Perspective

Perspective on "Some recent developments in the theory of molecular energy levels"

Longuet-Higgins HC (1961) Adv Spectrosc 2:429–472. The geometric phase effect

David R. Yarkony

Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218, USA

Abstract. Conical intersections of two potential-energy surfaces have the obvious, but important, effect of facilitating radiationless decay of the excited state. They also have a less obvious, but potentially more general, impact on single and multisurface dynamics through the geometric phase effect. The geometric phase effect, the subject of this perspective, requires that the adiabatic electronic wavefunction, real-valued and continuous with respect to nuclear coordinates, change sign when transported along a closed loop – a pseudorotation path – surrounding a single point of conical intersection. This was discovered by Longuet-Higgins in 1958 and carefully described in papers between 1958 and 1963. In the title article Longuet-Higgins demonstrates, in the context of a theoretical exposition of the dynamic Jahn–Teller (and Renner–Teller) effects, the connection between conical intersections and the geometric phase effect, and establishes the consequences of the geometric phase effect in nuclear dynamics. Since that time appreciation of the importance of the geometric phase effect has increased enormously aided in no small measure by Berry's 1984 work that established the role of the geometric phase effect in general adiabatic processes. That work spurred research in areas well outside the realm of molecular spectroscopy/dynamics. However, recent work demonstrating the prevalence of conical intersections of two Born–Oppenheimer states of the same symmetry suggests that conical intersections and the geometric phase effect will be issues of significant importance in molecular/chemical dynamics in the next century.

Key words: Geometric phase effect – Conical intersection – Molecular Aharonov–Bohm effect – Berry's phase

1 The 'origin' of the geometric phase effect

This perspective is concerned with the geometric phase effect, a property of a real-valued adiabatic wavefunc-

tion that results from a conical intersection involving the potential-energy surface of the state in question. It has profound and fundamental effects (modifying the basic Schrödinger equation) on nuclear motion. The geometric phase effect is known to be broadly applicable [1] as a result of Berry's highly influential 1984 work [2]; yet, the discovery of the geometric phase effect and the description of its potential impact, by Longuet-Higgins [3–5] 25 years earlier, are firmly rooted in the theoretical treatment of electronically nonadiabatic processes using the extension of the Born–Oppenheimer approximation, due to Born and Huang [6]. Interestingly although conical intersections were themselves known from the pioneering work of von Neumann and Wigner in 1929 [7] it was not until approximately 30 years later, long after the 1937 work of Jahn and Teller [8] on the effect bearing their names, that Longuet-Higgins [3–5] established the existence of the geometric phase effect in Jahn-Teller systems. The featured article, one of several papers Longuet-Higgins published between during the period 1958–1963 dealing with the geometric phase effect, presents a careful description of the geometric phase effect and its implications. Hence the choice of the article for this perspective.

1.1 Relation to the theory of nonadiabatic processes

Within the Born–Oppenheimer approximation the faster moving electrons create a potential-energy surface on which the nuclei move. This approximation forms the basis of our understanding of chemical bonding and molecular dynamics, see, for example, the article by Tully in this issue. Despite its central position in chemical theory, breakdowns of the Born–Oppenheimer approximation, electronically nonadiabatic processes, are ubiquitous. Nonadiabatic processes include charge-transfer [9] and electronic-quenching reactions, and many photochemical reactions are nonadiabatic [10], including some of nature's most basic processes: the initial radiationless energy transport step in photosynthesis [11] and the cis-trans isomerization that initiates the process of vision.

Most treatments of nonadiabatic processes do not abandon the Born–Oppenheimer idea of nuclear motion on potential-energy surfaces, instead in a nonadiabatic process the nuclei move on more than one Born–Oppenheimer potential-energy surface. Nonadiabatic transitions between potential-energy surfaces occur when the nuclei encounter a region where two potential-energy surfaces are in close proximity. Regions where the potential-energy surfaces intersect linearly, conical intersections, are of preeminent importance.

1.2 Conical intersections

A conical intersection of two potential-energy surfaces is depicted in Fig. 1 [12]. From this figure it is seen that for the excited state the conical intersection provides an efficient pathway for internal conversion: radiationless decay to the ground electronic state [10]. The effect of a conical intersection on ground-state dynamics is more subtle but is of enormous fundamental and practical importance. It might appear that for nuclear motion beginning on the ground-state potential-energy surface the conical intersection is of limited importance since it represents a mountain peak and therefore is comparatively inaccessible. In fact, for that reason nuclear motion on the ground-state potential-energy surface is not usually expected to sample the conical intersection directly; however the conical intersection can effect nuclear motion indirectly through the geometric phase effect [13]. In this case the particle need only traverse a closed path around the conical intersection. Proximity to the conical intersection is not the issue.

