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A tribute to the memory of Professor Couceiro da Costa

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6. ADIABATIC APPROXIMATION AND RELATED ISSUES INCLUDING TOPOLOGICAL IMPLICATIONS

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We provide a perspective on several issues of the adiabatic approximation to the fundamental equation of quantum chemistry as suggested by Born and Oppenheimer: separation of the electronic and nuclear motions, coupled-channel treatment, scaling properties, validity, and diabatic states. The need for its generalization such as to account for the topological implications that arise from the separation of the electronic (fast) and nuclear (slow) degrees of freedom is also described in some detail by focusing on Jahn-Teller systems. Although considerable work has been reported on the energetics and dynamics of two-fold degeneracies of the conical type, the list of references on higher electronic degeneracies is meager due to enhanced theoretical difficulty. For high degeneracies, it may therefore be convenient to avoid the dynamics altogether by making use instead of symmetry invariants. This short review will cover both types of approaches to the electron-nuclei coupling problem, but focusing on work carried out at the author's group.

6.1 Introduction

It is well established [1] that no problem in physics or chemistry can ever be solved exactly. Approximations are unavoidable, with the adiabatic approximation due to Born and Oppenheimer [2] (BO), often called a theorem [3], being most fundamental as it is instrumental for ascribing a shape to a molecule. Without it, the solution (albeit approximate) of the fundamental equation of quantum mechanics - the Schrödinger equation (SE) - cannot be obtained except for simple model systems. In fact, the SE can be solved exactly for the hydrogen atom but no exact solution exists for any multi-electron system. Strictly speak-

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*Email address: varandas@qtvs1.qui.uc.pt ing, the SE is itself an approximation as it does not account for relativistic effects, and in nature there is no such a thing as a non-relativistic Schrödinger atom or molecule. Similarly, Dirac's equation is exactly solvable for the hydrogen atom and accounts for relativity, but cannot account for the size and structure of the atomic nuclei (thus, for the atomic interaction with the electromagnetic field). In turn, quantum electrodynamics allows to achieve higher accuracy (by describing, say, the Lamb shift of levels), but this too only allows the calculation of properties at some order of approximation to the relativistic effects. The above cannot be viewed [4] as a pitiful temporary drawback but something that goes on forever reflecting the approach of physics to nature: physics is nothing but a hierarchy of approximations.

By allowing an accurate treatment of the electronic structure without concerning the nuclei, the BO approximation underpins the way most chemists think about molecules. In fact, such a dividing to conquer idea which may even predate the publication of the BO key paper [5], leads to the concept of potential energy surface (PES). Because this governs the nuclear motion, the BO approximation lies at the heart of both molecular spectroscopy and chemical kinetics. Manifestations of the breakdown of the BO approximation in systems that are expected to behave adiabatically are ubiquitous in the sense of being rather small, but they may be non-negligible if accuracy is on demand. In fact, since electrons are expected to follow imperfectly the nuclei in their vibrational and rotational motions, nonadiabatic effects are expected to be required whenever there is a need to take into account that the vibrational and rotational motions of the nuclei induce interactions with other electronic states. The BO approximation should therefore be most valuable if electronic properties are considered, although it becomes somewhat more problematic when vibrational-rotational properties are envisaged. For example, to obtain a dissociation energy of a diatomic in an adiabatic calculation one calculates first the potential energy curve and then subtracts the zero-point energy for vibration. Instead, a nonadiabatic calculation will give directly the observable dissociation energy of a molecule rather than the well depth of the PES. Yet, it is well established that, even for the most unfavorable case of the hydrogen molecule (where the electron/nucleus ratio is 1/1836), the calculated dissociation energy lies surprisingly close [6] to the experimental value. Of course, the BO approximation can manifest itself also on systems beyond electrons and nuclei, and we have recently suggested that such an effect may explain the undissociated equator-to-pole motion of an helium atom when moving around a much heavier fullerene molecule [7–9].

The adiabatic BO approximation lies therefore on the assumption that the electronic states are well separated with the motion of the nuclei being governed by just one electronic state. Yet, it is now well established that intersections may occur between PESs of the same spatial and spin symmetry. In $2D$ Hilbert space, the necessary and sufficient condition for such an intersection (known as a conical or diabolical intersection) to occur can be satisfied if the molecule has three atoms or more. Similarly, threefold degeneracies are possible for tetratomic and larger molecules, fourfold for five atoms or more, fivefold for at least seven atoms, and so on. Such topological features bear key implications on the validity of the BO approximation, a subject that will be discussed in the present work.

A special class of systems where conical intersections occur due to symmetry reasons is known under the names of Jahn and Teller [10–13] (JT) who established the following Theorem: *all molecules (other than linear ones) distort from a symmetric configuration $\boldsymbol{Q}_0$ if, by so doing, any electronic degeneracy can be lifted*. In the vicinity of $\boldsymbol{Q}_0$, the PES assumes the form $E_\pm = E_0 \pm c\rho$, where ρ is the radial polar coordinate in the subspace (v-space) that contains all JT distorted configurations[1]. If the PES does not satisfy such a requirement (by having an extremum at $\boldsymbol{Q}_0$, say), it is called non-JT: it may even touch tangentially the next non-JT excited state leading then to a pseudo-JT type instability [11, 13]. Generically, N-fold electronic degeneracies have associated the unitary and rotation groups in N dimensions [11].

The study of conical intersections in $2D$ Hilbert space [15–19] has been pi-

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[1] The only exception to such instabilities on linear systems are twofold spin degeneracies of Kramer's type [14]. These are of no concern as only orbital degeneracy is here envisaged. If quadratic coupling is included, the linear molecules will also not be an exception due to the so-called Renner-Teller (RT) effect, also out of the scope of the present work.

oneered by Herzberg and Longuet-Higgins [20]. In 1975, Longuet-Higgins [21] (LH) established the following two key theorems: *I. On going once around any closed path on the surface that contains the conical intersection the electronic wave function changes sign*; *II. If a real adiabatic electronic wavefunction changes sign when a polyatomic traverses a 1D closed loop on a 2D surface in the* $(3N-6)$*-D nuclear configuration space, then the corresponding electronic state must become discontinuous and degenerate with another one at an odd number of points lying on that surface and within that loop.* There is therefore a phase factor (geometrical phase or GP) experienced by an eigenfunction of the parameter-dependent Hamiltonian when transported adiabatically such as to complete a path closing to itself around the conical intersection. In fact, such an intersection can be demonstrated by verifying [22, 23] the LH theorem I, by evaluating the line integral of the derivative couplings along a closed loop [17, 24], or by using [23] the Pancharatnam [25] connection. Varandas, Tennyson and Murrell [22] have in turn demonstrated that a conical intersection needs not be forced by symmetry reasons.

Although the GP effect has been known for decades [20, 21], interest on it has largely been motivated by Mead and Truhlar [26] derivation of a general phase factor formula in the context of the molecular BO problem followed by its rederivation and recasting in a more general context by Berry [24]. It became then also known as the Berry phase. Because the involved differential equations are similar to those of a charged particle moving in the presence of a magnetic solenoid, it is further often called as the molecular Aharonov-Bohm effect. Note that the GP appears whenever the BO approximation is utilized to separate the fast motion of the electrons from the slow vibrational degrees of freedom (parameters) in studying the coupled vibrational-electronic (vibronic) system. [Parenthetically, it should be noted that mathematical tools such as fibre bundles and gauge theories have specialized to describe (an)holonomies like GP; an account of this can be found in Ref. 27] Since the total BO wave function is a product of the electronic and nuclear ones, with the former changing sign when transported adiabatically along a loop that encircles a conical intersection [20, 21, 24], a sign change of opposite effect must occur in the nuclear wave function such that their product becomes single-valued. This has important consequences on the quantized nuclear motion, particularly in determining the symmetry of the ground-state vibronic energy levels [13, 28]. Indeed, its signature on reaction dynamics has been a theme of much debate over the years [29–33].

Compared with the vast amount of research on twofold degeneracies [17, 24, 26, 34–42] (the list is by no means exhaustive), the number of studies on the GP effect at higher electronic degeneracies is meager [19, 28, 43–45]. Cullerne and O'Brien [46] have been the first to use both numerical and analytical methods to map the lowest adiabatic PESs of icosahedral molecular systems such as fullerenes with a view to understand the rich structure of their degenerate electronic and vibrational modes as well as the role of GP. They have remarked [46] "To discuss the complete structure of degeneracies and Berry phases over the full nine-dimensional (9*D*) space of $G \otimes (g \oplus h)^2$ would be a mammoth task. Indeed, it is a task that we did not even complete in the 4*D* and 5*D* phase spaces of the subsystems $G \otimes g$ and $G \otimes h$." In 1998, Manini and De los Rios [28] and, more recently, Lijnen and Ceulemans [47] investigated the GP effect on the manifold of JT potential minima (JTM) of such species. Other developments are due to Manolopoulos and Child [43] who have utilized a model Hamiltonian to investigate the possible sign changes that can occur when N real quantum states are transported adiabatically around a N-fold electronic degeneracy. and to Baer [44] that focused on the topological features and existence of pure diabatic states. In a recent series of papers, we have instead advocated [19, 45, 48] the use of Lie group symmetries to study such N-fold degeneracies in JT systems. Two major questions have been addressed: (*i*) how many of the electronically degenerate states are subject to GP? (*ii*) can the GP effect be treated in a way similar to what is commonly done for the 2*D* Hilbert-space case? The basic idea is then to provide relevant answers of chemical physics interest without having to perform a diagonalization of the JT matrix and follow up the GP change in

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[2] Although the notation is rather variable in the literature, we use the notation E for doublets, T for triplets, G for quartets and H for quintets.

configuration space, but rather make use of symmetry invariants that are inherent to each system. Interestingly, such a work has also suggested [48] that the LH theorem can provide a rationale for any arbitrary N-fold, JT type, electronic degeneracy.

The structure of this Chapter is as follows. After a presentation of the SE in section 6.2, the BO approximation follows in section 6.3 and its subsections, where the following issues are discussed: separation of the electronic and nuclear motions, coupled-channel treatment, scaling properties, BO validity, and diabatic states. A generalized BO formulation will then be discussed in section 6.4 for the $2D$ Hilbert space case, thus accounting for the topological implications due to conical intersections. After a brief presentation of function space in section 6.5, attention is driven to the treatment of higher-dimensionality JT manifolds in section 6.6, and to the generalization of the LH theorem in section 6.7. Section 6.8 explores the possibility of using the novel formalism also for solving the dynamics of the nuclear motion. The work presented is tentative and is currently being explored in our Group. Because specialized books and reviews have recently covered some of the topics discussed in the present report, this will focus primarily on the author's own work. The Chapter concludes with section 6.9.

6.2 The electronuclear Schrödinger equation

The SE describing the complete time-dependent many-body problem assumes the form

$$\imath\hbar\frac{\partial}{\partial t}\tilde{\Omega}(\mathbf{r}_e,\mathbf{r}_n,t)=\hat{H}(\mathbf{r}_n,\mathbf{r}_e)\tilde{\Omega}(\mathbf{r}_e,\mathbf{r}_n,t) \tag{6.1}$$

where t represents the time, $\mathbf{r}_e=\{x_i\}$ $(i=1,\ldots,3N)$ denotes the collective positions of the N electrons, $\mathbf{r}_n=\{X_I\}$ $(I=1,\ldots,3M)$ those of the M nuclei, the molecular Hamiltonian assumes the form

$$\hat{H}(\mathbf{r}_e,\mathbf{r}_n)=-\frac{\hbar^2}{2m_n}\Delta_n-\frac{\hbar^2}{2m_e}\Delta_e+V(\mathbf{r}_e,\mathbf{r}_n) \tag{6.2}$$

where m_e is the mass of the electron and, for simplicity, all nuclei have been assumed to have the same mass m_n; $\Delta_e=\sum_{i=1}^{N}\nabla_i^2$ and $\Delta_n=\sum_{I=1}^{M}\nabla_I^2$ are the corresponding Laplacians, with $\nabla_i = \nabla_{i,x}\hat{\imath} + \nabla_{i,y}\hat{\jmath} + \nabla_{i,z}\hat{k}$ and $\nabla_I = \nabla_{I,x}\hat{\imath} + \nabla_{I,y}\hat{\jmath} + \nabla_{I,z}\hat{k}$. Note that the potential energy $V(\mathbf{r}_e, \mathbf{r}_n)$ is assumed to be a real function [3]. Although $\Omega(\mathbf{r}_e, \mathbf{r}_n, t)$ is in general a function of the coordinates and time and cannot be expressed as a function only of time multiplied by another function only of coordinates, it turns out that we can express any solution of the SE as the sum of a series of separable ones. Substitution of the simple product $\tilde{\Omega}(\mathbf{r}_e, \mathbf{r}_n, t) = \Omega(\mathbf{r}_e, \mathbf{r}_n)\phi(t)$ into SE (6.1) and dividing both sides of the resulting equation by $\Omega(\mathbf{r}_e, \mathbf{r}_n)$ then yields:

$$\frac{\iota\hbar}{\phi(t)}\frac{d\phi(t)}{dt} = \frac{1}{\Omega(\mathbf{r}_e, \mathbf{r}_n)}\hat{H}(\mathbf{r}_e, \mathbf{r}_n)\Omega(\mathbf{r}_e, \mathbf{r}_n) \tag{6.3}$$

