J. Chem. Sci. Vol. 124, No. 1, January 2012, pp. 115–120. © Indian Academy of Sciences.

Dynamics study of a three-fold pseudo-Jahn–Teller system using the extended Longuet–Higgins formalism[#]

BIPLAB SARKAR[a,b] and A J C VARANDAS[a,*]

[a]Departmento de Química, Universidade de Coimbra, 3004 535 Coimbra, Portugal

[b]On study leave from the Department of Chemistry, North-Eastern Hill University, Shillong 793 022, India

e-mail: varandas@qtvs1.qui.uc.pt

Abstract. An extended Longuet–Higgins formalism recently utilized to obtain generalized Born–Oppenheimer equations including the geometrical phase effect has been used to study a three-fold pseudo-Jahn–Teller type electronic degeneracy. The results of dynamics calculations carried out with the novel formalism are compared with Born–Oppenheimer (geometrical phase ignored), extended Born–Oppenheimer, and coupled three-state ones for the same system. The theory shows unprecedented simplicity while depicting all features.

Keywords. Born–Oppenheimer approximation; geometrical phase effect; extended Longuet–Higgins theorem.

1. Introduction

The geometrical phase (GP) effect is a quantum phenomenon that plays an important role in molecular dynamics. The Born–Oppenheimer (BO) treatment[1] considers the fact that slow-moving nuclei are distinguishable from fast moving electrons in molecular systems. This distinction helps to impose the BO approximation,[2] which states that the nuclear and electronic motions are essentially uncoupled. Accordingly, the nuclei move on a single potential energy surface (PES). For polyatomic systems, such PES's can intersect conically with the topology of a diabolo, and under such a situation the BO approximation breaks down. Herzberg and Longuet–Higgins[3] have shown in their pioneering work that a real-valued electronic wave function changes sign when the nuclear coordinates traverse a closed path encircling a conical intersection, and corrected this deficiency with a complex phase factor in the electronic part that makes unique the total electronuclear wavefunction. An *ab initio* demonstration of the Longuet–Higgins (LH) theorem[4] has been provided, which stressed that the crossing need not be forced by symmetry.[5] Because a formal systematization of the involved closed-path geometrical phase in quantum mechanics has been given by Berry,[6] the effect is also known under his name. Moreover, due to the similarity of the involved differential equations with those of a charged particle moving in the presence of a magnetic solenoid, it is also often referred to[7] as the molecular Aharonov–Bohm effect. Suffice to say that it arises in the vibronic problem whenever one insists to separate the fast motion of the electrons from the slow vibrational degrees of freedom as it is done in the BO approximation.

Conical intersections have important consequences in dynamics, with the subject having achieved modern interest after the Mead and Truhlar vector potential approach.[8] The signature of GP in reaction dynamics has since been the theme of debate, and the subject has been studied extensively both by theoreticians and experimentalists for the last four decades.[9–19] The effect of GP has been observed in many Jahn–Teller molecules from the simplest H_3^+ ion[20] to fullerenes[21] (the list can be numerous and hence only two references have been indicated from which others can be obtained by cross-referencing).

The Jahn–Teller (JT) effect[22] arises from the coupling of degenerate electronic states with degenerate vibrational modes in highly symmetrical molecules, clusters or crystals.[10] Ham[23] has shown that the two-mode $E \otimes e$ Jahn–Teller system is an example of GP and later Aitchison[24] has also discussed it in a more general context. The linear octahedral $T \otimes (e \oplus t_2)$ JT system, which couples an electronic triplet state to triply and doubly degenerate phonon modes, has a sign change phenomenon similar to that found in $E \otimes e$.[25] Another important example is the coupling of a triply degenerate electronic state (T_2) with a triply degenerate normal mode (t_2) in systems of tetrahedral or cubic

[#]Dedicated to Prof. N Sathyamurthy on his 60th birthday

[*]For correspondence

symmetry, so-called $T_2 \otimes t_2$ JT effect.[26–28] The $T_2 \otimes t_2$ JT effect is a widespread phenomenon in transition-metal complexes or crystals of tetrahedral or cubic symmetry.[29] In organic chemistry, the methane cation (CH_4^+) is a fundamental system exhibiting the $T_2 \otimes t_2$ JT effect.[30]