1.3 Geometric phase effect

The geometric phase effect, the signature property of a conical intersection, requires that the adiabatic electronic wavefunction (chosen to be real-valued and continuous with respect to nuclear coordinates) change sign when
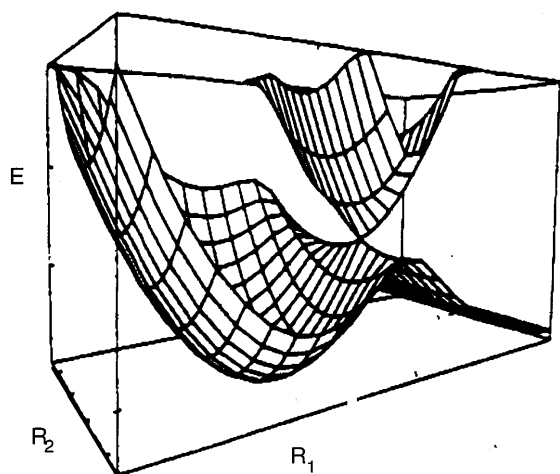

Fig. 1. A conical intersection of two potential-energy surfaces

transported along a closed loop – a pseudorotation path [14] – surrounding (only) a single point of conical intersection. The pseudorotation path for an X_3 molecule was presented in the featured work. Figure 2 presents a one-third of the pseudorotation path for H_3, following Ref. [15]. In the featured work Longuet-Higgins explains the mixing of the two wavefunctions, that are degenerate at the conical intersection point, along the pseudorotation path that leads to the sign change. This result can be understood using a simple Jahn–Teller model Hamiltonian. (see Sect. 3). Degeneracy is essential here. A nondegenerate wavefunction cannot exhibit the geometric phase effect since it must remain normalized, i.e., the leading coefficient in its perturbation expansion about a point $\mathbf{R}$ must always be large.

1.4 Implications: dynamic Jahn–Teller effect

Longuet-Higgins pointed out that the sign change in the electronic wavefunctions has profound implications for the associated nuclear Schrödinger equation. To see this note that since the electronic wavefunction changes sign along a circular path around the conical intersection, the vibrational wavefunction must compensate by also changing sign so that the overall wave function returns to itself after traversing the loop. Let θ denote the angle that transports nuclear configuration around the loop. Then a basis function for the nuclear wavefunction of the form $\Phi_m(\theta) = \exp im\theta$ is unacceptable since $\Phi_m(\theta + 2\pi) = \Phi_m(\theta)$. Rather functions of the form $\Phi_{m+1/2}(\theta) = \exp i(m + 1/2)\theta$ are required since $\Phi_{m+1/2}(\theta + 2\pi) = -\Phi_{m+1/2}(\theta)$. This is the origin of the well-known half-integer quantization in the dynamic Jahn–Teller effect [4].

2 Subsequent work

2.1 Molecular Aharonov–Bohm effect

The idea in the preceding section was subsequently used to consider to the single adiabatic state problem [16], where it is known as the molecular Aharonov–Bohm (MAB) effect [17] owing to its analogy with a magnetic effect discussed by Aharonov and Bohm [18]. In MAB theory the electronic wavefunction is altered to remove the sign change. It is multiplied by a phase factor so that it returns to itself after traversing a closed loop. The effect of this modification is to introduce into the nuclear Schrödinger equation a vector potential, analogous to the magnetic vector $\mathbf{A}$ in the standard semiclassical treatment of radiation [19]. This term must be included whether or not the system actually encounters the conical intersection. Thus through the geometric phase effect a conical intersection can exhibit a highly non local influence on nuclear dynamics.

Recently this idea has received much attention in the chemical physics community, brought about by accurate measurements [20–22] of rotational–vibrational energy transfer in collisions of H with H_2. Kuppermann [23–26]