Note that $\hat{H}$ has been chosen to be a function only of the spatial coordinates, and not of t, such as to make the first expression in this equation a function only of t, and the second a function only of $\mathbf{r}_e$ and $\mathbf{r}_n$. It can then be concluded that both expressions are equal to a third that can be neither a function of spatial coordinates nor of time. If this is designated by a constant E, two differential equations can be extracted:

$$\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = -\frac{\iota E}{\hbar} \tag{6.4}$$

and

$$\hat{H}(\mathbf{r}_n, \mathbf{r}_e)\Omega(\mathbf{r}_e, \mathbf{r}_n) = E\Omega(\mathbf{r}_e, \mathbf{r}_n) \tag{6.5}$$

The former can be solved to yield $\phi(t) = \exp\left(-\iota Et/\hbar\right)$. Because the Hamiltonian is a Hermitian operator, its eigenvalues (and hence E) must be real, with the solutions $\phi(t)$ being purely oscillatory. Thus, if

$$\tilde{\Omega}(\mathbf{r}_e, \mathbf{r}_n, t) = \Omega(\mathbf{r}_e, \mathbf{r}_n)\exp\left(-\iota Et/\hbar\right) \ , \tag{6.6}$$

the total wave function $\tilde{\Omega}(\mathbf{r}_e, \mathbf{r}_n, t)$ differs from $\Omega(\mathbf{r}_e, \mathbf{r}_n)$ only by a phase factor of constant magnitude. Of course, Eq. (6.6) is a particular solution of Eq. (6.1). A general solution will therefore be given by a linear combination of such particular solutions:

$$\tilde{\Omega}(\mathbf{r}_e, \mathbf{r}_n, t) = \sum_i c_i\Omega_i(\mathbf{r}_e, \mathbf{r}_n)\exp\left(-\iota E_i t/\hbar\right) \tag{6.7}$$

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[3] A complex potential acts as a source or sink of probability [49].

Finding solutions of the time-independent SE will then generate the components that are necessary for building the time dependent solutions. It is on the time-independent SE that the discussion will be focused hereinafter.

6.3 The BO approximation

Assuming the atomic system of units where $\hbar = m_e = 1$ and defining the mass ratio $\epsilon^4 = m_e/m_n$, Eq. (6.2) assumes the form

$$\hat{H}(\mathbf{r}_e, \mathbf{r}_n) = -\frac{\epsilon^4}{2}\Delta_n + \hat{H}_e(\mathbf{r}_e; \mathbf{r}_n) \tag{6.8}$$

where

$$\hat{H}_e(\mathbf{r}_e; \mathbf{r}_n) = -\frac{1}{2}\Delta_e + V(\mathbf{r}_e; \mathbf{r}_n) \tag{6.9}$$

is the electronic Hamiltonian that depends parametrically on $\mathbf{r}_n$ through $V(\mathbf{r}_e; \mathbf{r}_n)$. Clearly, in the limit of infinitely massive nuclei, these will not move from their positions and the electrons will feel only the Hamiltonian $\hat{H}_e$ for the frozen nuclei positions. This provides the motivation for decoupling the electronic and nuclear motions, since the latter are at least 1836 times as heavy as an electron. Because the nuclei move slowly, it is then a good approximation to assume that the electrons move subject to a Hamiltonian that depends on the position of the nuclei at a given instant.

An alternative derivation of the electronic SE is by assuming that the nuclei can be treated classically. The nuclei will then be described by trajectories $\mathbf{r}_n(t)$, with $\hat{H}_e$ being thought to depend on $\mathbf{r}_n$ or time. If such an assumption is made, the nuclei will move infinitely slowly as we have an Hamiltonian $\hat{H}_e(t)$ that changes very slowly with time. If the electrons begin in an eigenstate of $\hat{H}_e(0)$, they will then adiabatically follow this eigenstate along such a trajectory ending up in an eigenstate of $\hat{H}_e(t)$. Note, however, that the BO approximation does not treat the nuclei classically and that, for slowly moving nuclei, the electronic SE follows naturally.

6.3.1 The electronic Schrödinger equation

The time-independent electronic structure problem is defined by the eigenvalue equation

$$\hat{H}_e(\mathbf{r}_e;\mathbf{r}_n)|\Psi_i(\mathbf{r}_e;\mathbf{r}_n)\rangle = E_i(\mathbf{r}_n)|\Psi_i(\mathbf{r}_e;\mathbf{r}_n)\rangle \tag{6.10}$$

where $|\Psi_i(\mathbf{r}_e;\mathbf{r}_n)\rangle \in \mathcal{H}_f \equiv S_a L^2(\mathbb{R}^{3N})$: it belongs to the Hilbert space for the "fast" electronic degrees of freedom. Because the electrons are fermions, S_a will then project onto the antisymmetric wave functions. In addition to bound states, $\hat{H}_e(\mathbf{r}_e;\mathbf{r}_n)$ has in general a continuous spectrum, with the eigenvectors of Eq. (6.10) being normalized: $\langle\Psi_i(\mathbf{r}_e;\mathbf{r}_n)|\Psi_j(\mathbf{r}_e;\mathbf{r}_n)\rangle = \delta_{ij}$, with the eigenvalues labeled as $E_1(\mathbf{r}_n) \leq E_2(\mathbf{r}_n) \leq \ \ldots$ including multiplicity. The graph of $E_i(\mathbf{r}_n)$ will be called the i-th BO PES. As a rule, such a PES will display a complicated topology with crossings and avoided crossings. For the wave functions of the slow coordinates one has $\mathcal{H}_s \equiv L^2(\mathbb{R}^{3M})$, recalling that to impose the physically correct statistics for the nuclei requires extra considerations [26].

6.3.2 The nuclear Schrödinger equation

Once the electronic SE is solved, one can write down the effective Hamiltonian for the nuclei by simply adding back in the terms that were left out of $\hat{H}_e$:

$$\hat{H}_n = -\frac{\epsilon^4}{2}\Delta_n + E_i(\mathbf{r}_n) \tag{6.11}$$

Thus, the nuclei move on an effective PES that is defined by the electronic energy, with the wave functions for the nuclei alone being eigenfunctions of this Hamiltonian

$$\left[-\frac{\epsilon^4}{2}\Delta_n + E_i(\mathbf{r}_n)\right]|\Phi_{Ii}(\mathbf{r}_n)\rangle = E_{Ii}|\Phi_{Ii}(\mathbf{r}_n)\rangle \tag{6.12}$$

Note that Eqs. (6.10) to (6.12) do not treat the electrons and nuclei as independent particles: the parametric dependence of the electronic eigenstates, expressed as usual by the semicolon[4], introduces as we shall see a non-trivial coupling

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[4] The obvious dependence of $\Psi_i(\mathbf{r}_e;\mathbf{r}_n)$ and $\hat{H}_e(\mathbf{r}_e;\mathbf{r}_n)$ in the electronic coordinates will be omitted for brevity after Eq. (6.13).

between the two that reflects on topological implications. Thus, the electronic-nuclei decoupling needs not be complete for the BO approximation to be valid. In summary, if the electrons are in an electronic state i and the nuclei in the I-th state of the i-th electronic state, the total electronuclear wave function can be specified as

$$|\Omega(\mathbf{r}_e, \mathbf{r}_n)\rangle = \Phi_{Ii}(\mathbf{r}_n)|\Psi_i(\mathbf{r}_e; \mathbf{r}_n)\rangle \tag{6.13}$$

where we have used a mixed representation: the nuclei will be described using wave mechanics notation while the electrons employ the popular (brac-ket) Dirac's notation.

6.3.3 The Born-Huang ansatz and coupled-channel treatment

The BO approximation is extremely accurate by itself, as explained by its widespread use through chemistry. Even when it fails, the result may be explained by assuming that the system is adiabatic almost all time, with only a few isolated regions where corrections need to be accounted for. Thus, it is convenient to consider the exact SE expressed in the basis defined by the BO approximation.

Since the electronic eigenstates for any fixed choice of $\mathbf{r}_n$ form a complete basis that satisfies Eq. (6.10) and, correspondingly, the nuclear eigenstates form a complete basis that satisfies Eq. (6.12) for any i-state, one may conclude that the set of products $\{\Phi_{Ii}(\mathbf{r}_n)|\Psi_i(\mathbf{r}_n)\rangle\}$ forms a complete basis for expanding any wave function that describes the electrons and nuclei. The total electronuclear wave function can therefore be exactly expressed (C_{Jj} are expansion coefficients) in terms of the so-called Born-Huang ansatz as:

$$|\Omega(\mathbf{r}_e, \mathbf{r}_n)\rangle = \sum_{Jj} C_{Jj}\Phi_{Jj}(\mathbf{r}_n)|\Psi_j(\mathbf{r}_n)\rangle \tag{6.14}$$

By representing now the Hamiltonian as a matrix in the Born-Huang ansatz, one gets

$$\begin{aligned}\mathbf{H}_{j'J'jJ} = &\int \Phi^{\star}_{J'j'}(\mathbf{r}_n)\left[-\frac{\epsilon^4}{2}\Delta_n + E_j(\mathbf{r}_n)\right]\Phi_{Jj}\delta_{jj'}\,d\mathbf{r}_n \\ &- \epsilon^4\sum_I \int \Phi^{\star}_{J'j'}(\mathbf{r}_n)\nabla_I\Phi_{Jj}(\mathbf{r}_n).\mathbf{F}^I_{j'j}(\mathbf{r}_n)d\mathbf{r}_n\end{aligned}$$

$$-\frac{\epsilon^4}{2}\int \Phi^{\star}_{J'j'}(\mathbf{r}_n)\Phi_{Jj}(\mathbf{r}_n)\mathbf{G}^I_{j'j}(\mathbf{r}_n)d\mathbf{r}_n \tag{6.15}$$

where the non-adiabatic coupling matrix elements $\mathbf{F}^I_{j'j}(\mathbf{r}_n) = \langle\Psi_{j'}(\mathbf{r}_n)|\nabla_I\Psi_j(\mathbf{r}_n)\rangle$ and $\mathbf{G}^I_{j'j}(\mathbf{r}_n) = \langle\Psi_{j'}(\mathbf{r}_n)|\Delta_n\Psi_j(\mathbf{r}_n)\rangle$ are the so-called first- and second-derivative non-adiabatic coupling terms (NACTs), respectively. Clearly, the first term in Eq. (6.15) is the BO approximation, while the second and third are corrections to the latter that arise due to the parametric dependence of the electronic wave function on the nuclear coordinates. The magnitude of such corrections will depend on the rate of change (gradient) of the electronic wave function as we change the nuclear configuration. Note that $\mathbf{F}^I_{j'j}(\mathbf{r}_n)$ is a matrix where each of its elements is a vector that originates from the gradient of the electronic wave function with respect to the I-th nuclear coordinates. The direction of this gradient indicates the direction in which the electronic wave function is changing fastest, while its magnitude indicates how large the change is in absolute sense. One then takes the overlap of this gradient with the electronic function $\Psi_{j'}$. This shows, as we vary $\mathbf{r}_n$, how much the change in Ψ_j looks like a change from the current electronic state Ψ_j to another $\Psi_{j'}$. Indeed, the NACT represents the overlap of wave functions with differentiated functions. Because numerical differentiation of a function involves its calculation at distinct points, the determination of $\mathbf{F}^I_{jj'}(\mathbf{r}_n)$ involves "delayed" overlaps in the sense that the overlapping functions are calculated at separated nearby points. This leads one to expect that NACTs should manifest an overlap dependence which, for realistic Slater type orbitals, is expressed as an inverse exponential of the interatomic distance [50]. Another property of NACTs refers to their sign change. Indeed, because the BO eigenfunctions are determined only up to a sign, it is easy to conclude that the sign of the NACTs cannot be assigned uniquely. Criteria to fix it have been suggested [51, 52] but none is unique. Thus, there is a wealth of information in the $\mathbf{F}^I_{j'j}(\mathbf{r}_n)$ NACT: tells (via its magnitude) how likely non-adiabatic events are, what physical motions it can be associated with (through its direction), and which electronic states are involved (via overlap of the gradient of Ψ_j with $\Psi_{j'}$). If the electronic state changes rapidly over a small distance, the term involving

$\mathbf{F}^{I}_{j'j}(\mathbf{r}_n)$ is likely to be large. Conversely, the third term, so-called diagonal BO correction (DBOC), is small and often neglected. The above is known as the coupled channel representation: each electronic state is a distinct channel with the Hamiltonian governing their coupling.