Manolopoulos and Child[31] used a model of Hamiltonian to study the sets of possible sign changes when N real quantum states are transported adiabatically around a N-fold degeneracy. Baer *et al.*[32,33] and Sarkar and Adhikari[34,35] focused on the topological features and formulated an extended Born–Oppenheimer equation for a three-state electronic manifold. The relationship between the mixing angle and GP has also been established.[34–38] From the electronic structure point of view, the theme has been popularized by Yarkony.[13] Opalka and Domcke[30] having modelled a PES for a three-fold degeneracy in CH_4^+ system. Recently, Varandas[39] used Lie group symmetry to study N-fold degeneracies in JT systems and demonstrated by the method of *reductio ad absurdum* the following extension of the LH theorem: *No N-fold linear JT degeneracy can have more than one pair of adiabatic electronic states that change sign upon being parallel transported in configuration space along a loop that encircles the degeneracy point.* More recently, the systematic derivation of the dynamical equations for such a JT and pseudo-JT system has been communicated.[40] In the present work, we discuss the Generalized Born–Oppenheimer (GBO) formulation of such dynamical equations using the extended LH (ELH) theorem for three-fold electronic JT manifolds which is readily extendable to manifolds of arbitrary dimension. Comparisons of the dynamics using various methods on this model are also presented.

2. Theoretical development

The detailed approach from Schrödinger's equation (SE) of the complete many-body problem has been discussed earlier,[40] but for the sake of completeness we will give a brief account of the equations involved in the dynamics. Consider the nuclear motion restricted to a three-state electronic manifold. Without lacking generality, let the three states be real and decoupled from the rest keeping the three states coupled among themselves. Any two of them (say, the nuclear wave functions χ_i and χ_j) may be coupled first, followed by coupling of the resultant to the third (χ_k). Assuming that the electronic wave functions (say, ψ_i, ψ_j and ψ_k) form a real orthogonalized set, and following Longuet–Higgins,[4] define next the intermediate wave function

$$\tilde{\chi}_{ij} = \chi_i + \imath \chi_j \,, \tag{1}$$

where $\imath$ is the imaginary unit, and the complex nature of the wave function is indicated by the tilde. Using the fact that $V_i \simeq V_j$ in the vicinity of the degeneracy, where the nuclear wave functions (χ_i and χ_j) are also known[41] to approach zero, one may write after some mathematical manipulation[36,37]

$$\begin{aligned} -\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ij} + (V_i - E)\tilde{\chi}_{ij} - \frac{\hbar^2}{2\mu}(\langle\psi_i|\nabla\psi_j\rangle)^2\tilde{\chi}_{ij} \\ + \frac{\imath\hbar^2}{2\mu}[2\langle\psi_i|\nabla\psi_j\rangle\cdot\nabla + \nabla\langle\psi_i|\nabla\psi_j\rangle]\tilde{\chi}_{ij} \\ = 0, \end{aligned} \tag{2}$$

$$\begin{aligned} -\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ij} + (V_j - E)\tilde{\chi}_{ij} - \frac{\hbar^2}{2\mu}(\langle\psi_i|\nabla\psi_j\rangle)^2\tilde{\chi}_{ij} \\ + \frac{\imath\hbar^2}{2\mu}[2\langle\psi_i|\nabla\psi_j\rangle\cdot\nabla + \nabla\langle\psi_i|\nabla\psi_j\rangle]\tilde{\chi}_{ij} \\ = 0. \end{aligned} \tag{3}$$

Similarly, the new intermediate hybrid wave function $\tilde{\chi}_{ij}$, can now be coupled with χ_k. Defining next

$$\tilde{\chi}_{ijk} = \chi_i + \imath\chi_j + \imath\chi_k \,, \tag{4}$$

and recalling that $V_j \simeq V_k$ and the fact that χ_k is known to vanish at the conical intersection,[41] gives:

$$\begin{aligned} -\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ijk} + (V_j - E)\tilde{\chi}_{ijk} - \frac{\hbar^2}{2\mu}(\langle\psi_i|\nabla\psi_j\rangle)^2\tilde{\chi}_{ij} \\ + \frac{\imath\hbar^2}{2\mu}[2\langle\psi_i|\nabla\psi_j\rangle\cdot\nabla + \nabla\langle\psi_i|\nabla\psi_j\rangle]\tilde{\chi}_{ij} \\ - \frac{\hbar^2}{2\mu}(\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle)^2\tilde{\chi}_{ijk} \\ + \frac{\imath\hbar^2}{2\mu}[2\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle\cdot\nabla + \nabla\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle]\tilde{\chi}_{ijk} \\ = 0, \end{aligned} \tag{5}$$