Fig. 2. Symmetry-unique portion of the pseudorotation path for H_3, *outer plates*, around the D_{3h} conical intersection point, *center plates*, as originally discussed by Longuet-Higgins [4]. Each point on the path is the constructed from $(\cos\theta\, Q_y + \sin\theta\, Q_x)$. Present drawing from Ref. [15]. The third internal coordinate, not shown, is the D_{3h}-preserving ring breathing mode, Q_s
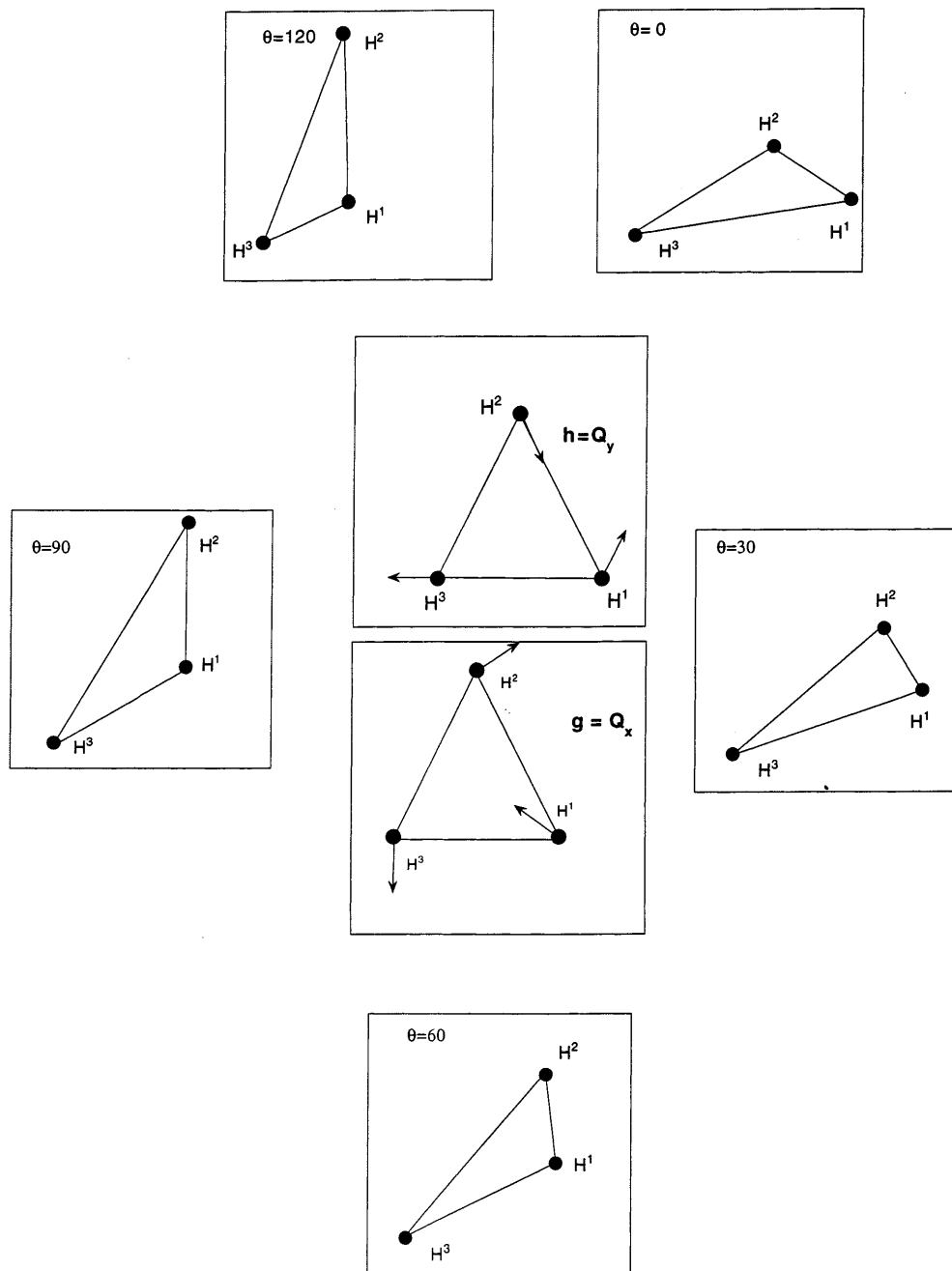
has argued that it is precisely the geometric phase effect that needs to be included in the adiabatic description of the reaction $H + H_2(v = 1, j) \rightarrow H + H_2(v = 0, j')$ to obtain agreement with experiment.

2.2 The quest for the geometric phase effect in optical spectroscopy

Berry's 1984 work led to manifestations of the geometric phase effect being detected outside the area of optical spectroscopy discussed by Longuet-Higgins. Observation of the geometric phase effect in molecular spectroscopy has proved surprisingly difficult. One reason for this difficulty is suggested in Sect. 3.

In 1986 the first apparent observation of a half-integer pseudorotation quantum number was reported [27]. The B band of Na_3 (interpreted as the $3^2E' - X^2E'$ transition) was observed through resonant two-photon ionization spectroscopy. A fit to the spectral data was obtained with a linear Jahn–Teller model, indicating the existence of the geometric phase effect; however, less than 2 years later ab initio calculations called this result into question, indicating that the transition in question was to the lowest, nondegenerate component, of a pseudo Jahn–Teller triple of electronic states [28]. Recent investigations at rotational resolution using resonant two-photon ionization and optical–optical double resonance spectroscopy [29, 30] have confirmed the absence of a geometric phase effect in this state. In fact it was not until

1998 that the first unambiguous demonstration of the geometric phase effect in Na_3 was reported on the basis of an analysis of the $A^2E'' \to X^2E'$ emission [31].

In the above-mentioned Na_3 studies the observation of the geometric phase effect was indirect, i.e., it is inferred by fitting the observed spectra to a detailed spectroscopic Hamiltonian that evinces the geometric phase effect. Preferable would be a direct observation, i.e., the observation of a 'spectral signature' of the geometric phase effect; however, this remains an elusive goal. It has been suggested the geometric phase effect could be "directly" observed using short-duration, coherent light pulses. In the experiment a nondegenerate ground state would be pumped to a degenerate excited state exhibiting the geometric phase effect and allowed to evolve until a second coherent pulse causes interference half a cycle later. The resulting interference would be evident in the fluorescence emission from the excited state [32–35]. This theoretical proposal of Cina has yet to be observed experimentally.

3 Current issues/mathematical formulation

Although the discovery of geometric phase effect is over 40 years old, it and related issues remain areas of active research. Below we illustrate in more precise terms the nature of the geometric phase effect as described above, and briefly outline some current issues in this field.