Let us examine briefly two subtleties of the NACTs before concluding this section. The first refers to their dependence on the choice of origin of the coordinate system [50, 53–60], as illustrated for various diatomic species, most recently [50] for LiF. In fact, this origin-dependence of NACTs can be problematic in the case of polyatomic species since the use of different coordinate systems is known to be convenient. Unfortunately, no such a study has, to our knowledge, been reported. A second subtlety, also raised by the origin dependence of NACTs, refers to the fact that the latter may not vanish asymptotically, and then present a problem in imposing the usual scattering boundary conditions. This emerges from the fact that the difference between NACTs calculated with respect to two different origins is proportional to the dipole transition matrix [56, 57, 60]. For example, in LiF the ground state curve dissociates to $\mathrm{Li}(^2S)+\mathrm{F}(^2P)$ while the next state of the same symmetry yields $\mathrm{Li}^{+}(^1S)+\mathrm{F}^{-}(^1S)$, and hence such a difference vanishes at $R \to \infty$ as the connection between ^1S and ^2P states by the electric dipole operator is spin forbidden [50]. Remedies to the asymptotic problem involve either the use of electron translation factors or appropriate reaction coordinates [54–57].

We are now in position to write the full SE by replacing Eq. (6.14) in Eq. (6.5) and multiplying on the left by $\langle \Psi_{j'}(\mathbf{r}_n)|$. This leads to an infinite set of coupled equations, which may be written in matrix form as[5]

$$\left\{ -\frac{\epsilon^4}{2}\left[\mathbf{I}\Delta_n + 2\mathbf{F}(\mathbf{r}_n)\cdot\boldsymbol{\nabla} + \mathbf{G}(\mathbf{r}_n)\right] + \boldsymbol{V}(\mathbf{r}_n) - E\mathbf{I} \right\} \boldsymbol{\Phi}(\mathbf{r}_n) = \mathbf{0} \tag{6.16}$$

where $\mathbf{I}$ is the identity matrix, $\boldsymbol{\Phi}(\mathbf{r}_n)$ is a column vector whose components are the nuclear wave functions, and $\boldsymbol{V}(\mathbf{r}_n)$ is now utilized as usual to represent the column vector of electronic PESs $\{E_j(\mathbf{r}_n)\}$.

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[5] When unlabeled (often indicated as $\nabla_{\mathbf{R}}$), the operator nabla refers to the nuclear coordinates.

6.3.4 Scaling properties

Born and Oppenheimer argued that the two terms on the right-hand-side of Eq. (6.15) can be neglected as ϵ^4 is a very small number. Indeed, if a typical nuclear mass is taken as $m_n = 10^4\, m_e$, then $\epsilon^4 = 10^{-4}$. Consider then a diatomic vibrating close to its equilibrium geometry X_e, and express the nuclear separation as $X = X_e + \epsilon u$, where the reduced distance u can be argued to be of the same order as X_e. Thus, $m_n \propto \epsilon^{-4}$, and $\partial/\partial X \propto \epsilon^{-1}$. This leads to the following typical scaling relationships [61]:

Typical vibrational energy	$\propto 1/\sqrt{m_n} \propto \epsilon^2$
Typical rotational energy	$\propto 1/(m_n X_e^2) \propto \epsilon^4$
First derivative coupling	$\propto \epsilon^4 \partial/\partial X \propto \epsilon^3$
Second derivative coupling	$\propto \epsilon^4$

6.3.5 When is the BO approximation expected to fail?

Although one is tempted to suggest that the BO approximation fails when the nuclei are light, this turns out not to be the major problem. To see this, consider a perturbative view where the first term (BO result) is treated as the zeroth-order Hamiltonian and the second is the perturbation (DBOC is ignored). Since an operator is uniquely determined by its matrix elements, the zeroth-order operator may assume the following form:

$$\hat{H}^0 = \sum_{\alpha\beta} |\Psi_\alpha\rangle \mathbf{H}^0_{\alpha\beta} \langle\Psi_\beta| \tag{6.17}$$

where $\mathbf{H}^0_{\alpha\beta} = \langle\Psi_\alpha|\hat{H}^0|\Psi_\beta\rangle$, and α and β are compound indexes belonging to the set of BO states that specify a particular choice of Jj. In fact, if it is assumed that

$$\hat{H}^0 = \sum_k |\Psi_k(\mathbf{r}_n)\rangle \left[-\frac{\epsilon^4}{2}\Delta_n + V_j(\mathbf{r}_n)\right] \langle\Psi_k(\mathbf{r}_n)|\,, \tag{6.18}$$

then $\mathbf{H}^0_{J'j'Jj}$ is identical to the set of matrix elements given by the Born-Oppenheimer term (first-term) of Eq. (6.15). Similarly, the perturbation operator assumes the form

$$\hat{U} = -\epsilon^4 \sum_{j'j} \int |\Psi_{j'}(\mathbf{r}_n)\rangle \sum_I \nabla_I \cdot \mathbf{F}^I_{j'j}(\mathbf{r}_n) \langle\Psi_j(\mathbf{r}_n)|\,, \tag{6.19}$$

since its matrix elements yield the perturbation correction (second term) in Eq. (6.15). Note that the perturbation operator $\hat{U}$ depends on the momenta of the nuclei. The probability of a non-adiabatic event will then depend on how fast the nuclei are moving. Such a probability, and hence non-adiabatic effects, are then expected to be the larger the faster the nuclei are moving. Since the BO states are eigenstates of $\hat{H}^0$, they will cease to be a good approximation to those of $\hat{H}$ when $\hat{U}$ is large. However, imposing that the dynamics evolves on a single PES may have also topological implications. How these can be overcome will be analyzed in section 6.3.7.

6.3.6 Diabatic states

We have seen that in the BO representation the Hamiltonian can be approximated by the sum of Eqs. (6.18) and (6.19). However, the first- and second-order NACTs are difficult to deal with since by using the Hellmann-Feynman theorem it may be shown to behave hyperbolically near the crossing seam where $V_i = V_j$. One may then write [62]

$$\mathbf{F}^I_{j'j}(\mathbf{r}_n) = \frac{\langle \Psi^a_{j'}(\mathbf{r}_n;\mathbf{r}_e)|\nabla^I H_e|\Psi^a_j(\mathbf{r}_n;\mathbf{r}_e)\rangle}{V^a_{j'}(\mathbf{r}_n) - V^a_j(\mathbf{r}_n)} \qquad (j' \neq j) \tag{6.20}$$

which shows that the NACTs cannot be neglected especially at regions where $V_{j'}$ approaches V_j. In fact, such a behavior is responsible for severe numerical computational difficulties in the adiabatic approximation. On the other hand, the potential matrix assumes its simplest form by being diagonal in the BO (adiabatic) approximation, $V_{j'j} = V_j\delta_{j'j}$. Clearly, one would then like to avoid the calculation of NACTs. Because they arise due to the fact that the electronic wave function depends parametrically on the nuclear coordinates, one may think of choosing a $\mathbf{r}_n$-independent basis set, say by defining a complete electronic basis set for a selected geometry of the nuclei. Of course, there are many ways for doing it, and any such basis will be referred to as a diabatic basis [63–66].

Consider now the following (adiabatic-to-diabatic) ATD unitary transformation:

$$|\Omega(\mathbf{r}_n, \mathbf{r}_e)\rangle = \sum_{jJ} C_{Jj}\Phi^a_{Jj}(\mathbf{r}_n)|\Psi^a_j(\mathbf{r}_n; \mathbf{r}_e)\rangle = \mathbf{C\Psi}^{a\dagger}\mathbf{UU}^\dagger\mathbf{\Phi}^a \equiv \mathbf{C\Psi}^{d\dagger}(\mathbf{r}; \mathbf{R})\mathbf{\Phi}^d(\mathbf{R}) \tag{6.21}$$

where the explicit dependence of the operators and wave functions is often ignored hereinafter for simplicity, and the superscript $a(d)$ has been added to indicate 'adiabatic' (diabatic). By replacing $\mathbf{\Phi}^a = \mathbf{U\Phi}^d$ in Eq. (6.16), where $\mathbf{U}$ is an orthogonal matrix, one obtains the following result [67]:

$$\left\{-\frac{\epsilon^4}{2}\mathbf{U}\Delta_n - \frac{\epsilon^4}{2}\left[\Delta_n\mathbf{U} + 2\mathbf{F}\left(\nabla\mathbf{U}\right) + \mathbf{GU}\right] - \epsilon^4\left(\nabla\mathbf{U} + \mathbf{FU}\right)\nabla + \left(\mathbf{V}^a - E\mathbf{I}\right)\mathbf{U}\right\}\mathbf{\Phi}^d = \mathbf{0} \tag{6.22}$$

Assuming now that $\mathbf{U}$ can ideally be chosen to solve

$$\nabla\mathbf{U} + \mathbf{FU} = 0\,, \tag{6.23}$$

it can be shown that Eq. (6.22) will then reduce to

$$\left(-\frac{\epsilon^4}{2}\mathbf{I}\Delta_n + \mathbf{V}^d - E\mathbf{I}\right)\mathbf{\Phi}^d = 0 \tag{6.24}$$

where

$$\mathbf{V}^d = \mathbf{U}^\dagger\mathbf{V}^a\mathbf{U} \tag{6.25}$$

Note that $|\Psi^d_j\rangle$ does not vary with $\mathbf{r}_n$, and hence $\mathbf{F}^I_{jj'} = 0$ in the diabatic basis. Conversely, the diabatic states will not diagonalize the electronic Hamiltonian, which becomes instead more complicated. This shows that the substitution of the adiabatic ansatz by the diabatic one does lead to a system of coupled differential equations similar to Eq. (6.16) but with some notable differences. First, the potential matrix becomes nondiagonal in the diabatic basis. In fact, the adiabatic potential matrix is diagonal, while in the diabatic basis it becomes a source of transitions between the surfaces. Second, the matrix elements of the nuclear kinetic energy operator disappear, but off-diagonal terms arise instead in the diabatic potential matrix. Of course, if a complete basis set is assumed, the unitary transformation in Eq. (6.25) warrants that the eigenvalues of the diabatic potential matrix coincide with the adiabatic potentials in Eq. (6.16). In practice, the diabatic basis is most useful very near a crossing or avoided crossing. Unfortunately, it is not possible to find strictly diabatic electronic states for which $\mathbf{F}^{I}_{j,j'}(\mathbf{r}_n)$ vanishes everywhere. Indeed, even if the adiabatic and diabatic results would coincide in the limit of an infinite basis, such diabatic states would not be very useful in practice due to the large number of them that would be required to describe the electronic structure. Often a linear combination of a small set of N_{ad} adiabatic states is instead chosen to be maximally diabatic:

$$|\tilde{\Psi}^{d}_{k}\rangle = \sum_{ki}^{N_{ad}} c_{ki}(\mathbf{r}_n)|\Psi^{ad}_{i}(\mathbf{r}_n)\rangle \tag{6.26}$$

If there is only one degree of freedom, we can even do this by choosing our maximal diabatic states [68] so that $\mathbf{d}^{I}_{jj'}(\mathbf{r}_n)$ is diagonal:

$$\left\langle \tilde{\Psi}^{d}_{j}(\mathbf{r}_n) \middle| \frac{\partial}{\partial r_n} \middle| \tilde{\Psi}^{d}_{j'}(\mathbf{r}_n) \right\rangle \propto \delta_{jj'} \tag{6.27}$$

In this case, the diabatic states become the set of electronic states that diagonalize the nuclear kinetic energy operator, whereas the adiabatic states diagonalize $\hat{H}_e(\mathbf{r}_n)$. The point to emphasize is that the PES is no longer single-sheeted, but (nonadiabatic) multi-sheeted by assuming the form of a potential matrix. Suffice it too add that there is considerable interest in methods that yield a diabatic potential matrix from an adiabatic one as this can facilitate drastically the nonadiabatic dynamics calculations.

A wide variety of methods for producing diabatic potentials has been reported in the literature [50, 69–86], as well as (diabatic) multi-sheeted PESs [70, 71, 73, 74, 80, 82, 84, 85, 87–96] (the list is by no means comprehensive). Such methods can be divided in two categories [85] according to whether they merge into the proper adiabatic states at the asymptotes or not. The direct diabatization approach gathers methods that yield directly the diabatic states [70, 71, 73–78, 80–84, 97], either from *ab initio* energies or diabatic electronic wave functions, thus without any intermediary. The second class includes three subclasses. One includes approaches that model the various diabats from regions of the adiabatic potentials where they are supposed to play the dominant

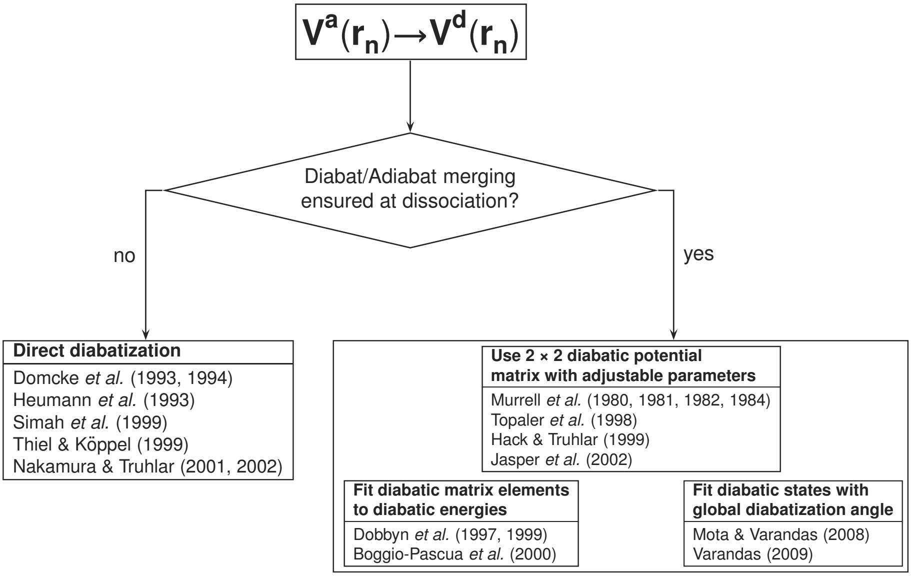

Figure 6.1. Schemes for adiabatic-to-diabatic transformation of PESs (see text).

role, thus warranting the desired asymptotic behavior by built-in construction. In another subclass the diabatic states are built with the help of molecular properties [69, 72, 79] that behave akin to the potential energy, in particular dipole or transition moments. In the third subclass, the various diabatic potentials are calculated and then assembled via a global diabatization angle. Figure 6.1 summarizes the various types of diabatization methods, with the reader being referred to Ref. 85 and the original papers for further details.