$$\begin{aligned} -\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ijk} + (V_k - E)\tilde{\chi}_{ijk} \\ - \frac{\hbar^2}{2\mu}(\langle\psi_i|\nabla\psi_j\rangle)^2\tilde{\chi}_{ij} \\ + \frac{\imath\hbar^2}{2\mu}[2\langle\psi_i|\nabla\psi_j\rangle\cdot\nabla + \nabla\langle\psi_i|\nabla\psi_j\rangle]\tilde{\chi}_{ij} \\ - \frac{\hbar^2}{2\mu}(\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle)^2\tilde{\chi}_{ijk} \\ + \frac{\imath\hbar^2}{2\mu}[2\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle\cdot\nabla + \nabla\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle]\tilde{\chi}_{ijk} \\ = 0, \end{aligned} \tag{6}$$

where the intermediate complex electronic wave function is $\tilde{\psi}_{ij} = \psi_i - \imath\psi_j$. Rewriting now equation 2 as

$$-\frac{\hbar^2}{2\mu}(\langle\psi_i|\nabla\psi_j\rangle)^2\tilde{\chi}_{ij} + \frac{\imath\hbar^2}{2\mu}[2\langle\psi_i|\nabla\psi_j\rangle\cdot\nabla + \nabla\langle\psi_i|\nabla\psi_j\rangle]\tilde{\chi}_{ij} = -\Big[-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ij} + (V_i - E)\tilde{\chi}_{ij}\Big] \quad (7)$$

one gets upon substitution in equations (5) and (6):

$$\Big[-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ijk} + (\bar{V}_j - E)\tilde{\chi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[2\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle\cdot\nabla + \nabla\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle\Big]\tilde{\chi}_{ijk}\Big] - \Big[-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ij} + (V_i - E)\tilde{\chi}_{ij}\Big] = 0 \quad (8)$$

$$\Big[-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ijk} + (\bar{V}_k - E)\tilde{\chi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[2\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle\cdot\nabla + \nabla\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle\Big]\tilde{\chi}_{ijk}\Big] - \Big[-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ij} + (V_i - E)\tilde{\chi}_{ij}\Big] = 0 \quad (9)$$

with $\bar{V}_\alpha = V_\alpha - \frac{\hbar^2}{2\mu}(\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle)^2$ for $\alpha = j$ and k. Careful examination of the above equations, finally gives

$$-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ij} + (V_i - E)\tilde{\chi}_{ij} = 0 \quad (10)$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ijk} + (\bar{V}_j - E)\tilde{\chi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[2\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle\cdot\nabla + \nabla\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle\Big]\tilde{\chi}_{ijk} = 0 \quad (11)$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ijk} + (\bar{V}_k - E)\tilde{\chi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[2\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle\cdot\nabla + \nabla\langle\tilde{\psi}_{ij}|\nabla\psi_k\rangle\Big]\tilde{\chi}_{ijk} = 0. \quad (12)$$

Expansion of the intermediate hybrid electronic wave function yields

$$-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ij} + V_i\tilde{\chi}_{ij} = E\tilde{\chi}_{ij} \quad (13)$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ijk} + \bar{V}_j\tilde{\chi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[2\{\langle\psi_i|\nabla\psi_k\rangle\cdot\nabla + \imath\langle\psi_j|\nabla\psi_k\rangle\cdot\nabla\}\Big]\tilde{\chi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[\nabla\{\langle\psi_i|\nabla\psi_k\rangle + \imath\langle\psi_j|\nabla\psi_k\rangle\}\Big]\tilde{\chi}_{ijk} = E\tilde{\chi}_{ijk} \quad (14)$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\chi}_{ijk} + \bar{V}_k\tilde{\chi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[2\{\langle\psi_i|\nabla\psi_k\rangle\cdot\nabla + \imath\langle\psi_j|\nabla\psi_k\rangle\cdot\nabla\}\Big]\tilde{\chi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[\nabla\{\langle\psi_i|\nabla\psi_k\rangle + \imath\langle\psi_j|\nabla\psi_k\rangle\}\Big]\tilde{\chi}_{ijk} = E\tilde{\chi}_{ijk}. \quad (15)$$

