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Compensation of the electronic geometric phase by the nuclear part of the wave-function

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Abstract. The nuclear equation in the Born–Oppenheimer scheme for electron–ion bound states is solved by a method that ensures that the nuclear part compensates for the geometrical (Berry) phase in the electronic part and that the total wave-function is single valued. The compensation occurs in a manner that keeps the energy of the state continuous even across a ‘topological transition’, i.e. for a change of parameters that removes the electronic degeneracy. The method ties the phase to the behaviour of the nuclear part near the conical intersection of potential surfaces. The consistency of the method is illustrated by *Gedankenexperiments* in a non-symmetric Jahn–Teller situation and a spin–orbit coupled doublet.

1. Introduction

Though the geometric or Berry phase is one of the most easily describable and demonstrable findings of modern physics, there are still some mystifying features in it [1–4]. In this note we shall limit our attention to quantal, molecular manifestations of the phase, with time reversal symmetry [5] (rather than classical or magnetically induced ones [6, 7]). Moreover, we shall dwell on the archetypal model, $E \otimes \varepsilon$ (the doubly degenerate electronic state interacting with a twofold vibrational mode), which gives rise to a conical intersection between adiabatic potential energy surfaces [8–12].

From the beginning, the role of degeneracies was regarded as essential (and even mandatory) for the existence of non-zero geometric phases (e.g. in section 3 of [1]). (In the discussion section we shall touch on the question of degeneracies for extended systems. This addresses the more recent discoveries of the phase in the electronic band-structure [13], in macroscopic polarization in solids [14–16].) Originally, in a molecular context, Longuet-Higgins [17] (and later Stone [18]) tied the multi-valuedness of an electronic wave function to the existence of degeneracy in the parameter space that is encircled by the system before it returns to its starting configuration.

However, the electronic wave-function is only one part of the quantal state of the material system. The other is the nuclear wave-function. This, or better its combination with the electronic part, has been the subject of numerous studies, both in solid state physics and molecular gas dynamics, especially with reference to the different procedures (adiabatic, non-adiabatic etc) used for disentangling the electronic from the nuclear motion [8, 19, 20]. In these, recent studies (which form the stepping board for the present work) it was found that in cases where an electronic degeneracy was involved, the choice of the procedures had immediate consequences in the calculation of molecular scattering cross-sections [21–24].

In previous studies in the literature it was made clear that the possibility of many-valuedness existed only for the electronic part (e.g. [9]). On the other hand, the full wavefunction (including all dynamical variables: those of the electrons and of the nuclei) had to be single valued in space, this requirement being fundamental in quantum mechanics, on which many quantization rules hinge (at the very least in a singly connected space, such that the particles have access to all points of the space). This means that the multi-valuedness of the electronic part has to be compensated by a similar multi-valuedness of the nuclear part. The latter is usually achieved by taking a non-integral value of the angular momentum associated with the nuclear vibrational motion [9, 12].

One of the issues which will be addressed is how the single valuedness of the total wavefunction is maintained as the location of the electronic degeneracy becomes displaced outside the closed trajectory of the nuclear motion. Then the nuclear part is also single valued, which would, by the foregoing considerations, require an integral angular momentum. But a finite change (e.g. from half-integral to integral value) in the angular momentum implies a finite change in the energy of the system. If we now go continuously from a degenerate situation to an infinitesimally close, non-degenerate situation, we reach the absurd conclusion that an infinitesimal cause (with almost no energy expenditure) engenders a finite energy change. We recall that in a magnetically induced Aharonov–Bohm effect the energy balance was shown to be ensured by the torque working on electrons [25]; in the molecular situation no similar compensation mechanism appears possible. The removal of degeneracy (named ‘topological transition’) was previously considered for the electronic part only [26].

In the next section we write out the nuclear equation [8, 19] and, applying a transformation introduced and used earlier [12, 27], we show that the energy of the system is (nearly) unchanged in a minute displacement of the degeneracy and that the single valuedness of the total wave function is ensured by the continuous variation of the phase.