A final comment to readdress the issue of dependence on the origin of the NACTs in adiabatic theory (section 6.3.3). Although one may be tempted to think this to be a definite advantage for doing the scattering within the diabatic picture (derivative couplings are replaced by potential couplings; Ref. 98, and references therein), this is not quite so as the NACTs are still required to get the diabatic potential matrix.

6.3.7 Topological implications of the BO approximation

As noted above, the nuclei can be treated classically in the BO approximation. They may then be described by trajectories $\mathbf{r}_n(t)$, with $\hat{H}_e$ thought to depend on

$\mathbf{r}_n$ or time. If such an assumption is made, the nuclei will move infinitely slow as the Hamiltonian $\hat{H}_e(t)$ changes slowly with time. Consider then an arbitrary path $\mathbf{r}_n(t)$. The non-stationary time-dependent electronic SE along such a path assumes then the form

$$\hat{H}_e\left(\mathbf{r}_n(t)\right)\Psi\left(\mathbf{r}_n(t)\right) = \iota\hbar\frac{\partial\Psi\left(\mathbf{r}_n(t)\right)}{\partial t} \tag{6.28}$$

where the obvious dependence of $\hat{H}_e$ and Ψ on $\mathbf{r}_e$ has been omitted for simplicity. Using the electronic basis set $\left\{\Psi_i\left(\mathbf{r}_n(t)\right)\right\}$, the wave function may now be expanded as

$$\Psi\left(\mathbf{r}_n(t)\right) = \sum_j c_j(t)\Psi_j\left(\mathbf{r}_n(t)\right)\exp\left[-\frac{\iota}{\hbar}\int^t E_j\left(t'\right)dt'\right] \tag{6.29}$$

where the term in the exponential is the dynamical phase. Eqs. (6.28,6.29) then yield

$$\begin{aligned}\iota\hbar\frac{dc_k}{dt} = \sum_j c_j\Bigg\{H_{ij} - E_j\delta_{ij} - \iota\hbar\langle\Psi_k\left(\mathbf{r}_n(t)\right)\left|\frac{\partial\Psi_j\left(\mathbf{r}_n(t)\right)}{\partial t}\right\rangle \\ \exp\left[-\frac{\iota}{\hbar}\int^t\left(E_j - E_k\right)dt'\right]\Bigg\}\end{aligned} \tag{6.30}$$

If the NACTs for $j \neq k$ are now neglected, and noting that $H_{kj} = S_{kj} = 0$ for the adiabatic basis set, it follows that

$$\frac{dc_k}{dt} = -\left\langle\Psi_k\left(\mathbf{r}_n(t)\right)\left|\frac{\partial\Psi_k\left(\mathbf{r}_n(t)\right)}{\partial t}\right.\right\rangle c_k \tag{6.31}$$

and hence

$$c_k = \exp\left[-\int^t\left\langle\Psi_k\left(\mathbf{r}_n(t')\right)\left|\frac{\partial\Psi_k\left(\mathbf{r}_n(t')\right)}{\partial t'}\right.\right\rangle dt'\right] = \exp\left[\iota A_k(t)\right] \tag{6.32}$$

where $A_k(t) = \iota\int^t\langle\Psi_k\left(\mathbf{r}_n(t')\right)|\partial\Psi_k\left(\mathbf{r}_n(t')\right)/\partial t'\rangle dt'$ is the GP. Thus, retaining only one term in the wave function expansion, one has

$$\Psi\left(\mathbf{R}(t)\right) = \Psi_i\left(\mathbf{r}_n(t)\right)\exp\left[-\frac{\iota}{\hbar}\int^t E_i\left(t'\right)dt'\right]\exp\left[\iota A_i(t)\right] \tag{6.33}$$

which has the form of a generalized Born-Huang ansatz. Besides the dynamical phase factor of time evolution (first factor), a GP must be included. If the

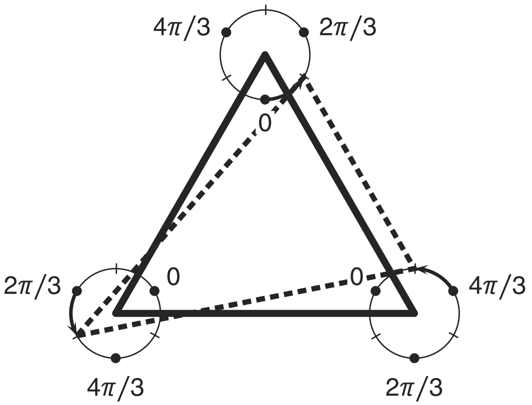

Figure 6.2. Distortions of a triatomic leading to appearance of GP in the $E \otimes e$ problem.

molecule performs a motion such that after some time $t = \tau$ it returns to its original position at time $t = 0$ $[\mathbf{R}(\tau) = \mathbf{R}(0)]$, then the wave function may not only have acquired a dynamical phase as described by $\exp[-(\iota/\hbar)\int^{t} E_i\left(t'\right) dt']$. Indeed, two possibilities exist: first, that the remaining part of the wave function has returned to its original value; second, that it has changed sign which simply requires that $A_i(\tau) = A_i(0) + \pi$. Recall that the sign of a wave function cannot be fixed, since it is its square that leads to an interpretation as a probability.

One may then ask when to expect the geometrical phase effect. The simplest case is that of H_3^+, a symmetric triatomic molecular ion which has the shape of an equilateral triangle [99]. Further examples are clusters built from hydrogen or alkali (lithium, sodium, potassium, etc) atoms. Such molecules may perform a motion, called pseudo-rotation, in which each of the three nuclei moves on a circle around its equilibrium position. If at the same time the molecule is in a degenerate electronic state, pseudo-rotational motion as illustrated in Figure 6.2 will build up a GP.

6.4 Generalized Born-Oppenheimer approximation

As noted above, the BO approximation breaks down at conical intersections since a real electronic wave function changes sign [20, 21, 100] whenever traversing a nuclear path that encircles the locus of degeneracy. Because the total electronuclear wave function must be continuous and single-valued, the nuclear wave function must change sign too such as to compensate the sign-change of the electronic counterpart. Although $\Psi_j(\mathbf{r}_n)$ and $\Phi_J(\mathbf{r}_n)$ may not be single-valued if real, there is no impediment to take them as complex in the Born-Huang [101] ansatz. For example, one may write

$$\Omega(\mathbf{r}_e, \mathbf{r}_n) = \sum_{Jj} \Phi_{Jj}(\mathbf{r}_n) \exp[iA_j(\mathbf{r}_n)] \Psi_j(\mathbf{r}_n) = \sum_{Jj} \Phi_{Jj}(\mathbf{r}_n) \tilde{\Psi}_j(\mathbf{r}_n) \tag{6.34}$$

where $A_j(\mathbf{r}_n)$ is the GP chosen to make the complex electronic wave function $\tilde{\Psi}_j(\mathbf{r}_n)$ [and hence $\Omega(\mathbf{r}_e, \mathbf{r}_n)$] be single-valued. Eq. (6.34) may alternatively be written as

$$\Omega(\mathbf{r}_e, \mathbf{r}_n) = \sum_{J} \tilde{\Phi}_{Jj}(\mathbf{r}_n) \Psi_j(\mathbf{r}_n) \tag{6.35}$$

where the complex nuclear wave functions $\left\{\tilde{\Phi}_{Jj}(\mathbf{r}_n)\right\}$ are now chosen to make $\Omega(\mathbf{r}_e, \mathbf{r}_n)$ be single-valued. If the ansatz in Eq. (6.35) is used, a set of coupled equations similar to Eq. (6.16) is obtained but with the real-valued nuclear wave functions replaced by the complex ones $\tilde{\Phi}_J(\mathbf{r}_n)$. If only the diagonal matrix elements are retained, then one gets

$$\left\{-\frac{\epsilon^4}{2}\left[\Delta_n + \mathbf{G}_{jj}(\mathbf{r}_n)\right] + V_j(\mathbf{r}_n) - E\right\} \tilde{\Phi}_j(\mathbf{r}_n) = 0 \tag{6.36}$$

Alternatively, if real nuclear wave functions as in Eq. (6.34) are employed, one has

$$\left\{-\frac{\epsilon^4}{2}\left[\nabla + \iota\nabla A_j(\mathbf{r}_n)\right]^2 + \bar{V}_j(\mathbf{r}_n) - E\right\} \Phi_j(\mathbf{r}_n) = 0 \tag{6.37}$$

where

$$\bar{V}_j(\mathbf{r}_n) = V_j(\mathbf{r}_n) - \frac{\epsilon^4}{2}\tilde{G}_{jj}(\mathbf{r}_n) \tag{6.38}$$

with $\tilde{G}_{jj}(\mathbf{r}_n)$ assuming the form given above but with the electronic wave functions tilded. Note that $\tilde{\mathbf{F}}_{jj}(\mathbf{r}_n) = \iota\nabla A_j(\mathbf{r}_n) + \mathbf{F}_{jj}(\mathbf{r}_n) = \iota\nabla A_j(\mathbf{r}_n)$ since, for real-valued electronic wave functions [102], $\mathbf{F}_{jj}(\mathbf{r}_n) = \langle\Psi_j(\mathbf{r}_n)|\nabla\Psi_j(\mathbf{r}_n)\rangle = 0$. Eq. (6.36) and Eq. (6.37) represent then a single-surface approach usually known as generalized BO approximation [40, 103]. Note that the ansatz in Eq. (6.34) leads to the appearance of a vector potential in the nuclear SE [26, 104, 105].

Note further that the $\mathbf{r}_n$-dependence of A_j must reflect the presence of any conical intersection in accordance with the GP [21, 24] condition, and hence can generally be constructed only once the conical intersections have been located. Although a general approach for determining $A_j(\mathbf{r}_n)$ has been suggested by Kendrick and Mead [103], it remains a nontrivial task. An alternative is to use Eq. (6.35), where the complex phase factor has been absorbed in the nuclear wave functions [106–108]. Such an approach is especially convenient for X_3-type systems when using hyperspherical coordinates [36, 109], although it can be generalized [40, 110, 111] to asymmetric cases. Of course, in the absence of a conical intersection, both Eq. (6.36) and Eq. (6.37) lead to the standard adiabatic nuclear SE

$$\left[-\frac{\epsilon^4}{2}\Delta_n + \bar{V}_j(\mathbf{r}_n) - E\right]\Phi_j(\mathbf{r}_n) = 0 \tag{6.39}$$

since $\tilde{D}^J_{jj}(\mathbf{r}_n) = D^J_{jj}(\mathbf{r}_n)$, and one may choose $A_j(\mathbf{r}_n) = 0$.

