



Analysis of a two dimensional molecular Berry phase system



R. Englman^{a,b,*}

^a Soreq NRC, Yavne 81800, Israel

^b Ariel University Center, Ariel 40700, Israel

ARTICLE INFO

Article history:

Received 2 April 2015

In final form 25 June 2015

Available online 9 July 2015

ABSTRACT

Discontinuities in the Born–Oppenheimer (infinite nuclear masses) limit of an artificial molecular system, absent for finite masses, have led Min et al. (2014) to a questioning of Berry phases in some molecular systems. We show here by a rigorous following of the analysis of Longuet-Higgins et al. (1958), that (a) the same phenomena of discontinuities occurs in typical degenerate molecular systems with regular Berry-phase effects, (b) they arise from the non-unique definition of the key quantity, electronic ‘vector field’, and (c) they can be removed by a different choice of normalization.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In a recent letter Min and coworkers [1] have questioned whether the electronic Berry (or geometric) phase [2] survives in a molecular system with a two dimensional nuclear parameter space, if taken beyond the Born–Oppenheimer (BO) approximation. The meaning of the last phrase is ‘when the nuclear masses may be regarded as infinite’ (as in reality they never are). Were they such, they could pass as classical objects and their movement in the molecule could be conceived as externally operated (i.e., time dependent parameters). The end result, reached by the authors through a numeric-intensive method, was that ‘the Berry phase is not a topological feature of the exact solution of the electronic-nuclear Schrödinger equation’. In their concluding section the authors were hesitant whether the examples worked out by them are representative of a general molecular situation or apply only to the specific (and rather artificial) example numerically studied by them. The novel (though tentative) conclusion of the authors was based mainly on comparison within and beyond the Born–Oppenheimer approximation of a newly defined quantity, ‘the two dimensional vector field’, described in this letter below and here renamed ‘Pseudo Average’.

Their conclusion could be of interest also outside molecular systems, in those in which Berry phase effects have been shown to play an important role and have also been experimentally verified. These include electrically polarized media [3], charge pumping [4], quantum and anomalous Hall effects [5], Bloch-band effects [6] and others. Back to molecular systems, geometric phases have been

broadly related to conical intersections, of importance, in e.g., relaxation phenomena [7–9]. Still, the preponderant application in this context has been the revealing of electronic degeneracies in molecular configuration space: here the nuclear ‘motion’ which shows the Berry-phase is not a physical event, but a calculational, computational process, whose idea originated in [10] and was intensively pursued later, with accounts in e.g., [7,8].

In the present work we show that the ‘Pseudo Average’ discontinuity of the electronic factor in the configuration space shown for the artificial system of [1] is also found in the archetypal case of the Berry phase, also known as the $E \otimes \epsilon$ Jahn–Teller effect. In this a doubly degenerate electronic state is linearly coupled to a twofold vibrational mode in a high symmetry molecule; a full treatment of which was provided by a classic paper of Longuet-Higgins et al. [11]. (There are overlaps between this basic work and that in [12]. An extension to a X_3 molecular system in D_3 symmetry was given by [13], whose discussion for the $k \gg 1$ strong coupling limit around Eq. (2.22) relies on the Longuet-Higgins et al.’s derivation. Gauge freedom aspects were introduced by [14,15].)

In the present work we are able to show analytically, by stepwise following the detailed treatment of Longuet-Higgins et al. [11], the development of the ‘Pseudo Average’ discontinuity of [1] as the BO limit is approached. We also show that the aforementioned discontinuity of the electronic factor in the molecular wave function in the BO limit is due to a choice of normalization of this factor, whereas a different and equally valid normalization removes the discontinuity. The different choices of normalizations are analogous to different gauge choices.

To demonstrate his result, this letter retraces in the next section the work of [11] for the ground state (‘vibronic’) doublet, indexing all results also with the formula number of that paper as [LH --]. This is followed by describing the states in the BO limit, after which

* Correspondence address: Soreq NRC, Yavne 81800, Israel.

E-mail address: englmanrobert@gmail.com

we evaluate averages of electronic coordinates, verifying the transition to discontinuity in the ‘Pseudo Average’ and its removal by changing the electronic normalization factor.