We begin by describing the origin of the geometric phase effect using the quadratic Jahn–Teller Hamiltonian of Longuet-Higgins [4]:

$$\boldsymbol{H}^{e}(\boldsymbol{Q}) = m(\boldsymbol{Q})\boldsymbol{I} + K^{(2)}(\boldsymbol{Q})\boldsymbol{\sigma}_z + \Lambda^{(2)}(\boldsymbol{Q})\boldsymbol{\sigma}_x \quad (1)$$

Here vectors (matrices) are written in boldface (bold italic), the $\mathbf{Q} = (Q_x, Q_y, Q_s)$ are the three standard Jahn–Teller coordinates, see Fig. 2, $\boldsymbol{\sigma}_w$ are the Pauli matrices, $K^{(l)}(\boldsymbol{Q}) = \sum_{i=1}^{l} k_i(\boldsymbol{Q})$, $\Lambda^{(l)}(\boldsymbol{Q}) = \sum_{i=1}^{l} \lambda_i(\mathbf{Q})$,

$$\begin{aligned} k_1(\boldsymbol{Q})/g_1(Q_s) &= Q_x \equiv \rho \cos\theta \\ \lambda_1(\boldsymbol{Q})/g_1(Q_s) &= Q_y \equiv \rho \sin\theta \end{aligned} \quad (2a)$$

$$\begin{aligned} k_2(\boldsymbol{Q})/g_2(Q_s) &= Q_x^2 - Q_y^2 = \rho^2 \cos 2\theta \\ \lambda_2(\boldsymbol{Q})/g_2(Q_s) &= -2Q_x Q_y = -\rho^2 \sin 2\theta \end{aligned} \quad (2b)$$

and $m(\boldsymbol{Q})$ is arbitrary in the present context. $g_1(Q_s)$ and $g_2(Q_s)$ are the Q_s-dependent parameters of the model. Note from Eq. (2a, b) that $\boldsymbol{H}^e$ has a conical intersection for $Q_x = Q_y = 0$ ($\rho = 0$).

$\boldsymbol{H}^e$ has eigenvalues [36]:

$$\begin{aligned} E_{\pm}&(\rho, \theta, Q_s) \\ &= m(\mathbf{Q}) \pm \rho|g_1(Q_s)| \\ &\quad \times \sqrt{[1 - \rho/\rho_c(Q_s)]^2 \pm 2\rho/\rho_c(Q_s)(\cos 3\theta \pm 1)} \;. \end{aligned} \quad (3)$$

Its eigenfunctions, the adiabatic electronic states, are

$$[\Psi^+(\mathbf{r}; \boldsymbol{Q}), \Psi^-(\mathbf{r}; \boldsymbol{Q})] = [(\psi_1(\mathbf{r}; \boldsymbol{Q}), \psi_2(\mathbf{r}; \boldsymbol{Q}))\boldsymbol{u}(\Theta(\boldsymbol{Q})]^{\dagger} \quad (4a)$$

where $\mathbf{r} \equiv (\mathbf{r}_1, \ldots, \mathbf{r}_{N^e})$ are the coordinates of the N^e electrons, ψ_1 and ψ_2 are the basis for $\boldsymbol{H}^e$, and $\boldsymbol{u}[\Theta(\boldsymbol{Q})]$ is given by

$$\boldsymbol{u}[\Theta(\boldsymbol{Q})] = \begin{pmatrix} \cos\Theta & \sin\Theta \\ -\sin\Theta & \cos\Theta \end{pmatrix} \quad (4b)$$

$$\tan 2\Theta(\rho, \theta, Q_s) = \frac{\sin\theta \mp (\rho/\rho_c)\sin 2\theta}{\cos\theta \pm (\rho/\rho_c)\cos 2\theta} \;. \quad (4c)$$

Here $\rho_c(Q_s) \equiv |g_1(Q_s)/g_2(Q_s)|$, and the upper (lower) signs in the radical in Eq. (3) and in Eq. (4c) are used if g_1g_2 is $> (<)0$.

From Eq. (4c) for small ρ, $\Theta = \theta/2$. In this case after a closed loop has been traversed, $\theta \to \theta + 2\pi$ but $\Theta \to \Theta + \pi$; therefore, from Eq. (4b) we see that $[\Psi^+(\mathbf{r}; \rho, \theta + 2\pi), \Psi^-(\mathbf{r}; \rho, \theta + 2\pi)] = -[\Psi^+(\mathbf{r}; \rho, \theta), \Psi^-(\mathbf{r}; \rho, \theta)]$. This is the geometric phase effect!

The situation is different for large ρ for which $\Theta = -\theta$ and so $[\Psi^+(\mathbf{r}; \rho, \theta + 2\pi), \Psi^-(\mathbf{r}; \rho, \theta + 2\pi)] = +[\Psi^+(\mathbf{r}; \rho, \theta), \Psi^-(\mathbf{r}; \rho, \theta)]$. The reason for this change is the existence of three more conical intersections at $\rho = \rho_c$ [36]. These additional conical intersections complicate the observation of the geometric phase effect. For further discussion of this point see Ref. [37].

As noted previously the key feature of the geometric phase effect is that it leads to a modification of the nuclear Schrödinger equation. This modification is described below.