2. The nuclear equations

As in earlier works [12, 28] we denote the pair of electronic and nuclear components, respectively, by $\zeta_1(r; \mathbf{q})$, $\zeta_2(r; \mathbf{q})$ and by $\chi_1(\mathbf{q})$, $\chi_2(\mathbf{q})$ with r and \mathbf{q} being the coordinates for electronic and (small amplitude) nuclear motions. (Several nuclear coordinates are implied by the (bold type) vector notation.) The total wave function is then

$$\psi(r; \mathbf{q}) = \sum_{i=1,2} \chi_i(\mathbf{q}) \zeta_i(r; \mathbf{q}) \quad (1)$$

in which the electronic parts are solutions of the equations

$$H_{el} \zeta_i(r; \mathbf{q}) = V_i(\mathbf{q}) \zeta_i(r; \mathbf{q}) \quad (i = 1, 2). \quad (2)$$

The electronic Hamiltonian H_{el} is a 2×2 matrix operator, depending parametrically on the nuclear coordinates. The V are adiabatic potential surfaces.

The nuclear equations are coupled differential equations for χ_1 and χ_2 involving the nuclear mass M , coordinates \mathbf{q} and the conjugate derivative operators ∇ ($\hbar = 1$). For their derivation and general form we refer to [8, 19, 27]

$$[-(2M)^{-1}(\nabla^2 + \tau_{11}^{(2)}) + V_1 - E] \chi_1 - (M)^{-1} \tau_{12}^{(1)} \nabla \chi_2 - (2M)^{-1} \tau_{12}^{(2)} \chi_2 = 0 \quad (3)$$

$$[-(2M)^{-1}(\nabla^2 + \tau_{22}^{(2)}) + V_2 - E] \chi_2 - (M)^{-1} \tau_{21}^{(1)} \nabla \chi_1 - (2M)^{-1} \tau_{21}^{(2)} \chi_1 = 0 \quad (4)$$

where

$$\tau_{12}^{(1)} = -\tau_{21}^{(1)*} = \langle \zeta_1 | \nabla | \zeta_2 \rangle = -\rho^2 \tau_{21}^{(1)} \quad (5)$$

$$\tau_{12}^{(2)} = -\tau_{21}^{(2)*} = \langle \zeta_1 | \nabla^2 | \zeta_2 \rangle = -\rho^2 \tau_{21}^{(2)} \quad (6)$$

$$\tau_{11}^{(2)} = \langle \zeta_1 | \nabla^2 | \zeta_1 \rangle = \tau_{22}^{(2)}.$$

The phase factor ρ ensures ‘parallel transport’ and is 1 for real electronic functions, but is complex for certain complex ones, such that it cannot be made real by a gauge transformation, as will be given in section 3.2. The asterisk denotes complex conjugation.

To solve (3) and (4) we set first

$$\chi = \chi_1 + i\rho\chi_2. \quad (7)$$

(A second solution is obtained by changing i to $-i$.) By adding up equation (3) and $i\rho$ times equation (4) we derive

$$\{-\nabla^2 - i(\rho)^{-1}\tau_{12}^{(1)}\nabla - i(\rho)^{-1}\tau_{12}^{(2)} - \tau_{11}^{(2)} - w\}\chi + \delta = 0 \quad (8)$$

where

$$w = 2M(E - V_1).$$

The last term given by

$$\delta = 2Mi(V_2 - V_1)\chi_2 \quad (9)$$

is small near the degeneracy, where $V_2 = V_1$. Now, we expect that the topological properties of the solution (e.g. its multivaluedness) are determined near the singularity [17]. Therefore, following [12, 27, 28], we temporarily proceed without δ . Next we assume a WKB type solution, of the form

$$\chi = \exp\left(i \int_{\Gamma} \mathbf{Q}(q) \cdot dq\right) \quad (10)$$

where the integration is along a path Γ connecting the initial and final points in the nuclear coordinate space. We now substitute equation (10) into equation (8), neglect in the spirit of WKB derivatives of \mathbf{Q} and obtain

$$\mathbf{Q}^2 + 2(\rho)^{-1}\tau_{12}^{(1)}\mathbf{Q} - (\rho)^{-1}\tau_{12}^{(2)} - \tau_{11}^{(2)} - w = 0. \quad (11)$$

The solutions to this equation are

$$\mathbf{Q} = -\tau_{12}^{(1)} \pm \sqrt{[(\rho)^{-1}\tau_{12}^{(1)}]^2 + (\rho)^{-1}\tau_{12}^{(2)} + \tau_{11}^{(2)} + w}. \quad (12)$$

This is a general result, valid semiclassically, whose quantum mechanical interpretation is that the exponential in (10) has to be summed for all paths (in the manner of path integrals). The presence of the potential V_1 in w will cause classically likely paths to be weighted strongly and to add up constructively.

