Curl condition revisited

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Abstract

In this Letter the Curl condition related to the nonadiabatic coupling terms, proved to be fulfilled by Born–Oppenheimer electronic eigenfunctions [Chem. Phys. Lett. 35 (1975) 112], is extended to include the points of singularity as recently discussed [Chem. Phys. 259 (2000) 123, Appendix B]. The study, related at this stage to a two-state system, is expected to add insight as to the origin of the non-adiabatic coupling terms. © 2001 Published by Elsevier Science B.V.

1. Introduction

The non-adiabatic coupling terms (NACTs) owe their existence to the Born–Oppenheimer–Huang assumption which says that the fast moving electrons can be treated separately from the (assumed) slow moving nuclei [1,2]. The NACTs are characterized by two features: they are vectors (in contrast to potentials that are scalars) and they may become singular (in contrast to potentials which do not). If arranged in matrices they acquire a third interesting feature, namely, the matrices are antisymmetric.

For a long time it was believed that the unique feature of the NACTs, namely, them being singular is a rare event in ab initio treatments. In fact what happens is that singular NACTs were found very frequently [3–10], actually much more than anticipated. The fact that they are so numerous implies that they are expected to play a dominant role in molecular physics and therefore calls for extensive studies of these objects, which will lead to a better understanding of their features. During the last few years major efforts were made in this respect.

As mentioned above the NACTs can be arranged in a matrix – the non-adiabatic coupling matrix (NACM) τ – which contains the vectorial elements τij where i and j label two adiabatic states, i.e. the ith and the jth states. Singular NACTs can be formed only between two adjacent adiabatic states (as is noticed from the Hellman–Feynmann theorem [11]) and we shall be interested only in this type of NACTs. In general two kinds of singular NACTs exist, one type which is known as conical intersection [12,13] and the other known as parabolic intersections [14,15].

In this Letter we consider an isolated system of two adiabatic states. In other words a sub-Hilbert space of two states is treated [16]. As a result only

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one (vectorial) nonadiabatic coupling term, namely, $\tau_{12}$ is encountered. In what follows this notation is simplified to $\tau$.

2. The non-adiabatic coupling term as a vector potential

For a given (isolated) system of Born–Oppenheimer–Huang states the above-mentioned non-adiabatic coupling matrix $\tau$ is known to fulfill the ‘Curl’ condition [16,17]

\[
\text{Curl } \tau - [\tau \times \tau] = 0.
\] (1)

This equation is valid as long as the components of $\tau$ are analytic functions at every point in configuration space. In case some of them become singular at a given point Eq. (1) may not be fulfilled at this particular point [16].

In order to simplify our discussion we limit ourselves, in the present publication, to the two-state system. For this case Eq. (1) becomes [16,17]

\[
\text{Curl } \tau = 0,
\] (1a)

which, again, is only fulfilled at the points where $\tau$ is regular.

In order to understand the meaning of this singularity and how to treat it, we start by considering the relevant Born–Oppenheimer–Huang equation [16,18]

\[
-\frac{1}{2m} (\nabla + \tau)^2 \Psi + (u - E) \Psi = 0.
\] (2)

Eq. (2) is a matrix equation where $\Psi$ is a two-component vector which contains the two relevant nuclear wave functions, $u$ is a diagonal potential matrix which contains the two adiabatic potentials and $\tau$ is the NACM of the form

\[
\tau = \begin{pmatrix} 0 & \tau \\ -\tau & 0 \end{pmatrix}.
\] (3)

Although Eq. (2) looks like a Schrödinger equation which contains a vector potential $\tau$, it can not be interpreted as such because $\tau$ is an antisymmetric matrix (thus, having diagonal terms which are equal to zero). This ‘inconvenience’ can be ‘repaired’ by employing the following unitary (constant) transformation [19–21]:

\[
\Psi = G\Phi,
\] (4)

where $G$ takes the form

\[
G = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix}.
\] (5)

As a result Eq. (2) becomes

\[
\frac{1}{2m} (-i\nabla + \tau)^2 \Phi + (w - E) \Phi = 0,
\] (6)

where $\tau$ is a diagonal matrix

\[
\tau = \begin{pmatrix} \tau & 0 \\ 0 & -\tau \end{pmatrix}
\] (7)

and $w$ is an ordinary potential matrix of the kind

\[
w = \frac{1}{2} \begin{pmatrix} u_1 + u_2 & - (u_2 - u_1) \\ -(u_2 - u_1) & u_1 + u_2 \end{pmatrix}.
\] (8)

The important fact is that by the transformation in Eqs. (4) and (5) we managed to show that $\tau$ is incorporated in the Schrödinger equation in the same way as would a vector potential due to a magnetic field. In other words the NACT $\tau$ behaves like a vector potential and therefore is expected to fulfill an equation of the kind [22a]

\[
\text{Curl } \tau = H,
\] (9)

where $H$ is pseudo-magnetic field. This equation differs from Eq. (1a) because $H$ is not necessarily zero. However we also limit the existence of Eq. (1a) (as well as Eq. (1)) to those points where $\tau$ is not singular [16]. Thus, in order to satisfy the two requirements we assume that $H$ differs from zero only at those singular points. In the present study we consider a case of one singular point.