Consider now a 2×2 potential matrix $\mathbf{W}$ that is invariant and restricted to E space:

$$\mathbf{W} = W_{A_1}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + W_{E_x}\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} + W_{E_y}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{6.40}$$

where W_{A_1}, W_{E_x}, W_{E_y} are functions of the nuclear coordinates transforming under[6] the C_{3v} symmetry group; as usual in polar coordinates, $x = \rho\cos\varphi$, and $y = \rho\sin\varphi$. The eigenvalues of $\mathbf{W}$, which reduce to the degenerate pair at the conical configuration, will then assume the form

$$W_{\pm} = W_{A_1} \pm W_\rho \tag{6.41}$$

where $W_\rho = \left(W_{E_x}^2 + W_{E_y}^2\right)^{1/2}$. To all orders, they assume the form [112]

$$W_{A_1} = f_1\left[z; \rho^2, \rho^3\cos(3\varphi)\right] \tag{6.42}$$

$$W_{E_x} = \rho\cos\varphi f_3\left[z; \rho^2, \rho^3\cos(3\varphi)\right] + \rho^2\cos(2\varphi) f_4\left[z; \rho^2, \rho^3\cos(3\varphi)\right] \tag{6.43}$$

$$W_{E_y} = \rho\sin\varphi f_3\left[z; \rho^2, \rho^3\cos(3\varphi)\right] - \rho^2\sin(2\varphi) f_4\left[z; \rho^2, \rho^3\cos(3\varphi)\right] \tag{6.44}$$

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[6] We may consider only this subgroup of D_{3h} since no out-of-plane bending is possible for a triatomic system. The component W_{A_2} must vanish, since $\mathbf{W}$ must be Hermitian, and in our case can be real.

where f_i (i=1−4) are functions formally representable as a double power series in their arguments other than z, with the coefficients being constant or functions of z. From Eq. (6.41) to Eq. (6.44), it follows:

$$W_{A_1} = W_{A_1}\left(z; \rho^2, \rho^3 \cos 3\varphi\right) \tag{6.45}$$

$$W_R = r\left(f^2 + \rho^2 g^2 + 2\rho f g \cos 3\varphi\right)^{1/2} \tag{6.46}$$

$$\to \rho w\left(z; \rho^2, \rho \cos 3\varphi\right) \qquad (\rho \to 0) \tag{6.47}$$

where $f = f(z; \rho^2, \rho^3 \cos 3\varphi)$, $g = g(z; \rho^2, \rho^3 \cos 3\varphi)$, and w are analytic functions. Eqs. (6.42)-(6.44) define the correct behavior of the PES in the vicinity of the conical intersection, and hence may be valuable in delineating fitting forms [112, 113]; for recent work on fitting and interpolation methods, the reader is referred to Refs. 114 and 115.

Let now $\tilde{\gamma}$ be an angle, itself a function of the nuclear coordinates, such that

$$W_{E_x} = W_\rho \cos\tilde{\gamma}, \quad W_{E_y} = W_\rho \sin\tilde{\gamma} \tag{6.48}$$

In terms of the degenerate pair of wave functions (ψ_x, ψ_y), we may write the two adiabatic ones (Ψ_+, Ψ_-) corresponding to the eigenvalues of Eq. (6.41) as

$$\Psi_+ = \psi_x \sin(\tilde{\gamma}/2) + \psi_y \cos(\tilde{\gamma}/2), \tag{6.49}$$

$$\Psi_- = \psi_x \cos(\tilde{\gamma}/2) - \psi_y \sin(\tilde{\gamma}/2) \tag{6.50}$$

which cannot be single-valued due to the appearance of $\tilde{\gamma}/2$ (note that both Ψ_+ and Ψ_- change sign when $\tilde{\gamma}$ increases by 2π). Thus, $\tilde{\gamma}/2$ is the mixing angle that yields the adiabatic states from the diabatic ones (*i.e.*, diagonalizes the diabatic potential matrix). Single-valuedness is warranted by defining [26, 104] the GP as $A_+(\mathbf{R}) = A_-(\mathbf{R}) = 3\varphi/2$, although other possibilities exist [40, 41] (see also Ref. 42). Since $\langle\Psi_+|\Psi_-\rangle = \delta_\pm$, one gets

$$\tilde{\mathbf{d}} = \mathbf{d} = \langle\tilde{\Psi}_-|\nabla\tilde{\Psi}_+\rangle = -\langle\tilde{\Psi}_+|\nabla\tilde{\Psi}_-\rangle \tag{6.51}$$

Using now Eq. (6.49) to Eq. (6.51), one obtains

$$\mathbf{d} = \mathbf{d}^{\mathrm{lon}} + \mathbf{d}^{\mathrm{tra}} \tag{6.52}$$

where the curl-free longitudinal and divergence-free transverse (solenoidal) parts of the derivative coupling are given by [112]

$$\mathbf{d}^{\mathrm{lon}} = \frac{1}{2}\nabla\tilde{\gamma} \tag{6.53}$$

$$\mathbf{d}^{\mathrm{tra}} = \langle\psi_x|\nabla\psi_y\rangle \tag{6.54}$$

a result which is a consequence of the general Helmoltz decomposition theorem.

The longitudinal part of **d** shows a singularity at the conical intersection but this singularity can be removed by a coordinate-dependent unitary transformation [116]. Moreover, from Eq. (6.43), Eq. (6.44) and Eq. (6.48), one may write [112]

$$\tan\tilde{\gamma} = \frac{f\sin\varphi - \rho g\sin(2\varphi)}{f\cos\varphi + \rho g\cos(2\varphi)} \tag{6.55}$$

and defining ϵ such that $\tilde{\gamma} = \varphi + \epsilon$, one has

$$\tan\epsilon = -\frac{\rho g\sin(3\varphi)}{f + \rho g\cos(3\varphi)} \tag{6.56}$$

Thus,

$$\mathbf{d}^{\mathrm{lon}} = \frac{1}{2}\nabla_{\mathbf{r}_n}\left\{\varphi - \tan^{-1}\left[\frac{\rho g\sin(3\varphi)}{f + \rho g\cos(3\varphi)}\right]\right\} \tag{6.57}$$

which defines the correct analytic properties of the nonadiabatic coupling near the seam of a potential energy surface exhibiting a C_{3v} conical intersection [112, 113, 117, 118].

Eq. (6.53) can be solved by integration along paths in the nuclear configuration space [119, 120]. The result will depend on the initial and final points of integration but not on the path chosen. Due to the LH theorem [20, 21, 100], if the integration is carried out along a closed loop $\mathcal{C}$, $\tilde{\gamma}/2$ should change by [24, 120, 121]

$$\xi_{\tilde{\gamma}} = \oint_{\mathcal{C}} \mathbf{d}^{\mathrm{lon}}(\mathbf{r_n})\, d\mathbf{r}_n = p\pi \tag{6.58}$$

where $p = 0$ if $\mathcal{C}$ does not enclose any conical intersection, but is 1 if it does enclose one.

The transverse part remains finite at the seam, and cannot generally be transformed away to zero for a polyatomic system [116, 119]. However, one may think of defining an (adiabatic-diabatic transformation, ATD) angle [66, 76, 119] $\alpha(\mathbf{r}_n)$ such that

$$\mathbf{d} = \nabla\alpha(\mathbf{r}_n) \tag{6.59}$$

which would be [up to a constant, *cf.* Eq. (6.53)] identical to the angle capable of transforming the adiabatic basis to a diabatic one or vice-versa. Similarly, a topological phase [122] can be defined as

$$\xi_\alpha = \oint_{\mathcal{C}} \mathbf{d}\,(\mathbf{r}_n)\,d\mathbf{r}_n \tag{6.60}$$

Since $\mathbf{d}$ does not generally satisfy Eq. (6.53), the result of such an integration will be path-dependent [116]. However, since the transverse part is finite (and possibly negligible upon optimal adiabatization [118]), one may expect to have $\xi_{\tilde{\gamma}} = \xi_\alpha$. As noted above, the mixing angle $\gamma(\mathbf{r}_n) = \tilde{\gamma}/2$ that diagonalizes the potential matrix is (up to a constant) identical to $\alpha(\mathbf{r}_n)$ [41], and also to the GP $A_j(\mathbf{r}_n)$ [40].

6.5 Configuration vs function space, and conservation laws

The configuration space forms the natural frame where to represent an adiabatic PES. For the purpose of studying the JT effect, only the subspace defined by the coordinates that are JT active is required since it contains all distorted configurations that may be reached by such vibrational modes. Their complete set subtends a real Cartesian space of dimension $\tau = [\Gamma^2] - 1$ known as [123] the *configuration space v* or simply *configuration space*. Figure 6.3 illustrates such a space the case of a triatomic belonging to the symmetry group C_{3v}, where the symmetric product leads to $[E_1^2] = A_1 \oplus E_1$. The v-space will then be defined by the e-type vibrations that span the $2D$ space $\{Q_{E_x}, Q_{E_y}\}$, which can be expressed in terms of the three bond distances (R_1, R_2, R_3) either as linear symmetrized combinations of bond distances

$$\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \begin{pmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \end{pmatrix} \begin{pmatrix} R_1 \\ R_2 \\ R_3 \end{pmatrix} \tag{6.61}$$

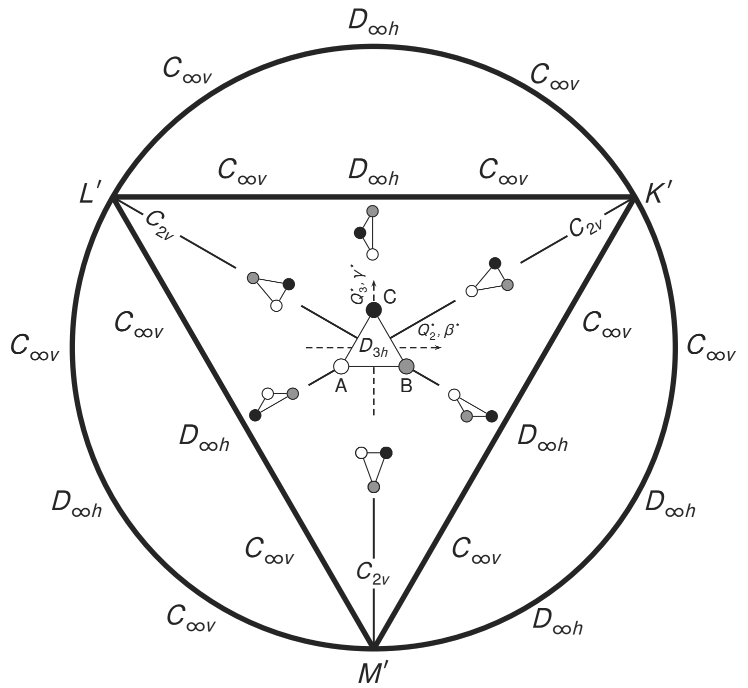

Figure 6.3. Locus of symmetry point groups assuming that the group operations are applied to three identical nuclei A, B, and C (denoted by the colored dots). The C_s symmetry is intrinsic to the entire physical circle based on the coordinates in Eq. (6.62) [corresponding considerations apply to the physical triangle when using Eq. (6.61)]. Molecular conformations obtained by following a closed path around the origin are also shown. K', L', and M' indicate the points where the 'physical triangle' and 'physical circle' centered at the origin of the coordinate system touch each other and the circunscribing equilateral triangle employed for the relaxed triangular plot [124]. Completion of a circular motion of the three atoms in panel (a) originates a circular path around the origin in Figure 6.2. Q_2 and Q_3 correspond to Q_{E_x} and Q_{E_y}, respectively. See the text.

or of their squares,

$$\begin{pmatrix} \mathcal{Q} \\ \beta \\ \gamma \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 \\ 0 & \sqrt{3} & -\sqrt{3} \\ 2 & -1 & -1 \end{pmatrix} \begin{pmatrix} R_1^2 \\ R_2^2 \\ R_3^2 \end{pmatrix} \tag{6.62}$$

Note that Q_1 and $\mathcal{Q}$ transform as A_1, while $\{Q_2, Q_3\}$ and (β, γ) transform as the degenerate pair of E-symmetry $\left\{Q_{E_x}, Q_{E_y}\right\}$. Note further that the locus of degeneracy is in this case a $0D$ manifold embedded in that space, a point that coincides with the JT origin ($Q_2 = 0, Q_3 = 0$). In the vicinity of the crossing point, the PES will appear in the (β, γ) representation as a double cone, as it could be

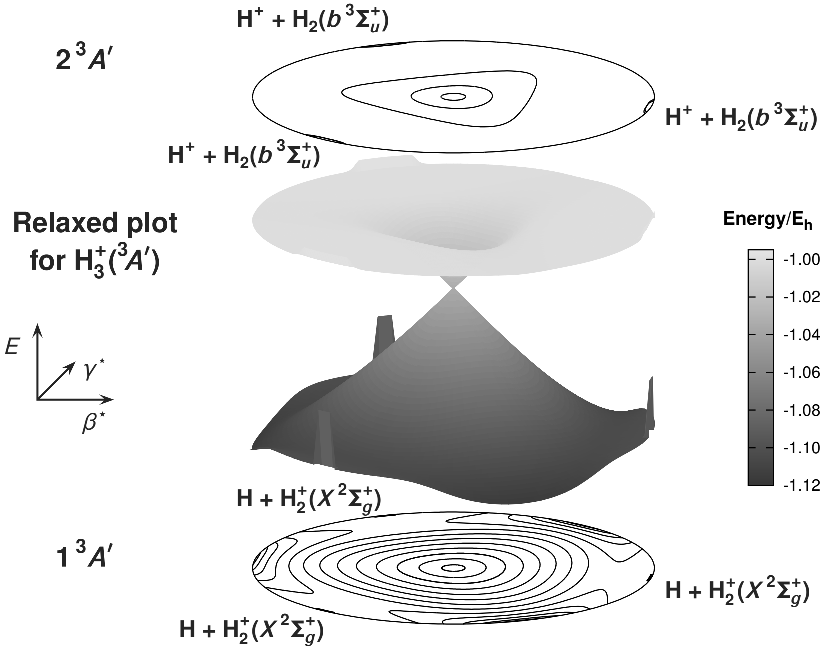

Figure 6.4. Perspective view [124] and contour plots of the adiabatic DMBE PESs of [125] $H_3^+(^4A')$ using hyperspherical coordinates. Also indicated are the asymptotic channels. Contours generated from $E_n/\mathrm{E_h} = -1.116 + 0.000447n^2$, where n is the contour number.

