}(2\tau\cdot\nabla+\nabla\tau)\chi=0. \tag{11}$$

It is noticed that Eq. (11), for the N-state case, is very similar to the two-state case we derived some time ago[6,7,9] except that $\tau\sqrt{N-1}$ [not $\tau(N-1)$] replaces τ at the required places. Also it is realized that for $N=2$ Eq. (11) becomes identical to the two-state equation.

III. THE PHASE FACTOR AND THE GEOMETRICAL PHASE

In Ref. 9 the two-state case was discussed and it was shown that the LH phase factor is determined by the nonadiabatic coupling term τ and given in the form:

$$\theta(S)=\theta(S_0)-\int_{\mathbf{s}_0}^{\mathbf{s}}\mathbf{ds}\cdot\tau, \tag{12}$$

where s and s_0 are two points in configuration space and **ds** is a differential vector element along a chosen path between s and s_0.

In what follows I shall show that also for the present N case one may define a phase factor very similar to the one introduced by LH. Moreover, once derived, I shall obtain the corresponding geometrical phase.

To treat this case I refer, again, to Eq. (1) (which is a matrix equation) and consider only the equation for one single (the lowest) electronic state. Next, I ignore all the τ matrix elements that couple this state to the higher electronic states so that Eq. (1) becomes[22]

$$-\frac{1}{2m}(\nabla^2+\tau_{11}^2)\chi_1+(u_1-E)\chi_1$$
$$-\frac{1}{2m}(2\tau_{11}\cdot\nabla+\nabla\tau_{11})\chi_1=0. \tag{13}$$

It is claimed that like the two-state case,[3(d)] also the present N-state case can be described in terms of one single phase factor. For this purpose the electronic eigenfunction $|\phi_1\rangle$ is assumed to be a complex function of the nuclear coordinates, namely:

$$|\phi_1\rangle=\exp(\mathbf{i}\theta)|\xi_1\rangle, \tag{14}$$

where ξ_1 is real and θ is an arbitrary phase which may depend on the nuclear coordinates (the phase may be arbitrary but is expected to fulfill certain requirements) it can be shown that:

$$\tau_{11}=\langle\phi_1|\nabla\phi_1\rangle=\nabla\theta. \tag{15}$$

Replacing τ_{11} in Eq. (13) leads to

$$-\frac{1}{2m}(\nabla^2-(\nabla\theta)^2)\chi_1+(u_1-E)\chi_1$$
$$-i\frac{1}{2m}(2\nabla\theta\cdot\nabla+\nabla^2\theta)\chi_1=0. \tag{16}$$

Comparing, now, Eq. (16) with Eq. (11) it is noticed that the two will become identical if $\nabla\theta$ is assumed to fulfill the (vector) equation:

$$\nabla\theta=\sqrt{(\mathbf{N}-1)}\tau, \tag{17}$$

where τ was introduced earlier [see Eq. (3)]. The solution for Eq. (17) is:[15–17]

$$\theta(S)=\theta(S_0)+\sqrt{(\mathbf{N}-1)}\int_{\mathbf{s}_0}^{\mathbf{s}}\mathbf{ds}\cdot\tau, \tag{18}$$

where s, s_0, and **ds** were introduced before. However, in order to have a unique solution (namely a solution that does not depend on the path that combines s and s_0) the following condition

$$\sqrt{(N-1)}\,\mathrm{curl}\ \tau=0\quad\Rightarrow\quad\mathrm{curl}\ \tau=0 \tag{19}$$

has to be fulfilled.[15–17]

Having an analytic expression for the phase factor we can also present the expression for the corresponding geometrical (Berry) phase γ_N.[20] Thus choosing a path that surrounds the region of the DVC we find for γ_N the expression:

$$\gamma_N=\sqrt{(N-1)}\oint_c\mathbf{ds}\cdot\tau. \tag{20}$$

Like in the case of Eq. (18), also here, a unique value is guaranteed if Eq. (19) is fulfilled.

The result of Eq. (20) is, to a certain extent, unexpected due to the square root sign in front of the integral. To continue the analysis we may remind the reader that the geometrical phase can be considered as a measure for the strength of the DVC. To get a deeper insight I shall compare, now, the strength of the present DVC due to N states at a point to the combined strength of $(N-1)$ ordinary two-state DVCs located at $(N-1)$ different points. For the sake of this comparison I shall assume that all $(N-1)$ two-state DVCs are similar to each other, namely, are characterized by an identical nonadiabatic coupling term τ. As a result, if c_i and c_j are loops that surround the ith and the jth degenerate points, respectively, we have

$$\oint_{\mathbf{c}_1} \mathbf{ds}\cdot\tau = \oint_{\mathbf{c}_j} \mathbf{ds}\cdot\tau. \tag{21}$$

Next, for such a group of two-state DVCs it is easy to see that the corresponding combined geometrical phase [which is the combined strength of the $(N-1)$ DVCs] is equal to:

$$\tilde{\gamma}_{\mathbf{N}} = (\mathbf{N}-1)\oint_{\mathbf{c}_0} \mathbf{ds}\cdot\tau. \tag{22}$$

Comparing the results of Eqs. (20) and (22) it is seen that the strength of DVC formed by N states at one single point is weaker then the strength formed by $(N-1)$ two-state DVCs. The ratio between the two measures is $(N-1)^{(1/2)}$.

IV. DISCUSSION AND CONCLUSIONS

In this paper I discussed DVC due to N states interacting at a single point, and arrived at two main conclusions: (a) Making a few simplifying (but still meaningful) assumptions one can treat such a case and derive, for a low energy case, the corresponding extended BO Schrödinger equation related to the lowest state (surface) only. (b) The analytic derivation led to the introduction of a novel phase factor (and a corresponding novel geometrical phase) suitable for a DVC formed by $N(N>2)$ states interacting at a point.

In what follows are, briefly, discussed two specific examples with the understanding that the above-mentioned assumptions are fulfilled.

(a) As a first example we consider the Jahn–Teller model discussed by BE.[6] There, the adiabatic–diabatic transformation angle θ, which was shown to be equal to the LH phase factor,[23] had been proved to be given (within the zero approximation) in the form:

$$\theta = (1/2)\varphi, \tag{23}$$

where φ is the polar angular coordinate. Consequently the geometrical phase, γ, becomes π. In case we have N such surfaces all degenerating at a single point, the corresponding phase factor will be $\sqrt{(\mathbf{N}-1)}(\varphi/2)$ and the geometrical phase γ becomes $\pi\sqrt{(\mathbf{N}-1)}$.

(b) The second example is the Renner–Teller case. Here it was shown[10] that the phase factor is φ (again within the zero approximation) and therefore for N degenerate states at a single point, it is $\varphi\sqrt{(\mathbf{N}-1)}$ and the corresponding geometrical phase is $2\pi\sqrt{(\mathbf{N}-1)}$.

In this article new relations were derived which are to many experts in the field of a surprise and therefore some of them may consider these relations to be incorrect or, if correct, not relevant to realistic cases. It is true that the present model may not be realistic but still it was demonstrated that also N-state systems, where $N>2$, may have phase factors and geometrical phases. So in this sense the present study can be considered as an existence theorem. It could very well be that the present model is the only case for which such phase factors and geometrical phases can be found; therefore, more studies on this subject are required.

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