The question is if in reality such magnetic fields exist. It turns out that such fields can be formed by long and narrow solenoids [22b]. It is well known that in this case the magnetic fields are nonzero only inside the solenoid but zero outside it [22]. Moreover it has a non-zero component along the solenoid axis only. Thus simulating the molecular seam [11] as a solenoid we can identify the NACT as a vector potential produced by an infinitesimal narrow solenoid.

The quantum mechanical importance of a vector potential $A$ even in regions where the
magnetic field is zero was first recognized by Aharonov and Bohm in their seminal 1959 paper [23]. Interpreting the meaning of τ as a vector potential associated with a magnetic field is reminiscent of what is known in physics as the Yang–Mills field [24].

To continue we assume the following situation: We concentrate on a plane which is chosen to be perpendicular to the seam. In this way the pseudo-magnetic field is guaranteed to be perpendicular to the plane and will have a non-zero component in the z-direction only. In addition we locate the origin at the point of the singularity i.e. at the crossing point between the plane and the seam. With these definitions the pseudo-magnetic field is of the form

$$H = H_z = 2\pi \frac{\delta(q)}{q} f(\theta).$$

(10)

Here δ(q) is the Dirac δ-function and f(θ) is an arbitrary, given, function (it can be shown that any function of the type f(q, θ) will lead to the same result). Considering Eq. (9) for the z-component we obtain (employing polar coordinates)

$$\frac{1}{q} \left( \frac{\partial \tau_\theta}{\partial \theta} - \frac{\partial \tau_q}{\partial \theta} \right) = 2\pi \frac{\delta(q)}{q} f(\theta).$$

(11)

Here (τ_θ, τ_q) are the radial and the angular components of τ (the z-component, i.e. the out of plane, is by definition equal to zero). Deleting the (1/q) term and integrating (Eq. (11)) along q for a fixed value of θ we get

$$\tau_\theta(q, \theta) - \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = \pi h(q) f(\theta),$$

(12)

where h(q) is the Heaviside function

$$h(q) = \begin{cases} 1, & q \geq 0, \\ 0, & q < 0. \end{cases}$$

(13)

In deriving Eq. (12) we did not include the term τ_θ(q = 0, θ) because it is expected to be included in the inhomogeneity term.

Since q is a radius it is always positive and therefore Eq. (12) can be written, without loss of generality, as

$$\tau_\theta(q, \theta) - \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = \pi f(\theta).$$

(14)

Next we consider the ‘quantization’ condition introduced sometime ago by Baer and Alijah, [19,20] namely

$$\oint_{\Gamma} ds \cdot \tau(s) = n\pi,$$

(15)

where Γ is a closed contour surrounding the origin and n is an odd integer in case of a conical intersection and an even integer in case of a parabolic intersection. Assuming Γ to be a circle with radius q, Eq. (15) implies

$$\int_0^{2\pi} \tau_\theta(q, \theta) d\theta = n\pi.$$

(16)

A similar integration, namely, over θ along the (0, 2π) range, can be carried out for Eq. (14). Thus let us first consider the integration over the second term

$$\int_0^{2\pi} d\theta \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = \int_0^q dq \int_0^{2\pi} \frac{\partial \tau_q}{\partial \theta} d\theta$$

$$= \int_0^q dq (\tau_q(q, \theta = 2\pi) - \tau_q(q, \theta = 0))$$

or due to the uniqueness of NACT function [28] we get

$$\int_0^{2\pi} d\theta \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = 0.$$  

(17)

Combining Eqs. (14), (16) and (17) yields the following outcome:

$$\int_0^{2\pi} f(\theta) d\theta = n.$$  

(18)

In other words, the quantization we encountered for the NACTs is associated with the ‘quantization’ of the intensity of the ‘magnetic’ field along the seam. Moreover, Eq. (18) reveals another feature, namely, that there are fields for which n is an odd integer, namely, conical intersections [12,13,20] and there are fields for which n is an even integer, namely, parabolic intersections [14,15,20].