anticipated from Eq. (6.48). A realistic example is illustrated in Figure 6.4 for the $H_3^+(^3A')$ ion, where we have utilized the symmetrized coordinates in Eq. (6.62) suitably relaxed [124] ($\beta^* = \beta/\mathcal{Q}$, $\gamma^* = \gamma/\mathcal{Q}$) such that $\mathcal{Q}$ corresponds at each point to the structure of lowest energy for that symmetry. They can be related to the hyperspherical coordinates [36] (ρ, θ, φ) through the relations

$$R_1^2 = \frac{1}{2} d_1^2 \rho^2 \left[1 + \sin\frac{\theta}{2} \cos(\varphi + \chi_3) \right] \tag{6.63}$$

$$R_2^2 = \frac{1}{2} d_2^2 \rho^2 \left(1 + \sin\frac{\theta}{2} \cos\varphi \right) \tag{6.64}$$

$$R_3^2 = \frac{1}{2} d_3^2 \rho^2 \left[1 + \sin\frac{\theta}{2} \cos(\varphi - \chi_1) \right] \tag{6.65}$$

where $d_i^2 = m_i/\mu \left(1 - m_i/M\right)$, $\chi_\mathrm{i} = 2\tan^{-1}\left(m_{i+2}/\mu\right)$, $\mu = \left(m_1 m_2 m_3/M\right)^{1/2}$, and $M = \sum_i m_i$. Thus, the plot in Figure 6.4 corresponds to a stereographic projection of the surface of an upper half sphere. The $\beta^\star$ coordinate corresponds to $\sin\left(\theta/2\right)\cos\varphi$, while $\gamma^\star$ denotes $\sin\left(\theta/2\right)\sin\varphi$. The hyperangle θ runs from zero at the north pole (center of plot) to $\pi/2$ at the equator. In turn, the hyperangle φ is measured from the positive $\beta^\star$ axis and grows on going counterclockwise. Note the three equivalent weak minima separated from each other by a tiny barrier that along the trough for pseudorotation.

A second example refers to threefold electronic degeneracies that are inherent to cubic groups T, T_d, O, O_h, and icosahedral groups I and I_h [11]. In the absence of inversion centers, $[T_1^2]=[T_2^2]=A_1\oplus E\oplus T_2$, while in the presence of inversion, the result is $[T_{1g}^2]=[T_{1u}^2]=[T_{2g}^2]=[T_{2u}^2]=A_{1g}\oplus E_g\oplus T_{2g}$. Thus, the JT active vibrations for a threefold degenerate electronic term (T_1 or T_2) are of e or t_2 symmetry: $T\otimes(e\oplus t_2)$ problem. If the coupling of the two t modes can be neglected, the analysis of the JT effect will be restricted to $5D$ space [126] defined by the normal coordinates $\left\{Q_{E_x}, Q_{E_y}\right\}$ for the e representation (tetragonal-type coordinates), and $\left\{Q_{T_x}, Q_{T_y}, Q_{T_z}\right\}$ for the t_2 representation (trigonal-type coordinates). Of course, such a space cannot be fully visualized. A possible way for reducing the dimensionality consists of assuming that the vibronic interaction with one of the two types of vibrations can be neglected. For other degenerate electronic terms interacting with degenerate vibrations, see Ref. 13.

Due to H invariance under time-reversal, the space of the electronic BO wave vectors can also be represented by a $(N-1)$-sphere in ND real space as the BO dynamics is known [123] to realize an adiabatic mapping of the v-space into such a *projective function space* (f-space). An arbitrary adiabatic electronic state assumes then the form

$$|\Gamma\gamma\rangle = \sum_{i=1,|\Gamma|} c_i|\Gamma\gamma_i\rangle \tag{6.66}$$

with norm preserving requirement $\sum_i c_i^\star c_i = 1$. The allowed transformations in f-space will then involve rotations or reflections of the points on the unit sphere. Its full symmetry group is $O(|\Gamma|)$, and the elements orthogonal matrices describing the transformation of the directional cosines c_i. Symmetry elements of the finite group G will then induce orthogonal matrix transformations, with the Γ matrix representation of G being a subgroup of $O(|\Gamma|)$. Of course, an advantage of the f-space is the lower number of parameters required to characterize an arbitrary state: $(N-1)$ *vs* τ for the f *vs* v spaces, respectively. The latter has been suggested by Ceulemans [123] to represent the PES itself, although we will utilize [48] it to characterize the GP effect by examining the outcome of matrix applications on an arbitrary electronic eigenvector.

Conservation laws and symmetries play a key role both in physics and mathematics as they allow to specify the dynamics of the system in terms of the first integrals of the motion. Noether's theorem plays in this context a prominent role by stating that the action admits an r-parameter Lie group as variational symmetries if there are r proper conservation laws. Thus, the vibronic Hamiltonian in the $E \otimes e$ system has the symmetry of the one-parameter axial group $O(2)$ because there is just one conserved quantity. In fact, diagonalization of the vibronic JT matrix shows that the component L_z of the angular momentum is the only constant of the motion, with the mixing (pseudo-rotation) angle that characterizes the unitary matrix being α_z. Similarly, the symmetry of the Hamiltonian of the $T \otimes (e \oplus t_2)$ system is [11] $SO(3)$, a 3-parameter Lie group. In this case, the 3×3 rotation matrix that diagonalizes the vibronic JT matrix assumes the form of a product of 3 planar rotations in configuration space, with a pseudo-rotation angle associated to every conserved component of the total angular momentum. Similar considerations hold for systems associated to other Lie groups; the symmetry invariances of the relevant linear JT Hamiltonian operators are discussed in the literature [11] (see also Table 2.3 of Ref. 19). It turns out that the group G has a dimension that does not generally coincide with the number of mixing angles required to describe an adiabatic electronic state in its associated function space. For example, only 2 mixing angles are necessary to describe the $T \otimes (e \oplus t_2)$ problem while 3 suffice for the $G \otimes (g \oplus h)$ one, respectively of dimensions 3 and 6. The former may be rationalized from the fact that only two combinations of its 3 invariants (the components of the angular momentum operator J_x, J_y and J_z), say J^2 and J_z, are known to commute. As a result, only 2 quantum numbers (or, equivalently, mixing angles) suffice to specify unambiguously an adiabatic electronic wave vector of the $T \otimes (e \oplus t_2)$ system. Similarly, although the orbital angular momentum in a $4D$ Cartesian space is described by 6 orbital angular momentum operators, only 4 commuting combinations arise, one corresponding to an operator that vanishes identically [127]. This indicates that 3 mixing angles only suffice to describe an adiabatic electronic wave vector for the $G \otimes (g \oplus h)$ problem. In fact, and more generally, although a set $N(N-1)/2$ components of the generalized orbital angular momentum can be defined for the N-fold problem, only $(N-1)$ commuting generalized orbital angular momentum operators are known to commute. Thus, they possess simultaneous eigenfunctions that depend on $(N-1)$ angular variables [128]. As above, this may explain why only $(N-1)$ angles are required to characterize unambiguously the corresponding adiabatic electronic wave vector [19, 45, 48].

The mapping in the electronic sphere is, however, two-valued since antipodal pairs of eigenvectors ($|\Gamma\gamma\rangle$ and $-|\Gamma\gamma\rangle$) refer to the same point in v-space: a physical state may be described by any wave vector in a ray [129]. This has implications on the GP analysis, since two classes of paths (closed loops) in v-space can be recognized [28]: paths that are continuously contractable to a point (class Π_1) and hence manifest no GP, and paths (Π_2) that manifest GP by showing a sign-change of the electronic state when going from a point A to its antipodal A'. Additionally, there are paths that connect a point to its antipodal without manifestation of GP, thus sign change. This is possible [28] provided that a point $\boldsymbol{Q}_d$ exists on the path where the mapping is degenerate by linking not just a pair of opposite points but a whole circle of linear combinations $\cos\theta|\psi_1(\boldsymbol{Q}_d)\rangle + \sin\theta|\psi_2(\boldsymbol{Q}_d)\rangle$ of two degenerate electronic states (path Δ in Figure 6.5).

6.6 Case studies of Jahn-Teller vibronic coupling

6.6.1 $e \otimes E$

The title JT problem has been much studied, and hence will serve here the purpose of comparing the two different formalisms discussed in the previous sections. Let the BO electronic wave vectors be $\{\psi_1, \psi_2\} = \{|E_x\rangle, |E_y\rangle\}$ [19, 45]. The two adiabatic wave vectors can then be unambiguously expressed in f-space

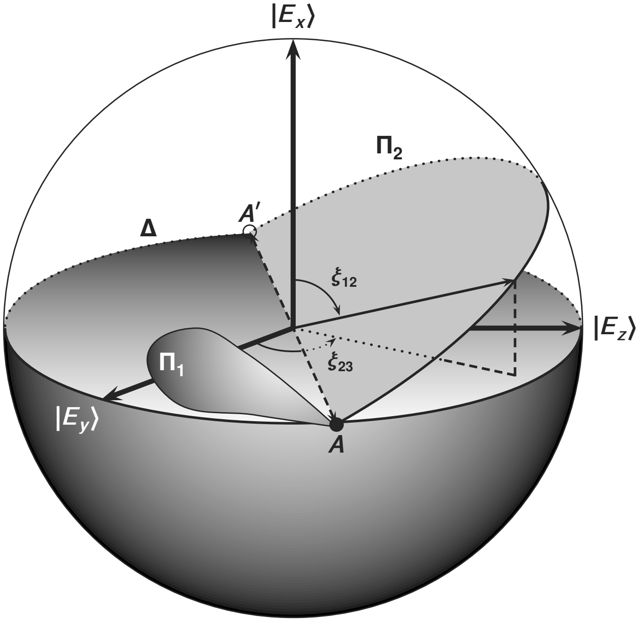

Figure 6.5. Paths in function space for $N=3$ (S^2 electronic sphere) that map onto closed loops in configuration space. Π_2 paths (from A to A', indicated by the solid and open circles, respectively) that involve a sign change and hence GP effect. With $\xi_{12}=0$ one gets: $|\Psi_1\rangle=|E_x\rangle$, $|\Psi_2\rangle=\cos\xi_{23}|E_y\rangle+\sin\xi_{23}|E_z\rangle$, and $|\Psi_3\rangle=-\sin\xi_{23}|E_y\rangle+\cos\xi_{23}|E_z\rangle$. In turn, for $\xi_{12}=\pi$: $|\Psi_1\rangle=-|E_x\rangle$, $|\Psi_2\rangle=-\cos\xi_{23}|E_y\rangle-\sin\xi_{23}|E_z\rangle$, and $|\Psi_3\rangle=-\sin\xi_{23}|E_y\rangle+\cos\xi_{23}|E_z\rangle$. For $\xi_{12}=0$ and π, all $|\Psi_i\rangle$ change sign upon the transformation $\xi_{23}\rightarrow\xi_{23}+\pi$, but $|\Psi_2\rangle$ does so by evolving from A to A' when $\xi_{12}=0$ and returning to A when $\xi_{12}=\pi$. Thus, $|\Psi_2\rangle$ leads to a Δ-type path (simply connected) under $\hat{\imath}_3$ by not manifesting GP. Also shown is a simply connected path of type Π_1.

as

$$\begin{pmatrix} \Psi_1(\mathbf{r}_n;\xi_z) \\ \Psi_2(\mathbf{r}_n;\xi_z) \end{pmatrix} = \begin{bmatrix} \cos\xi_z(\mathbf{r}_n) & \sin\xi_z(\mathbf{r}_n) \\ -\sin\xi_z(\mathbf{r}_n) & \cos\xi_z(\mathbf{r}_n) \end{bmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \tag{6.67}$$

where $\xi_z = \alpha_z/2$ is the mixing angle. Thus, $\langle\Psi_1|\nabla\Psi_2\rangle = -\langle\Psi_2|\nabla\Psi_1\rangle = \nabla\xi_z$. Defining [40]

$$\tilde{\Psi} = \frac{1}{\sqrt{2}}(\Psi_1 + \iota\Psi_2) \tag{6.68}$$

it is now easy to show that $\langle\tilde{\Psi}|\nabla\tilde{\Psi}\rangle = \iota\langle\Psi_1|\nabla\Psi_2\rangle$. Similarly, it follows that $\langle\tilde{\Psi}|\nabla\tilde{\Psi}\rangle=\iota\nabla A(\mathbf{r}_n)$. It then follows that $\nabla A(\mathbf{r}_n)=\nabla\xi_z(\mathbf{r}_n)$, a result corroborating the statement already made that the GP is (up to a constant term that has no physical implications) identical to the mixing angle and which will be of use again at a later stage.