Note that the equations 14 and 15 contain an anti-Hermitian operator (a Hermitian operator becomes anti-Hermitian whenever it is multiplied by $\imath$ or $-\imath$). Another way of considering the complex wave function is $\tilde{\chi}_{ji} = (\imath\chi_j + \chi_i)$, followed by $\tilde{\chi}_{kji} = \imath\chi_k + (\imath\chi_j + \chi_i)$, also leading to the same set of equations [like equations 13–15] but with the anti-Hermitian part exactly the opposite of the one in equations 13–15. Averaging this set of equations eliminates such an anti-Hermitian contribution yielding the following equation:

$$-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\phi}_{ij} + V_i\tilde{\phi}_{ij} = E\tilde{\phi}_{ij} \quad (16)$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\phi}_{ijk} + \bar{V}_j\tilde{\phi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[2\{\langle\psi_i^a|\nabla\psi_k^a\rangle\cdot\nabla + \langle\psi_k^b|\nabla\psi_i^b\rangle\cdot\nabla\}\Big]\tilde{\phi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[\nabla\{\langle\psi_i^a|\nabla\psi_k^a\rangle + \langle\psi_k^b|\nabla\psi_i^b\rangle\}\Big]\tilde{\phi}_{ijk} = E\tilde{\phi}_{ijk} \quad (17)$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\tilde{\phi}_{ijk} + \bar{V}_k\tilde{\phi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[2\{\langle\psi_i^a|\nabla\psi_k^a\rangle\cdot\nabla + \langle\psi_k^b|\nabla\psi_i^b\rangle\cdot\nabla\}\Big]\tilde{\phi}_{ijk} + \frac{\imath\hbar^2}{2\mu}\Big[\nabla\{\langle\psi_i^a|\nabla\psi_k^a\rangle + \langle\psi_k^b|\nabla\psi_i^b\rangle\}\Big]\tilde{\phi}_{ijk} = E\tilde{\phi}_{ijk}, \quad (18)$$

where $\tilde{\phi}_{ij} = \frac{1}{2}(\tilde{\chi}_{ij} + \tilde{\chi}_{ji})$ and $\tilde{\phi}_{ijk} = \frac{1}{2}(\tilde{\chi}_{ijk} + \tilde{\chi}_{kji})$. ψ_i^a's and ψ_i^b's are the real adiabatic electronic wave functions given by the three rows of a 3×3 unitary matrix

which can be obtained by proper choice of multiplication (clockwise and anticlockwise) of the planar rotation matrices, respectively. One of the possible choice is described in the next paragraph. Equations 17 and 18 contain coupling terms while equation 16 does not, indicating that GP is expected to manifest only from the former equations. In summary, GP will appear on electronic states ψ_j and ψ_k, with the PES's of these two electronic states having a non-zero slope at the degeneracy locus.[39] Indeed, as shown later, numerical calculations with GP included on the above two states give reactive transitions in good agreement with available results from other approaches.

For the three-fold electronic degeneracy in $T \otimes (e \oplus t_2)$, the JT Hamiltonian including linear vibronic coupling has Lie group symmetry $SO(3)$, which implies dimension 3 and hence 3 Lie group parameters. Since a norm-preserving adiabatic electronic wave vector one the electronic sphere S^2 can be unambiguously characterized by two angles (so called coordinates of the Lie group; for a finite-dimensional Lie group G, they vary in some region of the Euclidean space $\Re^p$ where p is the dimension of the group), there will be freedom of choice for selecting the latter out of the three coordinates in $SO(3)$.

The remaining parameter can, however, be sampled in principle by considering all three two-angle sets.[39] By labelling the chosen angles as ξ_{ij} and ξ_{jk} and assigning a 3×3 unitary planar rotation matrix[42] to each, the full rotation matrix assumes the form

$$\boldsymbol{T_{ijk}} = \boldsymbol{t}_{ij}(\xi_{ij})\boldsymbol{t}_{jk}(\xi_{jk}), \tag{19}$$