3. Applications

We shall now examine the solution in the previous section for two cases, in which the nuclear motion (not necessarily cyclic) is confined to a circle in a plane. The nuclear coordinates q_1, q_2 are then naturally written as (q, ϕ) where

$$q_1 = q \cos \phi \quad q_2 = q \sin \phi.$$

3.1. A shifted Jahn–Teller system

The electronic Hamiltonian is an asymmetric modification of the linear Jahn–Teller case $E \otimes e$ [8, 10], and is shown below in a traditional form:

$$H_1 = E_{vib} \begin{bmatrix} -(kq \cos \phi - \alpha) & kq \sin \phi - \beta \\ kq \sin \phi - \beta & kq \cos \phi - \alpha \end{bmatrix} \quad (13)$$

(E_{vib} is an energetic measure of the cohesion between the nuclei. k is a dimensionless electron–vibration coupling constant. q is also dimensionless.) The separation between the pair of adiabatic potentials arising from H_1 is in units of E_{vib}

$$2V_1(\phi, q) = 2|k|\sqrt{[(q \cos \phi - a)^2 + (q \sin \phi - b)^2]} \quad (14)$$

where

$$a = \alpha/|k| \quad b = \beta/|k| \text{ and (for future use) } \eta \equiv \tan^{-1}(\alpha/\beta). \quad (15)$$

States:

$$\begin{aligned} \zeta_1(r; q, \phi) &= \left\{ [|k|(q \cos \phi - a) + V_1] \begin{pmatrix} 1 \\ 0 \end{pmatrix} + [|k|(q \sin \phi - b)] \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right\} \\ &\quad \times \{ [|k|(q \cos \phi - a) + V_1]^2 + [|k|(q \sin \phi - b)]^2 \}^{-1/2} \\ \zeta_2(r; q, \phi) &= \left\{ - [|k|(q \sin \phi - b)] \begin{pmatrix} 1 \\ 0 \end{pmatrix} + [|k|(q \cos \phi - a) + V_1] \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right\} \\ &\quad \times \{ [|k|(q \cos \phi - a) + V_1]^2 + [|k|(q \sin \phi - b)]^2 \}^{-1/2}. \end{aligned}$$

The condition for a degeneracy to lie inside the circle $q = \text{constant}$ is that

$$\sqrt{(\alpha^2 + \beta^2)} < |kq| \quad (16a)$$

or, by virtue of (15)

$$\sqrt{(a^2 + b^2)} < q \quad (16b)$$

and then the point of degeneracy (conical intersection) is at $\phi = \eta (\equiv \tan^{-1}(b/a))$

$$q = \sqrt{(\alpha^2 + \beta^2)}/|k| \quad (\text{or } \sqrt{(a^2 + b^2)} = q). \quad (17)$$

This result exemplifies the statement that conical degeneracies are not necessarily due to symmetry [17].

We now add to H_1 a (diagonal) guiding potential that confines the nuclear motion to a circular path $q = q_0$. (Guiding potentials appear in many situations; e.g. in the Aharonov–Bohm effect [7].) Then the only remaining nuclear coordinate is $q_0\phi$ and the derivative ∇ in the previous section is simply $(\partial/\partial\phi)/q_0$. Evaluating the quantities (5) and (6) from the states ζ_1 and ζ_2 shown above, we find

$$\rho = 1$$

(since the electronic states are real) and

$$\begin{aligned} \tau_{12}^{(1)} &= \langle \zeta_1(r; q_0, \phi) | \partial/\partial\phi | \zeta_2(r; q_0, \phi) \rangle / q_0 = \{ 1 - [(a^2 + b^2) - q_0\sqrt{(a^2 + b^2)} \cos(\phi - \eta)] \\ &\quad / [q_0^2 + a^2 + b^2 - 2q_0\sqrt{(a^2 + b^2)} \cos(\phi - \eta)] \} / 2q_0. \end{aligned} \quad (18)$$