The total wave function for a molecule can be expanded as

$$\Psi_k^T(\mathbf{r}, \mathbf{R}) = \sum_{I=1}^{N^a} \tilde{\chi}_I^k(\mathbf{R})\tilde{\Psi}_I^a(\mathbf{r}; \mathbf{R}) \;, \quad (5)$$

where $\mathbf{R} \equiv (\mathbf{R}_1, \ldots, \mathbf{R}_{N^{nuc}})$ are the coordinates of the N^{nuc} nuclei, in a space fixed frame, $\tilde{\chi}_I^k(\mathbf{R})$ are the nuclear wave functions and $\tilde{\Psi}_I^a(\mathbf{r}; \mathbf{R})$ are the adiabatic electronic wavefunctions which satisfy the standard (Coulombic) electronic Schrödinger equation

$$[H^e(\mathbf{r}; \mathbf{R}) - E_I^a(\mathbf{R})]\tilde{\Psi}_I^a(\mathbf{r}; \mathbf{R}) = 0 \quad (6)$$

with the total Hamiltonian given by $H^T(\mathbf{r}, \mathbf{R}) = \sum_{\alpha=1}^{N^{nuc}} (\frac{1}{2M_\alpha})\mathbf{p}_\alpha \mathbf{p}_\alpha + H^e(\mathbf{r}; \mathbf{R})$.

The difference between $\Psi_I^a(\mathbf{r}; \mathbf{R})$ and $\tilde{\Psi}_I^a(\mathbf{r}; \mathbf{R}) \equiv \exp iA^I(\mathbf{R})\Psi_I^a(\mathbf{r}; \mathbf{R})$ is crucial. As a consequence of the geometric phase effect, at each $\mathbf{R}$ the sign of $\Psi_I^a(\mathbf{r}; \mathbf{R})$ is arbitrary and path-dependent. Such a function is called double-valued, since it can be either $\pm\Psi_I^a(\mathbf{r}; \mathbf{R})$; however, the total wave function must be single-valued and so as noted previously the geometric phase effect must be compensated for by either choosing the phase factor $\exp iA^I(\mathbf{R})$ such that $\tilde{\Psi}_I^a(\mathbf{r}; \mathbf{R})$ is single-valued, or by the phase properties of $\tilde{\chi}_I^k(\mathbf{R})$. The only requirement on $A^I(\mathbf{R})$, sometimes referred to as the Longuet-Higgins phase [38], is that it change sign when transported in a closed loop around a conical intersection. The determination of $A^I(\mathbf{R})$ has been a topic of recent discussion [39, 40]. The second option is less frequently used since in general, although not for the Jahn–Teller effect, it is more difficult to implement.

Using Eq. (5) in the total Schrödinger equation $(H^T - E_k)\Psi_k^T = 0$ and taking $\langle\tilde{\Psi}_I^a(\mathbf{r};\mathbf{R})|$ the nuclear Schrödinger equation becomes

$$\begin{aligned}&\left[\sum_{\alpha=1}^{N^{nuc}}\frac{1}{2M_\alpha}\Big[(\mathbf{p}_\alpha+\mathbf{A}_\alpha^I)^2-(\mathbf{p}_\alpha+\mathbf{A}_\alpha^I)\cdot i\mathbf{f}_\alpha^{II}(\mathbf{R})\right.\\&\left.-i\mathbf{f}_\alpha^{II}(\mathbf{R})\cdot(\mathbf{p}_\alpha+\mathbf{A}_\alpha^I)\Big]+\bar{E}_I(\mathbf{R})-E_k\right]\tilde{\chi}_I^k(\mathbf{R})\\&=-\sum_{J(\neq I)}^{N^a}\exp[iA_{JI}(\mathbf{R})]\sum_{\alpha=1}^{N^{nuc}}\left[\frac{1}{2M_\alpha}\{k_\alpha^{IJ}(\mathbf{R})+(\mathbf{p}_\alpha+\mathbf{A}_\alpha^J)\right.\\&\left.\cdot i\mathbf{f}_\alpha^{IJ}(\mathbf{R})+i\mathbf{f}_\alpha^{IJ}(\mathbf{R}).\,(\mathbf{p}_\alpha+\mathbf{A}_\alpha^J)\}\right]\tilde{\chi}_J^k(\mathbf{R})\;,\end{aligned}\tag{7}$$

where $\mathbf{A}_\alpha^I(\mathbf{R})=\nabla_\alpha A^I(\mathbf{R})$, $A_{JI}(\mathbf{R})=A_J(\mathbf{R})-A_I(\mathbf{R})$, the first derivative couplings or simply the derivative couplings [41], $\mathbf{f}_\alpha^{JI}(\mathbf{R})$, are given by

$$\mathbf{f}_\alpha^{JI}(\mathbf{R})=\langle\Psi_J(\mathbf{r};\mathbf{R})|\nabla_\alpha\Psi_I(\mathbf{r};\mathbf{R})\rangle_r\tag{8}$$

$$\bar{E}_I(\mathbf{R})=E_I(\mathbf{R})+\sum_{\alpha=1}^{N^{nuc}}\frac{k_\alpha^{II}}{2M_\alpha}\tag{9}$$

and

$$\begin{aligned}k_\alpha^{JI}(\mathbf{R})&=\langle\nabla_\alpha\Psi_J(\mathbf{r};\mathbf{R})\,|\cdot\nabla_\alpha\Psi_I(\mathbf{r};\mathbf{R})\rangle_r\\&=\sum_{K=1}^{N^{CSF}}\mathbf{f}_\alpha^{KJ}(\mathbf{R})^*\cdot\mathbf{f}_\alpha^{KI}(\mathbf{R})\;.\end{aligned}\tag{10}$$

If Ψ_I^a is chosen to be real then $\mathbf{f}_\alpha^{II}(\mathbf{R})=0$, otherwise it is purely imaginary.