where $[\boldsymbol{t}_{nm}]_{nn} = [\boldsymbol{t}_{nm}]_{mm} = \cos(\xi_{nm})$ and $[\boldsymbol{t}_{nm}]_{nm} = -[\boldsymbol{t}_{nm}]_{mn} = \sin(\xi_{nm})$ with all other entries satisfying $[\boldsymbol{t}_{nm}]_{ij} = \delta_{ij}$. As in the $E \otimes e$ problem, the electronic adiabatic wave vectors will now be given by the rows of the $\boldsymbol{T_{ijk}}$ matrix. The angle ξ_{ij} is the first mixing angle (describes the mixing of state ψ_i and ψ_j to form an intermediate adiabatic state $\tilde{\psi}_{ij}$, and ξ_{jk} is the second mixing angle (describes the mixing of state $\tilde{\psi}_{ij}$ and ψ_k). We may proceed by calculating the first derivative coupling terms as a function of mixing angles. After some algebra, one obtains

$$\begin{aligned}
\langle\psi_i|\nabla\psi_j\rangle &= -\nabla\xi_{ij}, \\
\langle\psi_i|\nabla\psi_k\rangle &= -\sin\xi_{ij}\nabla\xi_{jk}, \\
\langle\psi_j|\nabla\psi_k\rangle &= -\cos\xi_{ij}\nabla\xi_{jk}.
\end{aligned} \tag{20}$$

Including these values in equations 16–18 one can get the dynamical equations in terms of mixing angles, which provides an explicit relation between the GP angle and the mixing angles.

3. Numerical calculations

To study the reactive scattering in a three state JT system, we have modified the two-arrangement 'quasi-JT' scattering model of Baer *et al.*[33] with the adiabatic PES's chosen in such a way that they become degenerate at a single point,

$$V_1(x, y) = \frac{1}{2}\mu\omega_0^2 y^2 + Af(x, y) \tag{21}$$

$$V_2(x, y) = \frac{1}{2}\mu\omega_0^2 y^2 + A \tag{22}$$

$$V_3(x, y) = \frac{1}{2}\mu\omega_0^2 y^2 - (D - A)f(x, y) + D, \tag{23}$$

where x and y are Cartesian coordinates: $-\infty \leq x \leq \infty$ is the reaction coordinate (translational), and $-\infty \leq y \leq \infty$ the internal (vibrational) coordinate, while $f(x, y) = \exp(-\frac{x^2 + y^2}{\sigma^2})$. The parameters assume the values of $\mu = 0.58$ amu, $\omega_0 = 5.0 \times 10^{13}$ s^{-1}, $A = 3.0$ eV, $D = 6.0$ eV, $\sigma = 0.20$ Å(respectively), and hence differs slightly from the one used elsewhere.[40] The degeneracy lies nearly 3.0 eV above the asymptote, and hence the calculations will be for energies below the seam. One should note that the model obeys selection rules, namely: if reduced to a two-state conical intersection, only even↔odd transitions are allowed; for the three-state coupled case, only even→even and odd→odd are permitted. Thus, any deviation from such selection rules may be interpreted as a symmetry change.[33] Figure 1 shows the three adiabatic potential energy surfaces for the model system. In solving equation 17, we have considered the initial wave function $\tilde{\phi}_{ijk}$ as the product between the ground vibrational state for the harmonic mode (y coordinate)and the translational Gaussian wave packet (x coordinate) with various

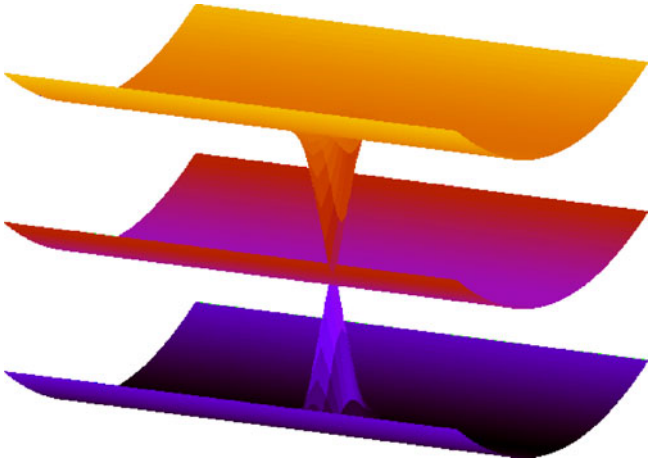

Figure 1. The three adiabatic potential energy surfaces.

Table 1. Reactive state-to-state transition probabilities.