Eq. (14) can be applied to obtain f(θ). Ab initio calculation for small enough q-values will yield τ_θ(0, q ~ 0) and these, as is seen from Eq. (14), can be directly related to f(θ).
\[ f(\theta) \sim \frac{1}{\pi} \tau_0(q \sim 0, \theta), \quad (19) \]

where the contribution of the second term on the left-hand side (for small enough \( q \)-values) is ignored.

3. The angular dependence of the internal magnetic field

As a the third subject, in this respect, we would like to discuss the possibility that \( \tau \), can be assumed to be of the form

\[ \tau = \left[ \vec{F}(q, \theta) \times \vec{q} \right], \quad (20) \]

where \( \vec{F}(q, \theta) \) is, at this stage, an unknown (vectorial) function assumed to be in the direction of the seam (which was assumed to be in the \( z \)-direction). This expression simply implies that \( \tau \) is located in a plane perpendicular to the seam, and that its radial component, \( \tau_r(q, \theta) \) is zero. Presenting the vector potential in this form looks like a generalization of the homogeneous magnetic field case as discussed in Ref. [22a], and which is also applied for instance in the context of the Zeeman effect [27] (for a homogeneous field). However, it has to be emphasized that writing \( \tau \) in this way does not imply that \( \vec{F}(q, \theta) \) is a magnetic field because the magnetic field is zero everywhere (except along the seam itself).

Inserting Eq. (20) in Eq. (11) yields for \(|\vec{F}(q, \theta)|\) the result

\[ F(q, \theta) = \frac{1}{q^2} \pi f(\theta), \quad (21) \]

which is compatible with Eq. (14) for the case that \( \tau_r(q, \theta) \) is zero (the vector sign and the absolute signs for \( F(q, \theta) \) were deleted for reasons of convenience).

So far the few ab initio calculations, as performed by Mebel et al. [9,10] and by Yarkony et al. [25,26] show that the values of \( \tau_r(q, \theta) \) are indeed smaller than the \( \tau_0(q, \theta) \)-values and sometimes even much smaller, but they are not negligibly small. These findings are also supported to some extent by perturbation expansions [25,26]. Thus, based on our limited experience, we may conclude that Eq. (21) is, probably, justified to a ‘first approximation’.

Returning now to Eq. (14) it is noticed that with this assumption the second term becomes negligible small and therefore can be deleted. As a result, Eq. (14) implies that \( \tau_0(q, \theta) \) depends only on \( \theta \) but not on \( q \), for any \( q \)-value. This result, for which we found so far, only a limited support, [9,10,25,26] is of major importance because it allows us to calculate \( \tau_0(q, \theta) \) for one single value of \( q \) and then apply it for all other \( q \)-values.

4. Conclusions

This Letter is devoted to the idea that the electronic NACTs can be simulated as an ordinary vector potential. To carry out this study we considered a two-state system, shifted (rigorously) the off-diagonal NACTs to the diagonal and employed the relevant Maxwell equation. These are the main findings:

1. From earlier studies [16] it became clear that the Curl condition in Eq. (1) is not fulfilled at every point in CS. In the present publication this missing part in the theory is complemented by attributing it to a singular, angular dependent, pseudo-magnetic field located along the seam.

2. The fact that the NACT has to be quantized led, in a most straightforward way, to the ‘quantization’ of the pseudo-magnetic field.

3. We examined the possibility that the NACT is in a right angle to a vector from the seam (which implies that the radial component of the NACT is zero). Such situations are frequently examined (as for instance in case of the Zeeman effect [27]) and it could be of interest to do it here as well. Perturbation studies as well as ab initio calculations suggest that the radial component of the NACT is usually much smaller than the angular one [25,26] so that this assumption has at least some support from realistic situations. However it is not clear, at this stage if they can be ignored altogether.

4. It is important to mention that if the radial component of the NACTs can indeed be ignored then \( \tau_0(q, \theta) \) becomes independent of \( q \) – a feature which enables the application of
a set of NACTs as calculated at one single radius $g$ around a conical intersection, for a whole plane.

5. Finally we would like to elaborate (semi-classically) on the origin of the above magnetic field if, indeed, its existence can be confirmed. We recall that the pseudo-magnetic field is assumed to exist along the seam. One-way of forming the seam is following the position of the conical intersection as a function of (non-relevant) vibrational coordinates. Since each of these coordinates is associated with a vibrational motion (even in its ground state) these vibrational motions lead to a quasi-periodic motion of the system along the seam. Assuming that some charge is distributed along the seam this vibrational motion may produce a pseudo-magnetic field as discussed in this Letter.

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