Of particular interest is the adiabatic, or MAB, limit $N^a=1$ where $\Psi_k^T=\exp[iA^I(\mathbf{R})]\Psi^a(\mathbf{r};\mathbf{R})\tilde{\chi}_I^k(\mathbf{R})$ and Ψ^a is real-valued. The nuclear Schrödinger equation is

$$\left[\sum_{\alpha=1}^{N^{nuc}}\frac{+1}{2M_\alpha}\Big[(\mathbf{p}_\alpha+\mathbf{A}_\alpha^I)^2\Big]+E_I(\mathbf{R})-E_k\right]\tilde{\chi}_I^k(\mathbf{R})=0\;.\tag{11}$$

This clearly demonstrates that the effect of the conical intersection is to add a vector potential, analogous to the vector potential $\mathbf{A}$ in semiclassical electromagnetic theory, to the nuclear Schrödinger equation in the adiabatic limit. Calculations based on Eq. (11) have recently been reported [39, 42, 43].

For the Jahn–Teller problem $N^a=2$ is required. The evaluation of $k_\alpha^{JI}(\mathbf{R})$ in Eq. (7) is quite costly [44, 45]. It is therefore convenient to approximate $k_\alpha^{JI}(\mathbf{R})$ by the second term in Eq. (10) with $N^{CSF}=N^a$. A somewhat stronger version of this assumption is found in the featured work. In this case for real $\Psi_I^a(\mathbf{r};\mathbf{R})$ and assuming $\mathbf{A}^J=\mathbf{A}^I=\mathbf{A}$, Eq. (7) becomes

Equation (12) illustrates the standard interpretation of $\mathbf{f}_\alpha^{IJ}$ as coupling the two electronic states in question. It is therefore interesting to observe the effect of the following transformation to a complex electronic basis used by Longuet-Higgins in the featured article (see also Ref. [46]).

$$\Psi^T\equiv\tilde{\Psi}_+\tilde{\chi}_-+\tilde{\Psi}_-\tilde{\chi}_+\;,\tag{13a}$$

where

$$\begin{aligned}\tilde{\Psi}_+&=(1/\sqrt{2})(\tilde{\Psi}_I^a+i\tilde{\Psi}_J^a)\quad\tilde{\Psi}_-=(1/\sqrt{2})(\tilde{\Psi}_I^a-i\tilde{\Psi}_J^a)\\\tilde{\chi}_-&=(1/\sqrt{2})(\tilde{\chi}_I-i\tilde{\chi}_J)\quad\tilde{\chi}_+=(1/\sqrt{2})(\tilde{\chi}_I+i\tilde{\chi}_J)\;.\end{aligned}\tag{13b}$$

Then $\tilde{\chi}_\pm$ satisfy (see also Ref. [46])

$$\begin{aligned}&\begin{pmatrix}h(\mathbf{p}_\alpha,\mathbf{A}_\alpha,\mathbf{f}_\alpha^{IJ})+\bar{E}_{IJ}^{avg}(\mathbf{R})-E_k&(E_I^a-E_J^a)/2\\(E_I^a-E_J^a)/2&h(\mathbf{p}_\alpha,\mathbf{A}_\alpha,-\mathbf{f}_\alpha^{IJ})+\bar{E}_{IJ}^{avg}(\mathbf{R})-E_k\end{pmatrix}\\&\times\begin{pmatrix}\tilde{\chi}_-^k(\mathbf{R})\\\tilde{\chi}_+^k(\mathbf{R})\end{pmatrix}=\begin{pmatrix}0\\0\end{pmatrix}\;,\end{aligned}\tag{14a}$$

where $\bar{E}_{IJ}^{avg}(\mathbf{R})=[\bar{E}_I^a(\mathbf{R})+\bar{E}_J^a(\mathbf{R})]/2$ and

$$\begin{aligned}h(\mathbf{p}_\alpha,\mathbf{A}_\alpha,\mathbf{f}_\alpha^{IJ})&=\sum_{\alpha=1}^{N^{nuc}}\frac{1}{2M_\alpha}\Big[(\mathbf{p}_\alpha+\mathbf{A}_\alpha)^2-(p_\alpha+\mathbf{A}_\alpha)\cdot\\&i\mathbf{f}_\alpha^{JI}(\mathbf{R})-i\mathbf{f}_\alpha^{JI}(\mathbf{R})\cdot(\mathbf{p}_\alpha+\mathbf{A}_\alpha)\Big]\;.\end{aligned}$$

Using the replacement $\tilde{\chi}=\chi\exp(-iA)$ the total wavefunction can be rewritten in terms of double-valued functions as $\Psi_k^T\equiv\Psi_+\chi_-^k+\Psi_-\chi_+^k$. In terms of $\chi_\pm$ Eq. (14a) becomes

$$\begin{aligned}&\left[\sum_{\alpha=1}^{N^{nuc}}\frac{1}{2M_\alpha}(\mathbf{p}_\alpha+\mathbf{f}_\alpha^{IJ})^2+E_I(\mathbf{R})-E_k\right]\chi_-^k\\&+i\Big[(E_I^a-E_J^a)/\sqrt{2}\Big]\chi_2^k=0\\&-i\Big[(E_I^a-E_J^a)/\sqrt{2}\Big]\chi_2^k+\left[\sum_{\alpha=1}^{N^{nuc}}\frac{1}{2M_\alpha}(\mathbf{p}_\alpha-\mathbf{f}_\alpha^{IJ})^2\right.\\&\left.+E_J(\mathbf{R})-E\right]\chi_-^k=0.\end{aligned}\tag{14b}$$

The most interesting aspect of Eq. (14a, b) is that the derivative coupling is transferred from the off-diagonal term to the diagonal term and the coupling is purely of the potential form.

