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LETTERS TO THE EDITOR

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NOTES

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The effects of doubly degenerate electronic states in general and of conical intersections in particular on molecular spectra and scattering processes have been studied continuously for the last 40 years.[1–7] These effects can be shown to be related to the fact that some relevant electronic nonadiabatic coupling terms are nonanalytic at some point (or region) in configuration space.[8] In particular it is important to call attention to five reviews which cover that subject each from a different point of view.[2]

In a recent publication Baer and Englman (BE)[6] derived a new (approximate) single-surface Born–Oppenheimer (BO) equation which is an extension of the ordinary BO equation, as it includes the possible effects due to electronic nonadiabatic processes. This equation is reminiscent of an equation derived some time ago by Mead and Truhlar (MT)[5] employing Longuet-Higgins *et al.*'s (L-H) phase.[3] In the present communication I shall show that the BE and the MT equations are identical (in case the two-state approximation is valid) and that the L-H phase is not arbitrary but fulfills a first order differential equation identical to that fulfilled by the electronic two-state adiabatic-diabatic transformation (ADT) angle.[8]

The starting point of the derivation is the matrix equation

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

where the $\underset{\approx}{\tau}^{(1)}$ matrix contains the nonadiabatic coupling elements defined as (the bra–ket notations are applied with respect to the electronic coordinates)

$$\tau_{ij}^{(1)} = \langle \zeta_i | \nabla \zeta_j \rangle, \tag{2}$$

$\underset{\approx}{u}$ is the potential matrix which contains the adiabatic potential energy surfaces, $\underset{\approx}{I}$ is the unity matrix, $\underset{\sim}{\chi}$ is a column matrix which contains the nuclear wave functions related to the various potential energy surfaces, and ∇ is given in the form

$$\nabla = \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \dots, \frac{\partial}{\partial q_N}\right). \tag{3}$$

Here, ζ_i are the adiabatic electronic eigenfunctions and the $(q_1, \dots, q_N)$ are nuclear coordinates. Eq. (1) is an outcome of the BO close-coupling expansion.[2(a),2(b),8]

In what follows we distinguish between two types of approximations both of them applying to the situation where the system energy is low enough so that only the lowest electronic state is classically open. These are

(a) The single-state approximation: In this case the components of all nonadiabatic coupling terms to higher electronic states (including those of $\tau_{12}^{(1)}$) are simply ignored so that Eq. (1) becomes

$$\left(-\frac{1}{2m}\nabla^2 + u_1 - E\right)\chi_1 - \frac{1}{2m}(2\tau_{11}\cdot\nabla + \tau_{11}^2 + \nabla\tau_{11})\chi_1 = 0, \tag{4}$$

where τ_{11} stands for $\tau_{11}^{(1)}$. In case the electronic basis set is chosen to be real (as a function of the nuclear coordinates) the value of τ_{11} can be shown to equal zero and Eq. (11) reduces to the ordinary single BO equation. However, choosing the electronic eigenfunction ζ_1 as a complex function of the nuclear coordinates will yield a nonzero value for τ_{11}. According to Longuet-Higgins *et al.*[3] ζ_1 can be written in the form

$$\zeta_1 = \exp(i\theta)\xi_1, \tag{5}$$

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). Substituting Eq. (5), for ζ_1, in Eq. (2) yields for τ_{11}, the following nonzero result:

$$\tau_{11} = i\nabla\theta. \tag{6}$$

Next, replacing τ_{11} in Eq. (4) leads to[5]

$$\left(-\frac{1}{2m}\nabla^2 + \tilde{u}_1 + E\right)\chi_1 - i\frac{1}{2m}(2\nabla\theta\cdot\nabla + \nabla^2\theta)\chi_1 = 0, \tag{7}$$

where $\tilde{u}_1$ is defined as

$$\tilde{u}_1 = u_1 + \frac{1}{2m}(\nabla\theta)^2. \tag{8}$$

Equation (7) is an extended single-surface BO equation where the extension (the last two terms) is expressed in terms of the L-H phase.