and moreover, it is shown in [19] and [20] that

$$\tau_{12}^{(2)} = \tau'_{12} \quad (19)$$

and

$$\tau_{11}^{(2)} = [\tau_{12}^{(1)}]^2 \quad (20)$$

where

$$\tau'_{12} = (1/q_0) \partial/\partial\phi (\tau_{12}^{(1)}). \quad (21)$$

We substitute these results in equation (12) to obtain a simpler expression

$$Q = -\tau_{12}^{(1)} \pm \sqrt{(\tau'_{12} + w)}. \quad (22)$$

Since we wish to see what happens to the wave-function as the degeneracy is lifted from the system, we evaluate (19) at near-degeneracy, namely when the parameter $a^2 + b^2$ is approximately 1. From the expressions of $\tau_{12}^{(1)}$ given above it is apparent that τ'_{12} is zero and analytic at and near the degeneracy. Thus, we obtain

$$\chi_{\pm}(\phi) \approx \exp[-i \int_0^{\phi} d\phi' \tau_{12}^{(1)}(\phi') \pm i\phi\sqrt{w}]q_0. \quad (23)$$

For any choice of the energy E or w such that $(\sqrt{w})q_0$ is an integer, *independently* of whether the system has or has not a degeneracy, $\chi(\phi)$ has the right property of multi- or single valuedness (needed to match the analogous property of the electronic part). This arises from the integration of the result (19) (e.g. using formula 3.613 in [29]), between 0 and 2π to give

$$\begin{aligned} q_0 \int d\phi' \tau_{12}^{(1)}(\phi') &= \pi && \text{for } \sqrt{(a^2 + b^2)} < q_0 && (24) \\ &= 0 && \text{for } \sqrt{(a^2 + b^2)} > q_0. && (24') \end{aligned}$$

Thus, the energy does not change discontinuously as the circle $q = q_0$ along which the electron moves crosses the point of degeneracy. Clearly the nuclear factors compensate for the sign change in the electronic wave-function, as required, and this occurs for any value of the energy E of the electron–nuclear system. This ensures that, in a *Gedankenexperiment* where the inequality in (24) passes smoothly into that in (24') by a continuous change in the parameters (k , a or b) of the Hamiltonian, the total wave-function maintains the correct single valuedness, without a jump in the energy.

As an alternative to the preceding method, for solving the coupled nuclear equations (3) and (4), it might be tried to uncouple them by neglecting the last two terms (those involving τ_{12}). This approximation is termed the ‘single-surface’ approach in [27]. In equation (11) for Q , it is equivalent to the neglect of the middle two terms. Then Q is, for a general value of E , a continuous function of the parameters k , a and b (entering w through the adiabatic potential V_1). As a consequence, to perform the compensating switch in the nuclear phase angle, the energy must change discontinuously as the potential changes smoothly. This is an unsavoury situation and unlike the magnetic case [25] it is difficult to envisage an energy-balancing mechanism that can justify it. The source of the difficulty underlying this approach is that τ_{12} is singular at $q = 0$, and therefore cannot be neglected. Our approach, while approximative in other respects (namely by the neglect of δ in equation (8)), keeps τ_{12} properly.

3.2. A spin–orbit coupled doublet

While the previous example was relatively simple in that $\tau_{12}^{(1)}$ was essentially the derivative of the transformation angle ($\approx\phi/2$) divided by q , in the following example, due to Stone [18], this is no longer so. The spin–orbit coupling between the orbital doublet, whose strength may be positive or negative and of any magnitude, causes the adiabatic electronic wave-function to be complex. The electronic phase change (the Berry phase) round the closed loop $q = \text{constant}$ in the nuclear parameter plane is according to [18]

$$\Omega = \pi[1 - \gamma/\sqrt{(k^2q^2 + \gamma^2)}] \quad (25)$$

and differs from a simple sign change. The question to be explored is whether the phase change in the nuclear part (not treated in [18], or elsewhere) compensates the electronic phase change Ω and whether it does so continuously as the parameters of the Hamiltonian (e.g. k , γ) are varied.