Note the similarity between the term involving $(\mathbf{p}_\alpha+\mathbf{f}_\alpha^{IJ})^2$ in Eq. (14b) and that involving $(\mathbf{p}_\alpha+\mathbf{A}_\alpha^I)^2$ in Eq. (11). Thus it is interesting to ask whether the replacement $\mathbf{A}_\alpha^I\to\mathbf{f}_\alpha^{IJ}$ is appropriate. In a sense it is, but

$$\begin{pmatrix}\sum_{\alpha=1}^{N^{nuc}}\frac{1}{2M_\alpha}(\mathbf{p}_\alpha+\mathbf{A}_\alpha)^2+\bar{E}_I(\mathbf{R})-E_k&\sum_{\alpha=1}^{N^{nuc}}\frac{-1}{2M_\alpha}\Big[(\mathbf{p}_\alpha+\mathbf{A}_\alpha)\cdot i\mathbf{f}_\alpha^{IJ}(\mathbf{R})+i\mathbf{f}_\alpha^{IJ}(\mathbf{R})\cdot(\mathbf{p}_\alpha+\mathbf{A}_\alpha)\Big]\\\sum_{\alpha=1}^{N^{nuc}}\frac{-1}{2M_\alpha}\Big[(\mathbf{p}_\alpha+\mathbf{A}_\alpha)\cdot i\mathbf{f}_\alpha^{JI}(\mathbf{R})+i\mathbf{f}_\alpha^{JI}(\mathbf{R})\cdot(\mathbf{p}_\alpha+\mathbf{A}_\alpha)\Big]&\sum_{\alpha=1}^{N^{nuc}}\frac{1}{2M_\alpha}(\mathbf{p}_\alpha+\mathbf{A}_\alpha)^2+\bar{E}_J(\mathbf{R})-E_k\end{pmatrix}\begin{pmatrix}\tilde{\chi}_I^k(\mathbf{R})\\\tilde{\chi}_J^k(\mathbf{R})\end{pmatrix}$$
$$=\begin{pmatrix}0\\0\end{pmatrix}\;.\tag{12}$$

ONLY when certain approximations are valid. To see this define a candidate $\bar{A}^I$ by

$$\bar{A}^I[\alpha, C_\rho(\mathbf{R}), \mathbf{f}^{IJ}] = \int_{\alpha, C_\rho} \mathbf{f}^{IJ}(\mathbf{R}') \cdot d\mathbf{R}' \ , \tag{15}$$

where $C_\rho(\mathbf{R})$ is a circle of radius ρ centered at $\mathbf{R}$, $[\alpha, C_\rho(\mathbf{R})]$ denotes an arc of $\alpha°$ on $C_\rho(\mathbf{R})$ and $\mathbf{f}^{IJ} = (\mathbf{f}_1^{IJ}, \ldots, \mathbf{f}_{N^{nuc}}^{IJ})$. Then we have the following [47]:

$$\bar{A}^I[2\pi, C_\rho(\mathbf{Q}), \mathbf{f}^{IJ}] \xrightarrow[\rho \to 0]{} \pi \quad \text{if } \mathbf{Q} = \mathbf{R}_x \tag{16a}$$

$$\bar{A}^I[2\pi, C_\rho(\mathbf{Q}), \mathbf{f}^{IJ}] \xrightarrow[\rho \to 0]{} 0 \quad \text{if } \mathbf{Q} \neq \mathbf{R}_x \ , \tag{16b}$$

where $\mathbf{R}_x$ is a point of conical intersection of states I and J. This is the requisite property for an $\mathbf{A}^I$. However, it must hold for circles of arbitrary ρ. For finite ρ Eq. (16a, b) is only an approximation since $\mathbf{f}^{IJ}$ has a nonvanishing curl [48]. Within the two-state approximation, $N^{CSF} = N^a$, the curl does in fact vanish [49]. Thus in this case the identification of $\bar{A}^I$ with A^I is appropriate; although, for $N^{CSF} > N^a$ it is only an approximation [50].

One way around this dilemma is to use an approximate derivative coupling that has the same singularity as $\mathbf{f}^{IJ}$, so that Eq. (16a, b) is satisfied, but is explicitly the gradient of a scalar so that its curl vanishes. The details of such a construction – applicable in favorable situations – can be found in Ref. [40].

4 The future

The geometric phase effect described in the title work results from a symmetry-required conical intersection, a comparatively rare occurrence in molecular systems. However the recent development of efficient algorithms [51, 52] for locating accidental conical intersections of two states of the same symmetry, an issue in which Longuet-Higgins also played a seminal role [53], has shown that conical intersections, rather than being rare occurrences, are a common phenomenon. The absence of point group symmetry as a prerequisite for these intersections and the recent discovery of unexpected loci for the seams of conical intersection [54] suggest that in the future conical intersections in general and the geometric phase effect in particular will be encountered often and in unexpected situations.