(b) The two-states approximation. We extract from Eq. (1) two (coupled) equations related to the two lowest adiabatic electronic states.[6,7(a)] Here, the assumption is that all

nonadiabatic coupling terms to states outside the two-state manifold are ignored (namely assumed to be small enough so that they can be ignored) and so there are left only the nonadiabatic coupling terms within the two-state manifold. Thus

$$\left[-\frac{1}{2m}\nabla^2+\bar{u}_1-E\right]\chi_1-\frac{1}{m}\tau_{12}\cdot\nabla\chi_2-\frac{1}{2m}\nabla\tau_{12}\chi_2=0,$$
(9a)

$$\left[-\frac{1}{2m}\nabla^2+\bar{u}_2-E\right]\chi_2+\frac{1}{m}\tau_{12}\cdot\nabla\chi_1+\frac{1}{2m}\nabla\tau_{12}\chi_1=0,$$
(9b)

where τ_{12} is a vector whose components are scalars (not matrices) and the $\bar{u}_i$'s are given in the form

$$\bar{u}_i=u_i+\frac{1}{2m}(\tau_{12})^2;\quad i=1,2.$$
(10)

It is important to emphasize that Eqs. (9) were obtained using real electronic eigenfunctions and consequently $\tau_{11}\equiv\tau_{22}\equiv0$.

As was mentioned above, Eqs. (9) will now be treated for the case where the upper electronic state is classically forbidden. In such a situation χ_2 is usually small at every point in configuration space a fact that can be used to construct one single equation from the two given in Eqs. (9). This was recently done by BE,[6] and is based on introducing a new function, ψ, defined as

$$\psi=\chi_1+i\chi_2.$$
(11)

The equation for ψ is obtained by multiplying Eq. (9b) by i and adding it to Eq. (9a). Thus

$$\left(-\frac{1}{2m}\nabla^2+\bar{u}_1-E\right)\psi+i\frac{1}{2m}(2\tau_{12}\cdot\nabla+\nabla\tau_{12})\psi=0.$$
(12)

To derive Eq. (12) we neglect the term $i(u_1-u_2)\chi_2$ which is not expected to contribute, because, as mentioned above, χ_2 is negligibly small and u_1 and u_2 are finite. It could be that χ_2 will have large values at regions where the two PESs coincide (namely, where τ_{12} becomes very large) but then $u_1=u_2$.

Now, comparing Eq. (7) with Eq. (12) it is seen that the two are very similar and will become identical if the phase θ is assumed to fulfill the following (vector) equation:

$$\nabla\theta=-\tau_{12}.$$
(13)

This equation has a simple solution (the conditions for having this solution were discussed in detail in Ref. 8(a) and they are fulfilled when the nonadiabatic coupling terms to higher states are small so that they can be ignored):

$$\theta(s_1)=\theta(s_0)-\int_{s_0}^{s_1}ds\cdot\tau_{12},$$
(14)

where s_0 and s_1 are two points along a path $\Gamma(s)$ and **ds** is a differential vector along this path. In case the path is a closed loop, Eq. (14) is reminiscent of the equation for the Berry phase[10] but is, as be seen, not the same.

Let us now summarize what has been achieved: Since a two-state approximation is always more accurate than a single-state approximation and since Eqs. (12) and (7) are so similar, it is plausible that the L-H phase has its origin in the electronic nonadiabatic coupling term τ_{12} and is therefore, up to a constant of integration, solely determined by Eq. (14).

The L-H phase was originally introduced for reasons of symmetry effects caused by conical intersections and what has been done here is to connect quantitatively this phase to dynamical magnitudes. It is important to emphasize that this connection can be done only in case the nonadiabatic coupling terms relating to states outside the two-state manifold are ignored.

Finally, I shall refer to a recent important publication by Yarkony[1(j)] which followed our Ref. 7(a). In this publication Yarkony calculated for a practical example, namely, the H_3 MCSCF/CI wave functions, the so-called Berry phase, using Eq. (14). In his conclusions Yarkony wrote: ''This choice'' (namely, that the L-H phase can be the ADT angle—M.B.) ''although certainly not necessary, is valid in the immediate vicinity of the conical intersection.'' I agree only with part of this statement and in my opinion it should be, ''in case the two-state approximation is valid the ADT angle *is* the L-H phase and there is no other, immaterial of the proximity to a conical intersection.'' Of course, the two angles will differ when the two-state approximation breaks down but then, also, a treatment within the two-state system will lead to irrelevant and even to erroneous results.

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