E/eV	$0 \to 0$	$0 \to 1$	$0 \to 2$	$0 \to 3$	$0 \to 4$	$0 \to 5$
1.00[a]	0.331	0.021	0.309	0.003		
1.00[b]	0.020	0.547	0.035	0.050		
1.00[c]	0.344	0.000	0.319	0.000		
1.00[d]	0.324	0.093	0.239	0.021		
1.00[e]	0.349	0.000	0.384	0.000		
1.25	0.331	0.019	0.246	0.003	0.099	
1.25	0.064	0.495	0.067	0.042	0.023	
1.25	0.343	0.000	0.252	0.000	0.102	
1.25	0.379	0.070	0.182	0.012	0.087	
1.25	0.315	0.000	0.289	0.000	0.111	
1.50	0.443	0.022	0.194	0.003	0.084	0.001
1.50	0.012	0.645	0.019	0.043	0.004	0.021
1.50	0.455	0.000	0.201	0.000	0.089	0.000
1.50	0.405	0.057	0.198	0.014	0.107	0.013
1.50	0.434	0.000	0.272	0.000	0.113	0.000

[a]GBO (13), [b]GBO (12) or GBO (23), [c]BO, [d]EBO, and [e]coupled three-state results.

kinetic energies for the scattering mode. This adiabatic wave function is then propagated as a function of time by using the newly derived single surface GBO equation,[40] and the BO and Extended BO (EBO)[34,38] ones, in addition to the solution of the three-state coupled equations.[33] For this, the discrete variable representation (DVR) method[43] has been utilized, with the final wave functions at $t \to \infty$ being projected on the asymptotic eigenfunctions of the Hamiltonian such as to obtain the state-to-state vibrational transition probabilities at different energies. We have used the the functional form of GP angle/mixing angles (ξ_{ij} and ξ_{jk}) as $\frac{1}{2}\tan^{-1}(y/x)$. All these dynamical calculations have been done at total energies of 1.00, 1.25, and 1.50 eV. The calculated reactive state-to-state transition probabilities are given in table 1.

The first row of table 1 shows the GBO results having the phases (ι) in states 1 and 3, case (13), which is predicted to yield the proper combination from the theory.[39] Cases (12) and (23) are expected to give distinct results, as shown in the second entries, while the third and fourth rows give the BO and EBO reactive transition probabilities, respectively. The results from the three coupled-state calculations are given in the fifth entries. It is clear from the table that the GBO values for case (13) are in excellent agreement with the results from other approaches. In contrast, cases (12) and (23) predict the largest reaction probabilities for even→odd vibrational transitions such as $0 \to 1$ while even→even ones are very small. This is typical of a two-state conical intersection (which predicts the latter to vanish), which contrasts with the results expected for a three-state conical intersection. In summary, GP will appear on electronic states ψ_1 and ψ_3, with the PES's of these two electronic states having a nonzero slope at the degeneracy locus.[39] Clearly, the GBO formalism reported here is strictly valid in the vicinity of the degeneracy seam, although generality can be warranted by invoking the fact that such regions influence in a dominant way the dynamics even when the energetics allows sampling wider areas of configuration space[44] surrounding the degeneracy point. Extension to larger manifolds is warranted by the ELH theorem.[39]

4. Conclusion

We have discussed a new approach to deal with the GP in the dynamics of scattering processes. It finds support on a *reductio ad absurdum* extension of the LH theorem,[39] and is readily extendable to manifolds of arbitrary dimension. For example, in the case of a N-fold JT electronic degeneracy, propagation of the adiabatic electronic wave vectors around the point of degeneracy can be represented as a rotation in $N-1$ parameters in the N-dimensional electronic wave-vector space. Specifically, for the $N = 3$ case, such a rotation occurs on the $3D$ electronic wave-vector space, showing that only two adiabatic electronic wave vectors (namely 1 and 3) are subject to GP effect.

Acknowledgements

We thank for the financial support received from Fundação para a Ciência e a Tecnologia, Portugal under

projects PTDC/QUI-QUI/099744/2008, PTDC/AAC-AMB/099737/2008 and SFRH/BPD/68406/2010. The support from European Space Agency (ESTEC contract No. 21790/08/NL/HE) is also acknowledged.