Consider now the equations of nuclear motion for the title $2D$ coupled problem[7]:

$$\left[-\frac{\hbar^2}{2\mu}\left(\nabla^2+\langle\Psi_1|\nabla^2\Psi_1\rangle\right)+V_1-E\right]\Phi_1=\frac{\hbar^2}{2\mu}\left[\langle\Psi_1|\nabla^2\Psi_2\rangle+2\langle\Psi_1|\nabla\Psi_2\rangle\cdot\nabla\right]\Phi_2 \tag{6.69}$$

$$\left[-\frac{\hbar^2}{2\mu}\left(\nabla^2+\langle\Psi_2|\nabla^2\Psi_2\rangle\right)+V_2-E\right]\Phi_2=\frac{\hbar^2}{2\mu}\left[\langle\Psi_2|\nabla^2\Psi_1\rangle+2\langle\Psi_2|\nabla\Psi_1\rangle\cdot\nabla\right]\Phi_1 \tag{6.70}$$

By writing [100] the complex nuclear wave function

$$\tilde{\Phi}=\frac{1}{\sqrt{2}}(\Phi_1+\iota\Phi_2) \tag{6.71}$$

and using the NACTs given above as well as $\langle\nabla\Psi_i|\nabla\Psi_i\rangle=[\nabla\xi_z(\mathbf{r}_n)]^2$, $\langle\nabla\Psi_i|\nabla\Psi_j\rangle=0$, $\langle\Psi_i|\nabla^2\Psi_j\rangle=\nabla^2\xi_z(\mathbf{r}_n)$, and $\langle\Psi_j|\nabla^2\Psi_i\rangle=-\nabla^2\xi_z(\mathbf{r}_n)$, yields

$$\left\{-\frac{\hbar^2}{2\mu}\left[\nabla^2-(\nabla\xi_z)^2\right]+E_i-E\right\}\tilde{\Phi}+\frac{\iota}{\sqrt{2}}\left(V_j-V_i\right)\Phi_j= \\ -\iota\frac{\hbar^2}{2\mu}\left(\nabla^2\xi_z+2\nabla\xi_z\cdot\nabla\right)\tilde{\Phi}\quad i,j=1,2 \tag{6.72}$$

Near the crossing seam, the term $\left(V_j-V_i\right)$ should be negligibly small, reducing to [40]

$$\left\{-\frac{\hbar^2}{2\mu}\left[\nabla^2-(\nabla\xi_z)^2\right]+V-E\right\}\tilde{\Phi}=-\iota\frac{\hbar^2}{2\mu}\left(\nabla^2\xi_z+2\nabla\xi_z\cdot\nabla\right)\tilde{\Phi} \tag{6.73}$$

a single (uncoupled) equation that should be accurate there both for $V=V_1$ and V_2. Note that the above differs from the Baer-Englman [37, 130] treatment in that Eq. (6.73) is valid for both sheets. Furthermore, unlike the latter, it uses the mixing angle $\xi_z(\mathbf{R})$ and no assumption is made that the upper sheet is closed to the dynamics. Of course, the BO approximation is recovered for derivative coupling constant or zero.

The implications of the GP in the dynamics can now be found by comparing the results obtained by solving the dynamics of nuclear motion in Eq. (6.73) with inclusion of GP and without it. Such studies have been carried out for a wealth of systems [18, 39, 110, 111, 115, 131–135], with the reader being referred

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[7] For clarity, we return to the explicit use of $\hbar$, and reduced mass.

to the original papers for details. Suffice it to say that the nuclear SE including GP may be written as $\hat{H}\tilde{\Phi} = E\tilde{\Phi}$, where $\hat{H} = \hat{H}_0 + \imath\hat{H}_1$. Explicitly, it assumes in hyperspherical coordinates [36] the form

$$\begin{aligned}
\hat{H}_0 =& -\frac{\hbar^2}{2\mu}\left\{\frac{\partial^2}{\partial\rho^2}+\frac{16}{\rho^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{4\sin^2(\theta/2)}\frac{\partial^2}{\partial\phi^2}\right]\right\} \\
&+\frac{\hat{J}^2-\hat{J}_z^2}{\mu\rho^2\cos^2(\theta/2)}+\frac{\hat{J}_z^2+4\imath\hbar\hat{J}_z\cos(\theta/2)(\partial/\partial\phi)}{2\mu\rho^2\sin^2(\theta/2)}+\frac{15\hbar^2}{8\mu\rho^2} \\
&+\frac{\sin(\theta/2)}{\mu\rho^2\cos^2(\theta/2)}\frac{1}{2}\left[\hat{J}_+^2+\hat{J}_-^2\right]+V(\rho,\theta,\phi)+\frac{\hbar^2}{2\mu}\left[\nabla\xi_z(\rho,\theta,\phi)\right]^2 \\
\hat{H}_1 =& -\frac{\hbar^2}{2\mu}\left[\nabla^2\xi_z(\rho,\theta,\phi)+2\nabla\xi_z(\rho,\theta,\phi)\cdot\nabla\right]
\end{aligned}$$

with all symbols having their usual meaning. Note that singularities may arise at $\rho = 0$ and $\theta = 0$, which requires special care. Note especially that the generalized BO approximation requires the gradient of GP rather than the GP itself. Early applications of the theory are reviewed in Ref. 18, to where the reader is addressed for details.

Consider now Eq. (6.67) written in matrix form as

$$\boldsymbol{\Psi}(\mathbf{r}_n;\xi_z) = \mathbf{R}_2(\xi_z)\boldsymbol{\psi} \tag{6.74}$$

which shows that a vector state will define in function space a point on the circle of unit radius centered at its origin. A rotation $\xi_z \to \xi_z+\pi$ characterized by the operator $\hat{R}_2$ will then lead to $\mathbf{R}_2(\xi_z+\pi) = -\mathbf{R}_2(\xi_z)$. Since both adiabatic electronic wave vectors Ψ_1 and Ψ_2 change sign upon acting with $\hat{R}_2$, the result mimics the one obtained for a closed loop in v-space ($\alpha_z \to \alpha_z+2\pi$) or the topological impossibility of unpinning the electronic circle from an enclosed point of degeneracy. As seen from Figure 6.6 (cf Figure 6.5 for a realistic system), the JTM forms a $1D$ trough in the lower sheet of the $E\otimes e$ problem [11, 13], so-called the 'Mexican hat', with the motion along the distortion coordinate α_z being equivalent to the concerted motion of each atom around a circle [*i.e.*, pseudo-rotation in Figure 6.2], The GP effect for systems with an orbital doublet degeneracy may then be stated as [19, 45, 48]: *an electronically adiabatic state that experiences the GP effect will change sign after completing a loop around the*

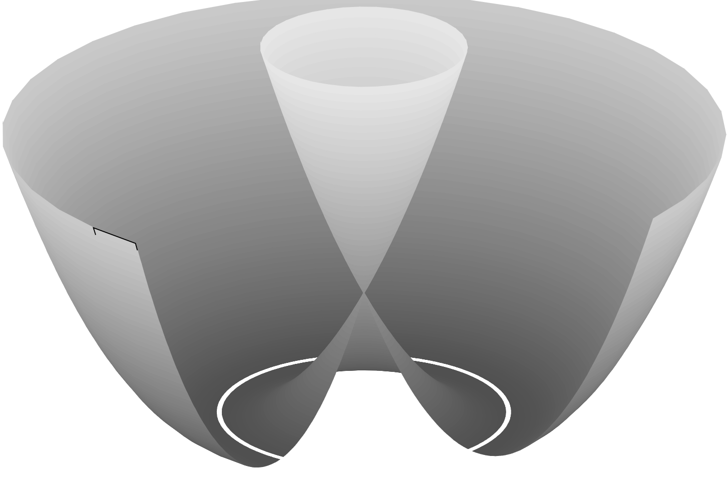

Figure 6.6. The “Mexican hat”. Besides the diagonal kinetic energy matrix, the linear JT Hamiltonian is characterized in the $\left\{Q_{E_x}, Q_{E_y}\right\}$ phase space by the potential matrix $\frac{1}{2}\omega_E^2\left(Q_{E_x}^2+Q_{E_y}^2\right)\boldsymbol{\sigma}_0+V_E\left(Q_{E_x}\boldsymbol{\sigma}_x+Q_{E_y}\boldsymbol{\sigma}_y\right)$, where $\boldsymbol{\sigma}_0=\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$, $\boldsymbol{\sigma}_x=\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$, and $\boldsymbol{\sigma}_y=\begin{bmatrix}0 & \iota\\ -\iota & 0\end{bmatrix}$ are Pauli matrices. In turn, ω_E characterizes the two harmonic oscillators and V_E the strength of the linear JT interaction. [10–12] Shown by the white line is the JTM, which corresponds to a circle of radius $\rho=(Q_{E_x}^2+Q_{E_y}^2)^{1/2}$ centered at the vertex of the diabolo, $\rho=0$, with an energy of $-V_E^2/2\omega^2$.

conical intersection in v-space or, equivalently, upon use of the rotation operator $\hat{R}_2$ *in f-space.* Although this may appear a trivial result since a path connecting a point to its antipodal must lead to a sign change of $|\Psi_1\rangle$ and $|\Psi_2\rangle$, it is not so when $N\geq 3$.

6.6.2 $\boldsymbol{T\otimes(e\oplus t_2)}$

Consider now the threefold electronic degeneracy in $T\otimes(e\oplus t_2)$. The JT Hamiltonian including linear vibronic coupling has now Lie group symmetry $SO(3)$ [11], which implies dimension 3 and hence 3 Lie group parameters. Since a norm-preserving adiabatic electronic wave vector on the electronic sphere S^2 can be unambiguously characterized in terms of two angles, there is freedom of choice for selecting the latter out of the three coordinates in $SO(3)$. The remaining one can, however, be sampled by considering all three two-angle sets. By assigning a 3 × 3 unitary planar rotation matrix to each of the chosen coordinates (ξ_{12} and ξ_{23}), the full rotation matrix assumes the form

$$\mathbf{R}_3 = \boldsymbol{\rho}_{12}(\xi_{12})\boldsymbol{\rho}_{23}(\xi_{23}) \tag{6.75}$$

where $\left[\boldsymbol{\rho}_{nm}\right]_{nn} = \left[\boldsymbol{\rho}_{nm}\right]_{mm} = \cos\xi_{nm}$, and $\left[\boldsymbol{\rho}_{nm}\right]_{nm} = -\left[\boldsymbol{\rho}_{nm}\right]_{mn} = \sin\xi_{nm}$; all other entries satisfy $\left[\boldsymbol{\rho}_{nm}\right]_{ij} = \delta_{ij}$. As in the $E\otimes e$ problem, the electronic adiabatic wave vectors will now be given by the rows of the following $\mathbf{R}_3$ matrix:

$$\begin{pmatrix} \Psi_1(\mathbf{r}_n;\xi_{23},\xi_{12}) \\ \Psi_2(\mathbf{r}_n;\xi_{23},\xi_{12}) \\ \Psi_3(\mathbf{r}_n;\xi_{23},\xi_{12}) \end{pmatrix} = \begin{bmatrix} \cos\xi_{12} & \sin\xi_{12}\cos\xi_{23} & \sin\xi_{12}\sin\xi_{23} \\ -\sin\xi_{12} & \cos\xi_{12}\cos\xi_{23} & \cos\xi_{12}\sin\xi_{23} \\ 0 & -\sin\xi_{23} & \cos\xi_{23} \end{bmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} \tag{6.76}$$

where $\xi_{12}(\mathbf{r}_n)$ is the first mixing angle (describes the mixing of ψ_1 and ψ_2 to form an intermediate adiabatic state Ψ_{12}), and $\xi_{23}(\mathbf{r}_n)$ is the second mixing angle (describes the mixing of Ψ_{12} and ψ_3). Upon use of the matrix $\mathbf{R}_3$ associated to the double-rotation in f-space defined by $\xi_{12}\rightarrow\pi-\xi_{12}$ and $\xi_{23}\rightarrow\xi_{23}+\pi$, Ψ_1 and Ψ_3 are seen to be the only eigenstates that change sign. Note that the two angles define normwise the degeneracy locus of an adiabatic state, being equivalent to the pseudo-rotational angles in v-space.