2. The ‘low energy states’

For a two-(electronic) level molecular system, (such as in six-coordinated Cu^{2+}) in which the electrons interact with two degenerate vibrations $x + iy = Re^{i\phi}$ [LH2.1, (but differing from that by writing R for the vibrational amplitude, instead of r which is reserved for the electronic coordinate as in [1])], we write the dimensionless Hamiltonian (as in [LH2.4], [LH2.9]), including the electron-vibrational coupling constant $k(\geq 0)$,

$$\begin{aligned} \frac{H}{\hbar\omega} &= \left[\frac{H_0}{\hbar\omega} \right] + \frac{H'}{\hbar\omega} + \frac{H_{A\phi}}{\hbar\omega} \\ &= \left[-\frac{1}{2} \left(\frac{\partial^2}{\partial R^2} + \frac{1}{R} \frac{\partial}{\partial R} + \frac{1}{R^2} \frac{\partial^2}{\partial \phi^2} \right) + \frac{1}{2} R^2 \right] \\ &\quad + 2kR \cos(2\theta - \phi) + \frac{1}{2R} \left(A_\phi \frac{\partial}{\partial \phi} + \frac{\partial}{\partial \phi} A_\phi \right) - \frac{1}{2} A_\phi^2 \end{aligned} \quad (1)$$

with the orthonormal $\sqrt{\frac{1}{2}} \cos \theta$, $\sqrt{\frac{1}{2}} \sin \theta$ being the representatives of a degenerate electronic orbital doublet. Differing from [11], we add gauge-potential terms in the last line, to be used later on and we also retain the basic vibrational energy unit $\hbar\omega$ in the formalism. The reason for this is that the approach to the infinite nuclear mass, Born–Oppenheimer (BO) limit is understood as the limit $\omega \rightarrow 0$, and equivalently as $k \rightarrow \infty$. As in [1], we shall work in this limit, mainly, but not exclusively. The ‘low energy states’ [LH Section 6] are those for $\ell = \pm \frac{1}{2}$ given by [LH6.4, LH6.5, LH6.6]

$$\begin{aligned} \Psi_\ell &= e^{i\ell\phi} \left\{ (\rho_\ell^+(R) + \rho_\ell^-(R)) \cos \left(\theta - \frac{\phi}{2} \right) \right. \\ &\quad \left. + i(\rho_\ell^+(R) - \rho_\ell^-(R)) \sin \left(\theta - \frac{\phi}{2} \right) \right\} \\ &= e^{i\ell\phi} \left\{ \left[u(-R) \cos \frac{\phi}{2} - i(-1)^{\ell-\frac{1}{2}} u(R) \sin \frac{\phi}{2} \right] \cos \theta \right. \\ &\quad \left. + \left[u(-R) \sin \frac{\phi}{2} + i(-1)^{\ell-\frac{1}{2}} u(R) \cos \frac{\phi}{2} \right] \sin \theta \right\} \end{aligned} \quad (2)$$

The two solutions with $\ell = +\frac{1}{2}$ and $-\frac{1}{2}$ are complex conjugates of each other; they are also energy-degenerate and are orthogonal in the sense that the θ , q , ϕ integration of their cross-product vanishes. These properties will also hold for any pair of orthonormal, linear combinations of the form $\Psi^1 = A\Psi_{\frac{1}{2}} + B\Psi_{-\frac{1}{2}}$ and $\Psi^2 = B^*\Psi_{\frac{1}{2}} - A^*\Psi_{-\frac{1}{2}}$ where A, B are complex constants and A^*, B^* their conjugates. We shall later look at arbitrary values of A, B , but for the time being, in order to line up with the working of [1], whose wave functions were real, we shall take $A=B=1$ (with wave-function normalization to be considered subsequently). We can now exhibit the two functions analogous to those in [1], but will simplify the notation by replacing the cos-sin representatives with the spinor set $\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

As in [1], we factorize the two molecular functions

$$\Psi^N(r; R, \phi) = \chi(R) \Phi_N(r; R, \phi), \quad N = 1, 2 \quad (3)$$

into a pure vibrational and an electronic factor, the latter depending parametrically on the vibrational coordinates. r arises from the electronic spinor’s up and down alternatives and is here an ‘electronic coordinate’ in the following sense: in the σ_z eigenstate

representation it takes two discrete values which are just $+1$ and -1 .