References

1. Shapere A, Wilczek F (eds) (1989) Geometric phases in physics. World Scientific, Singapore
2. Berry MV (1984) Proc R Soc Lond Ser A 392: 45
3. Longuet-Higgins HC, Öpik U, Pryce MHL, Sack RA (1958) Proc Roy Soc Lond Ser A 244: 1
4. Longuet-Higgins HC (1961) Adv Spectrosc 2: 429
5. Herzberg G, Longuet-Higgins HC (1963) Discuss Faraday Soc 35: 77
6. Born M, Huang K (1954) Dynamical theory of crystal lattices. Oxford University Press, Oxford
7. von Neumann J, Wigner E (1929) Phys Z 30: 467
8. Jahn HA, Teller E (1937) Proc R Soc Lond Ser A 161: 220
9. Baer M, Ng CY (eds) (1991) State-selected and state-to-state ion-molecule reaction dynamics: parts 1 and 2, Vol 82. Wiley, New York
10. Michl J, Bonacic-Koutecky V (1990) Electronic aspects of organic photochemistry. Wiley, New York
11. Hu X, Schulten K (1997) Phys Today 50: 28
12. Kash PW, Waschewsky GCG, Morss RE, Butler LJ, Francl MM (1994) J Chem Phys 100: 3463
13. Mead CA (1980) J Chem Phys 72: 3839
14. Berry RS (1960) J Chem Phys 32: 933
15. Yarkony DR (1996) J Phys Chem 100: 18612
16. Mead CA, Truhlar DG (1979) J Chem Phys 70: 2284
17. Mead CA (1980) Chem Phys 49: 23
18. Aharonov Y, Bohm B (1959) Phys Rev 115: 485
19. Schiff LI (1960) Quantum mechanics. McGraw-Hill, New York
20. Kliner DAV, Rinnen K-D, Zare RN (1990) Chem Phys Lett 166: 107
21. Kliner DAV, Adelman DE, Zare RN (1991) J Chem Phys 95: 1648
22. Neuhauser D, Judson RS, Kouri DJ, Adelman DE, Shafer NE, Kliner DAV, Zare RN (1992) Science 257: 519
23. Kuppermann A, Wu Y-SM (1993) Chem Phys Lett 205: 577
24. Wu Y-SM, Kuppermann A (1993) Chem Phys Lett 201: 178
25. Wu Y-SM, Kuppermann A (1995) Chem Phys Lett 235: 105
26. Kuppermann A (1996) In: Wyatt RE, Zhang JZH (eds) Dynamics of molecules and chemical reactions. Dekker, New York, pp 411–472
27. Delacrétaz G, Grant ER, Whetten RL, Wöste L, Zwanziger JW (1986) Phys Rev Lett 56: 2598
28. Cocchini F, Upton TH, Andreoni W (1988) J Chem Phys 88: 6068
29. Ernst WE, Rakowsky S (1995) Phys Rev Lett 74: 58
30. Ernst WE, Rakowsky S (1995) Ber Bunsenges Phys Chem 99: 441
31. Busch HV, Dev V, Eckel H-A, Kasahara S, Wang J, Demtröder W, Sebald P, Meyer W (1998) Phys Rev Lett 81: 4584
32. Romero-Rochín V, Cina JA (1989) J Chem Phys 91: 6103
33. Cina JA, Romero-Rochin V (1990) J Chem Phys 93: 3844
34. Cina JA (1991) Phys Rev Lett 66: 1146
35. Cina JA, Smith TJ, Romero-Rochín V (1993) In: Prigogine I, Rice SA (eds) Advances in Chemical Physics, Vol 83. Wiley, p 1
36. Zwanziger JW, Grant ER (1987) J Chem Phys 87: 2954
37. Sadygov RG, Yarkony DR (1999) J Chem Phys 110: 3639
38. Baer M (1997) J Chem Phys 107: 2694
39. Kendrick B, Pack RT (1996) J Chem Phys 104: 7502
40. Yarkony DR (1996) J Chem Phys 110: 701
41. Lengsfield BH, Yarkony DR (1992) In: Baer M, Ng C-Y (eds) State-selected and state-to-state ion-molecule reaction dynamics: part 2 theory, Vol 82. Wiley, New York, pp 1–71
42. Kendrick B, Pack RT (1996) J Chem Phys 104: 7475
43. Kendrick B (1997) Phys Rev Lett 79: 2431
44. Saxe P, Yarkony DR (1987) J Chem Phys 86: 321
45. Jensen JO, Yarkony DR (1988) J Chem Phys 89: 3853
46. Baer M (1997) J Chem Phys 107: 10662
47. Yarkony DR (1997) J Phys Chem A 101: 4263
48. Mead CA, Truhlar DG (1982) J Chem Phys 77: 6090
49. Baer M (1975) Chem Phys Lett 35: 112
50. Mead CA (1983) J Chem Phys 78: 807
51. Radazos IN, Robb MA, Bernardi MA, Olivucci M (1992) Chem Phys Lett 197: 217
52. Yarkony DR (1996) Rev Mod Phys 68: 985
53. Longuet-Higgins HC (1975) Proc R Soc Lond Ser A 344: 147
54. Yarkony DR (1998) Acc Chem Res 31: 511