Keeping as far as possible to Stone's notation, but retaining the column vector representation for the electronic base, we write for the electronic wave function components perturbed by the spin-orbit interaction

$$\psi'_1 = \zeta_1 = \begin{pmatrix} cC + isS \\ cS - isC \end{pmatrix} \quad (26)$$

$$\psi'_2 = \zeta_2 = \begin{pmatrix} cS + isC \\ -cC + isS \end{pmatrix} \quad (27)$$

where we have introduced the abbreviated notations:

$$s \equiv \sin \alpha \quad c \equiv \cos \alpha \quad (28)$$

with

$$\tan 2\alpha \equiv \gamma/kq \quad (29)$$

$$S \equiv \sin(\phi/2) \quad C \equiv \cos(\phi/2). \quad (30)$$

Further electronic wave-functions $\Psi_1(\phi)$ and $\Psi_2(\phi)$ were introduced in [18], that have the property of parallel transport, namely

$$\langle \Psi(\phi) | (\partial/\partial\phi) \Psi(\phi) \rangle = 0$$

and that differ from ψ'_1 and ψ'_2 by phase factors. A simple calculation shows that

$$\Psi_1(\phi) = \rho^{-1/2} \psi'_1 \quad (31)$$

and

$$\Psi_2(\phi) = \rho^{1/2} \psi'_2 \quad (32)$$

where the phase factor ρ introduced earlier in (5) is given by

$$\begin{aligned} \rho &= \exp(i\phi \sin 2\alpha) \quad (\sin 2\alpha = \gamma/\sqrt{(k^2q^2 + \gamma^2)}) \\ &= (\rho^{-1})^*. \end{aligned} \quad (33)$$

It is now straightforward to calculate the quantities entering the nuclear equations:

$$\tau_{12}^{(1)} = \langle \Psi_1 | \nabla | \Psi_2 \rangle = \rho k/2\sqrt{(k^2q^2 + \gamma^2)} = -\tau_{21}^{(1)*} \quad (34)$$

$$\tau_{12}^{(2)} = \langle \Psi_1 | \nabla^2 | \Psi_2 \rangle = i\rho\gamma k/[2q(k^2q^2 + \gamma^2)] = -\tau_{21}^{(2)*}. \quad (35)$$

Moreover,

$$\tau_{11}^{(1)} = \tau_{22}^{(1)} = 0 \quad (36)$$

$$\tau_{11}^{(2)} = \tau_{22}^{(2)} = -k^2/(k^2q^2 + \gamma^2). \quad (37)$$

We can now substitute these quantities into the solution of the nuclear equation for circular motion in the (q, ϕ) plane (equations (10)–(12)). The angle independence of these quantities makes the angular integration in the exponent in (10) trivial and one obtains the following nuclear function:

$$\chi = \exp i\phi/2\{kq/\sqrt{(k^2q^2 + \gamma^2)} + \sqrt{[8Mq^2(E - V_1) + \gamma kq/(2(k^2q^2 + \gamma^2))]\}. \quad (38)$$

(There are further solutions with different signs in the exponent. The following considerations are unaffected by these differences.)

We have noted above in equation (25) that the phase of the electronic component changes in a cycle ($\phi = 2\pi$) by the angle

$$\Omega = \pi[1 - \gamma/\sqrt{(k^2q^2 + \gamma^2)}]. \quad (39)$$

The choice of an appropriate energy E introduces a compensatory change in the nuclear factor and ensures the one-valuedness of the total wave-function. For our purposes it is essential to note that, as either the spin-orbit coupling strength γ is continuously varied (e.g. by a suitably oriented application of pressure on the system), or the parameter k is altered, the energy E will adjust continuously, as it should.