References

1. Born M and Oppenheimer J R 1927 *Ann. Phys.* **84** 457
2. Born M and Huang K 1954 *Dynamical theory of crystal lattices* (Oxford: Clarendon Press)
3. Herzberg G and Longuet-Higgins H C 1963 *Discuss. Faraday Soc.* **35** 77
4. Longuet-Higgins H C 1975 *Proc. R. Soc. Ser. A* **344** 147
5. Varandas A J C, Tennyson J and Murrell J N 1979 *Chem. Phys. Lett.* **61** 431
6. Berry M V 1984 *Proc. R. Soc. London, Ser. A* **392** 45
7. Mead C A 1980 *Chem. Phys.* **49** 23
8. Mead C A and Truhlar D G 1979 *J. Chem. Phys.* **70** 2284
9. Ceulemans A 1987 *J. Chem. Phys.* **87** 5374
10. Chancey C C and O'Brien M C M 1988 *J. Phys. A: Math. Gen.* **21** 3347
11. Ceulemans A and Fowler P W 1990 *J. Chem. Phys.* **93** 1221
12. Mead C A 1992 *Rev. Mod. Phys.* **64** 51
13. Yarkony D R 1996 *Rev. Mod. Phys.* **68** 985
14. Chancey C C and O'Brien M C M 1997 *The Jahn–Teller effect in C_{60} and other icosahedral complexes* (NJ: Princeton University Press)
15. Varandas A J C and Xu Z R 2002 in *Adv. Chem. Phys.* (eds) M Baer and G D Billing (New York: Wiley) pp. 659–741
16. Althorpe S C, Stecher T and Bouakline F 2008 *J. Chem. Phys.* **129** 214117
17. Viegas L P and Varandas A J C 2008 *Phys. Rev. A* **77** 032505
18. Goldberg N T, Zhang J, Koszinowski K, Bouakline F, Althorpe S C and Zare R N 2008 *Proc. Natl. Acad. Sci. USA* **105** 18194
19. Bouakline F, Althorpe S C, Larregaray P and Bonnet L 2010 *Mol. Phys.* **108** 969
20. Juanes-Marcos J C, Varandas A J C and Althorpe S C 2008 *J. Chem. Phys.* **128** 211101
21. Lijnen E and Ceulemans A 2005 *Phys. Rev. B* **71** 014305
22. Jahn H A and Teller E 1937 *Proc. R. Soc. London, Ser. A* **161** 220
23. Ham F S 1987 *Phys. Rev. Lett.* **58** 725
24. Aitchison I J R 1988 *Phys. Scripta* **T23** 12
25. O'Brien, M C M 1969, *Phys. Rev.* **187** 407
26. Sturge M D 1967 in *Solid state physics: Advances in research and applications* (eds) D T F Seitz and H Ehrenreich (New York: Acadamic) p. 91
27. Englman R 1972 *The Jahn–Teller effect in molecules and crystals* (New York: Wiley)
28. Bersuker I B 2006 *The Jahn–Teller effect* (Cambridge: Cambridge University Press)
29. Bersuker I B 1996 *Electronic structure and properties of transition metal compounds* (New York: Wiley)
30. Opalka D and Domcke W 2010 *J. Chem. Phys.* **132** 154108
31. Manolopoulos D E and Child M S 1999 *Phys. Rev. Lett.* **82** 2223
32. Baer M, Lin S H, Alijah A, Adhikari S and Billing G D 2000 *Phys. Rev. A* **62** 032506
33. Adhikari S, Billing G D, Alijah A, Lin S H and Baer M 2000 *Phys. Rev. A* **62** 032507
34. Sarkar B and Adhikari S 2006 *J. Chem. Phys.* **124** 074101
35. Sarkar B and Adhikari S 2008 *Int. J. Quantum Chem.* **60** 650
36. Baer M and Englman R 1997 *Chem. Phys. Lett.* **265** 105
37. Varandas A J C and Xu Z R 2000 *J. Chem. Phys.* **112** 2121
38. Paul A K, Sardar S, Sarkar B and Adhikari S 2009 *J. Chem. Phys.* **131** 124312
39. Varandas A J C 2010 *Chem. Phys. Lett.* **487** 139
40. Varandas A J C and Sarkar B 2011 *Phys. Chem. Chem. Phys.* doi:10.1039/c0cp02598d
41. Varandas A J C and Xu Z R 2000 *Chem. Phys. Lett.* **316** 248
42. Leon S J 1990 *Linear algebra with applications* (New York: MacMillan Publishing Company)
43. Puzari P, Sarkar B and Adhikari S 2007 *J. Chem. Phys.* **121** 707
44. Xu Z R and Varandas A J C 2001 *J. Phys. Chem. A* **105** 2246