We now write out the two real superpositions of the states in Eq. (2) (the first using the coefficients $A=B=1$, as already noted, and the second its orthogonal partner) as the transposes (T) of $\Phi_N(r; R, \phi)$ together with their normalization factors. We shorten the notation by using

$$u(R) + u(-R) = f(R)C(R); \quad u(R) - u(-R) = f(R)S(R) \quad (4)$$

with an explanation for the choice of the symbols to be given shortly. We obtain

$$\Phi_1(r; R, \phi)^T = \frac{[C(R) + S(R) \cos(\phi), -S(R) \sin(\phi)]}{\sqrt{(C(R) + S(R) \cos(\phi))^2 + (S(R) \sin(\phi))^2}} \quad (5)$$

$$\Phi_2(r; R, \phi)^T = \frac{[-S(R) \sin(\phi), C(R) - S(R) \cos(\phi)]}{\sqrt{(S(R) \sin(\phi))^2 + (C(R) - S(R) \cos(\phi))^2}} \quad (6)$$

It can be shown that the two states are energy-degenerate (since they are obtained as a unitary transformation upon a complex conjugate pair, as in [17]); their orthogonality is obtained from an angle integration of the cross product over the range $\phi = (0, 2\pi)$. The normalization ensures a norm of 1 upon taking the self-inner product, equivalent to an integration over the electronic variable, as with the corresponding wave functions in [1].

It is clear that the change $\phi \rightarrow \phi + 2\pi$ leaves the functions sign-invariant, that is, there is no Berry phase in the full wave function, in agreement with the assertions made in several basic papers, e.g., [11, 15, 21]. The adiabaticity criterion is satisfied by the constraint to a single degenerate set, out of the multitudes of eigenfunctions of the Hamiltonian.

2.1. Explanation of the nomenclature

In [11] Section 6 and [LH6.11, LH6.14–LH6.16], for large k^2 , $u(R)$ was identified with the ground state wave function of the radial factor of a displaced 2D harmonic oscillator. In this limit, then

$$\begin{aligned} u(R) \begin{pmatrix} + \\ - \end{pmatrix} u(-R) &\propto R^{-\frac{1}{2}} \left\{ e^{-\frac{(R-k)^2}{2}} \begin{pmatrix} + \\ - \end{pmatrix} e^{-\frac{(R+k)^2}{2}} \right\} \\ &= 2R^{-\frac{1}{2}} e^{-\frac{R^2+k^2}{2}} \begin{pmatrix} \text{Cosh}(kR) \\ \text{Sinh}(kR) \end{pmatrix} \propto f(R) \begin{pmatrix} \text{Cosh}(kR) \\ \text{Sinh}(kR) \end{pmatrix} \end{aligned} \quad (7)$$

Thus, in the large k^2 limit $C(R), S(R)$ of Eq. (4) are actually the *Cosh*, *Sinh* functions, though this may not hold for lower values of k . However, it was shown in [16–18] that the same identification fits quantitatively extremely well the numerically obtained exact solutions of [11] for cubic symmetry and in [19] the numerical data of [20] for dihedral symmetries. Therefore, in the computed results to be presented in the sequel we shall identify C and S with the hyperbolic functions throughout the k range, bearing in mind that by the Longuet-Higgins et al. paper this is exact only for the large k , or near BO range. But, of course, this is the region of interest in this work.

3. The Born–Oppenheimer limit

We take now the $k \rightarrow \infty$ limit and, as noted in the lines just before [LH 6.9], this can also be written as $|u(-|R|)|/|u(|R|)| \rightarrow 0$. In our formalism (Eq. (4)) the BO limit is simply described by

$$S(R) \rightarrow C(R) \quad (8)$$

Download English Version:

<https://daneshyari.com/en/article/5379730>

Download Persian Version:

<https://daneshyari.com/article/5379730>

[Daneshyari.com](https://daneshyari.com)