The situation is quite different in the ‘one-surface’ approximation, when we investigate how the energy adjusts in the limits (already considered by Stone [18]) of very small γ and q . In this approximation one neglects in (3) terms in χ_2 or equivalently in (11) the second and third term containing τ_{12} . Then one obtains

$$Q = \sqrt{(\tau_{11}^{(2)} + w)}.$$

When we substitute this in (10), using (37) we obtain

$$\chi(2\pi) = \exp\{i2\pi\sqrt{[2M(E - V_1)q^2 - k^2q^2/(k^2q^2 + \gamma^2)]}\}. \quad (40)$$

Here the energy E is to be so chosen as to compensate the multivaluedness of the electronic phase in (39). Evidently this can always be done. However, let us examine the exponent for the case where first $|\gamma|$ is arbitrarily small and then $|kq|$ decreases (by shrinking the orbit) to $|\gamma|$ and below it. Clearly, for a minute variation of the parameter q , the negative term will make a finite jump between -1 and 0 . Then also q^2E will make a finite jump (to maintain the single-valuedness of the total wave-function). But, since q itself is arbitrarily small, this means that E (which is an observable) makes an infinitely large jump under a continuous change of the Hamiltonian.

We conclude from the examples 3.1 and 3.2, that the single-surface approximation fails in describing the topological properties of the combined electron-nuclear system, precisely where the treatment of [12, 27, 28] gives consistent answers.

4. Discussion

We have shown, by detailed study of the cases above, that consistency in the single valuedness of the total wave-function can be achieved by tracing the phase near the degeneracy. This idea is of course germane to the works of Longuet-Higgins and Stone for the electronic wave-function component.

The approach was tested on a model which possesses a conical intersection with resemblance to an $H-H_2$ scattering configuration [28]. A numerical study using our (approximative) approach, namely that based on our equation (8) with $\delta = 0$, has given probabilities for the reactive state-to-state transitions that are very close to the exact ones (our equations (3) and (4)). (e.g. with a collision energy of 2 eV the $0 \rightarrow 1$ transition probabilities are 0.082 and 0.083 in the two methods respectively, table III in [28]. For comparison, the lower potential at its lowest is 5 eV below the upper one and the intersection lies at 3 eV.) Also the selection rule for $0 \rightarrow 1$ as an allowed transition by both methods contrasts with the forbiddenness in the ‘single-surface’ method. Likewise (as seen in table IV of [28]), inelastic scattering probabilities computed with the approximative approach gave good quantitative agreement with exact computations, unlike the ‘single-surface’ method. (For the $0 \rightarrow 0$ transition the values are 0.029, 0.030 and 0.185, respectively.) In a different paper, the cyclic integral of $\tau_{12}^{(1)}$ calculated for the triatomic molecule CH_2 was found to depend on the distance from the singularity, approaching π with decreasing distance [3]. This supports our taking $\tau_{12}^{(1)}$ as a derivative coupling, as in equation (34), near the intersection point.

At the same time, the effect of neglecting δ away from the intersection needs to be investigated. In a perturbational approach the first-order perturbation correction to the energy

raises the energy of the upper component χ_2 by just the right amount. The corresponding (first-order) correction to the wave-function

$$\delta\chi_2 = \sum \langle \chi_r | \delta \rangle \chi_r / (E - E_r) \quad (41)$$

(in which the summation runs over all solutions of (3) and (4)), excepting χ_2) vanishes due to the orthogonality of $\exp(ir\phi)$ for integer r . Higher order corrections and the convergence of the corrections need to be investigated. It is clear, however, that the topological properties of all terms are the same as those of χ_1 or χ_2 . Thus it can be claimed that the method of neglecting δ is appropriate for establishing the topological features of the wave-function, while incomplete as regards to the functional form of the solution (e.g. when the dependence on the radial nuclear coordinate q is reinstated).

In the issue of degeneracy, one source of the difficulty is that the geometrical phase angle relates to (and is conventionally expressed in terms of) a single wave-function [1], so that a partner wave-function, with which the former might be degenerate, seems uncalled for. However, as noted on p 901 of [15], 'Within a finite system, two alternative descriptions [in terms of the squared modulus of the wave-function, or in terms of its phase] are equivalent' and, moreover, we have elsewhere given integral relations that show that when the geometrical phase (more precisely, the 'connection') varies with time, so does the squared modulus (and vice versa) [30]. Now, the change of the latter implies the presence of at least one further wave-function component (which takes up, or supplies, the change in the modulus so that the norm is time independent, e.g. 1). Thus, one expects that for *all* finite systems, a degeneracy with some of these components will occur somewhere in the relevant portion of the parameter space. (As an example, Resta invokes other wave-function components to prove the gauge invariance of the geometrical phase, equation (44) in [15].)

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