Figure 6.5 shows that a path connecting a point to its antipodal in f-space leads to a manifestation of the GP effect for Ψ_1 and Ψ_3 but not Ψ_2. Following Ref 48, this can be understood as follows. Consider the angle ξ_{12} fixed at $\xi_{12}=0$ such that the point A and its antipodal A' lie on the equator of the electronic sphere, with the path Π_2 passing on its north pole. Thus, $\Psi_1 = \psi_1$, $\Psi_2 = \cos\xi_{23}\psi_2 + \sin\xi_{23}\psi_3$, and $\Psi_3 = -\sin\xi_{23}\psi_2 + \cos\xi_{23}\psi_3$. For ξ_{12} fixed at 0, Ψ_2 and Ψ_3 will change sign upon the transformation $\xi_{23}\rightarrow\xi_{23}+\pi$. By considering now $\xi_{12}=\pi$, one obtains $\Psi_1\rightarrow-\Psi_1$ and $\Psi_2 = -\cos\xi_{23}\psi_2 - \sin\xi_{23}\psi_3 = \cos(\xi_{23}+\pi)\psi_2 + \sin(\xi_{23}+\pi)\psi_3$ while Ψ_3 shows the same dependence on ξ_{23} as for $\xi_{12}=0$. Thus, upon the transformation $\xi_{23}\rightarrow\xi_{23}+\pi$, Ψ_2 evolves from A to A' (changes sign) when $\xi_{12}=0$, but closes the loop (*i.e.*, changes sign again) by returning to A when $\xi_{12}=\pi$. The notable feature is then the cancelation of signs that occurs when both ξ_{12} and ξ_{23} vary simultaneously. Equivalently, Ψ_2 keeps its sign unchanged upon acting with the matrix $\mathbf{R}_3$. The same conclusions can be extracted irrespectively of the initial and final values of ξ_{12} provided that they differ by π. The important observation is the cancelation of signs in Ψ_2 owing to the fact that the path from A to A' becomes a closed one (*i.e.*, Δ-type). Similar results are obtained irrespective of the chosen angles, provided that the matrices in Eq. (6.75) form an ordered sequence yielding physical solutions: *under the action of $\hat{R}_3$, an arbitrary wave vector must either change sign or remain sign unchanged*. State labeling in Eq. (6.76) is also arbitrary showing that only one pair of adiabatic electronic states changes sign.

The above results indicate that the three branches of the three-valued PES and the electronic S^2-sphere show a different connectedness. While the latter is simply connected (any closed path or loop can be smoothly contracted to a point), the former may well have 'holes' in their topologies and hence be multiply connected. Thus, besides trivial paths of class Π_1, there may be nontrivial ones of Π_2 type. In fact, these two classes of paths seem to be topologically distinct in states Ψ_1 and Ψ_3 (*i.e.*, loops belonging to class Π_2 can never evolve smoothly to Π_1-type ones), thence explaining their multiple-connectedness property. Thus, our predictions agree with previous findings [28, 35] that show the multiple-connectedness property of the JTM in the linear $T \otimes h$ problem. Instead, for state Ψ_2, the Π_2 path evolves to one of class Π_1 by becoming of the Δ-type, and hence smoothly contractable to a point: no GP effect is observed. In other words, there is a point $\boldsymbol{Q}_d$ in configuration space where the mapping is degenerate: it links $\boldsymbol{Q}_d$ not just to a pair of opposite points $\pm\Psi_2(\boldsymbol{Q}_d)$ on the electronic sphere but to the whole circle of linear combinations $\cos\xi_{23}(\boldsymbol{Q}_d)\psi_2+\sin\xi_{23}(\boldsymbol{Q}_d)\psi_3$.

Similarly to the $E \otimes e$ system, $\theta = 2\xi_{12}$ and $\phi = 2\xi_{23}$ define pseudo-rotational angles with the lowest adiabatic PES displaying a continuum of equipotential minima points that form a $2D$ trough on the $5D$ surface. In terms of ξ_{12} and ξ_{13} distortion angles, the motion along the bottom of the JTM can then be viewed as an internal free rotation of quadrupole distortions of a sphere where the direction of the distortion gradually changes along the (ξ_{12}, ξ_{13}) directions [12,13]; Figure 6.7. The presence/absence of GP effect manifests then as a property inherent to sign change of the adiabatic electronic wave vectors upon action of $\hat{R}_3$ in f-space, thus corroborating the observation [35] that GP in the $T \otimes (e \oplus t_2)$

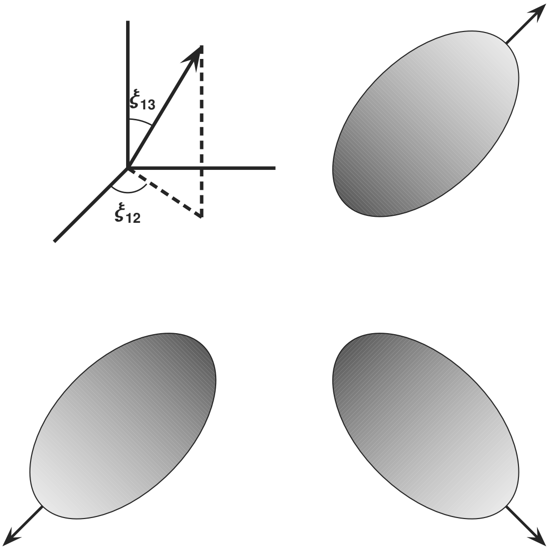

Figure 6.7. Internal free rotation of quadrupole distortions of a sphere where the direction of the distortion gradually changes along the (ξ_{12}, ξ_{13}) directions.

system is tied to the occurrence of a ground-state triplet (see Ref. 136).

6.6.3 High electronic orbital degeneracies

Fourfold and fivefold orbital degenerate electronic terms arise in icosahedral systems, with typical problems being [12] $G \otimes (g \oplus h)$ and $H \otimes (g \oplus 2h)$, respectively. These will be briefly surveyed in this section. A parametrization of the $\hat{R}_N$ ($N = 4, 5$) operator is then required, with two convenient and independent ways being available to parametrize N dimensions with angular coordinates [137]. The one followed here, which is most frequently encountered in physical applications, is the polar parametrization [19,45,46,128,137]. Such N-dimensional polar (also known as hyperspherical polar) coordinates were used by Louck [128] in pioneering work on the generalized orbital angular momentum for the N-fold degenerate harmonic oscillator, although a parametrization with biharmonic coordinates has also been used [46]. The rotation matrix in $O(N)$ assumes then the form:

$$\mathbf{R}_N = \boldsymbol{\rho}_{12}(\xi_{12})\boldsymbol{\rho}_{23}(\xi_{23})\boldsymbol{\rho}_{34}(\xi_{34})\cdots\boldsymbol{\rho}_{N-1,N}(\xi_{N-1,N}) \qquad (6.77)$$

thence showing a dependence on $(N-1)$ mixing angles.

Consider now the the $G \otimes (g \oplus h)$ problem whose Lie symmetry of the linear JT Hamiltonian is [11] $SO(4)$, thus having six Lie-group parameters. A norm-preserving adiabatic electronic vector for this problem will then be defined by three mixing angles with the rotation matrix $\mathbf{R}_4$ given by the product of three 4×4 independent unitary planar rotation matrices $\boldsymbol{\rho}_{ij}$. Any 3 mixing angles [chosen from the 6 available parameters in $SO(4)$] will then be suitable to specify an adiabatic wave vector, provided that under $\hat{R}_4$ it either changes sign or remains sign unchanged. Thus,

$$\mathbf{R}_4 = \begin{bmatrix} c_{12} & s_{12}c_{23} & s_{12}s_{23}c_{34} & s_{12}s_{23}s_{34} \\ -s_{12} & c_{12}c_{23} & c_{12}s_{23}c_{34} & c_{12}s_{23}s_{34} \\ 0 & -s_{23} & c_{23}c_{34} & c_{23}s_{34} \\ 0 & 0 & -s_{34} & c_{34} \end{bmatrix} \tag{6.78}$$

where $c_{ij} = \cos\xi_{ij}$, $s_{ij} = \sin\xi_{ij}$, and the angles are interpreted in a way similar to previous cases. being associated to pseudo-rotational angular coordinates in v-space. The action of $\hat{R}_4$ in f-space will then consist of the following rotations: $\xi_{12} \rightarrow \pi - \xi_{12}$, $\xi_{23} \rightarrow \pi - \xi_{23}$, and $\xi_{34} \rightarrow \xi_{34} + \pi$. Upon acting with $\hat{R}_4$, Ψ_1 and Ψ_4 are seen to change sign while Ψ_2 and Ψ_3 remain sign-unchanged. Following Ref. 48, this may be rationalized by fixing ξ_{12} and ξ_{34} at specific values. If one considers $\xi_{12} = 0 \rightarrow \pi$ at $\xi_{34} = \pi/2$, one gets for the Ψ_2 components: $(0, c_{23}, 0, s_{23}) \rightarrow (0, -c_{23}, 0, -s_{23})$. The situation is then analogous to that of the $N=3$ problem: both before and after the transformation $\xi_{12} \rightarrow \pi - \xi_{12}$, Ψ_2 is found to change sign but through complementary paths that close the loop and hence lead to sign cancelation as the final result (topologically, one has a path of Δ type). A similar observation applies to Ψ_3 when $\xi_{23} = 0 \rightarrow \pi$: $(0, 0, c_{34}, s_{34}) \rightarrow (0, 0, -c_{34}, -s_{34})$. The above explains why Ψ_2 and Ψ_3 keep their signs unchanged under $\hat{R}_4$ in f-space.

A situation where only two states change sign out of four belongs to case $(2, 2)$; the first digit stands for the number of sign changes, the other for that of no sign changes (also referred to as [44] JT and RT cases, respectively), where also the cases $(4, 0)$ and $(0, 4)$ are observed. However, it finds no correspondence in the model Hamiltonian work of Ref. 43 where only cases $(4, 0)$ and $(0, 4)$ are found. If $2\xi_{12}$, $2\xi_{23}$ and $2\xi_{34}$ are viewed as pseudo-rotation angles in the

$9D$ space of the g and h vibrations ($[G^2] = A+G+H$, with an equal coupling assumed for the G and H modes), one obtains [46, 138] a $3D$ JTM extending over the $9D$ coordinate space, a situation analogous to the one in $5D$ for the cubic quadruplet terms [$\Gamma_8 \otimes (e \oplus t_2)$ problem] [11]. Of course, it cannot be anticipated whether a warping of the adiabatic PESs occurs as this depends on the JT matrix. In fact, when the dimension of the normal-mode space is smaller than that of the function space, the PES is usually characterized by some amount of corrugation [13]. Our theory can then predict how many states manifest GP but not its presence/absence in JTM.

We now turn to fivefold electronic degeneracies, the highest known in molecular symmetry groups (except for axial ones, not interesting in JT theory), which arise in fullerenes like C_{60} via the icosahedral $H \otimes (g \oplus 2h)$ system [12]. Belonging to the symmetry group [11] $SO(5)$, the analysis for the coupling of a fivefold degenerate electronic state of H symmetry and a $9D$ space of nuclear distortions ($g + h$) leads to the prediction of a $4D$ JTM trough in the $9D$ PES. This is due to the fact that a norm-preserving eigenvector will show rotational invariance to changes in its direction related to an equipotential displacement on the bottom of the trough. Depending on a single-mode splitting parameter, two coupling regimes favoring either pentagonal or trigonal minima may be observed. For a nonzero splitting, the surface of the trough becomes warped with the appearance of minima of D_{3d} and D_{5d} symmetries (Refs. 12, 47, and therein).

In line with the other JT problems, use will then be made of the rotation matrix

$$\mathbf{R}_5 = \begin{bmatrix} c_{12} & s_{12}c_{23} & s_{12}s_{23}c_{34} & s_{12}s_{23}s_{34}c_{45} & s_{12}s_{23}s_{34}s_{45} \\ -s_{12} & c_{12}c_{23} & c_{12}s_{23}c_{34} & c_{12}s_{23}s_{34}c_{45} & c_{12}s_{23}s_{34}s_{45} \\ 0 & -s_{23} & c_{23}c_{34} & c_{23}s_{34}c_{45} & c_{23}s_{34}s_{45} \\ 0 & 0 & -s_{34} & c_{34}c_{45} & c_{34}s_{45} \\ 0 & 0 & 0 & -s_{45} & c_{45} \end{bmatrix} \tag{6.79}$$

where the angles ξ_{ij} are defined as above. In this case too, only two adiabatic sheets of the fivefold manifold are predicted to manifest GP: case (2, 3). Such a result seem at first to contradict existing evidence on the nature of the dynamic ground state adiabatic PES, which has been examined in detail [47, 139, 140].

In fact, the JT effect of the icosahedral quintuplet term in the trigonal regime shows an intriguing crossover of dynamic states from a degenerate to a singlet state, with coupling strength showing an apparent correlation with the phase of the tunneling paths through such minima. At stronger coupling the dominant tunneling process is believed to consist of closed loops spanning cycles of five wells, with a vanishing GP associated with these loops. Moate *et al.* [139] and Manini and De Los Rios [140] studied the $H \otimes h$ problem and have given distinct topological explanations for the absence of GP in such loops by considering their projection in a plane formed by normals to a pentagonal symmetry axis which permutes the five wells in a cyclic fashion. A connection between such topological explanations has been given by Lijnen and Ceulemans [47], who have scanned the topology of the full coordinate space using a net of triangular cross sections between the ten D_{3d} minima. By expressing the GP of every loop on the PES in terms of such 2D triangular cross sections, they have found [47] that the absence of GP for the cycles containing five trigonal wells originates from two seams of conical intersections going through these cycles. Suffice it to note that the absence of GP effect on the adiabatic ground state PES does not invalidate our prediction that only two sheets of the fivefold electronic manifold manifest GP. Of course, one may argue that, if both a conical and a tangential contact occur, one expects the former to lie lower in energy due to its nonzero slope. Yet, one can contest that the energy-ordering criterion is applicable only to adiabatic states, which need not necessarily be invoked here. In other words, a given diabatic state may be the dominant contribution to the adiabatic ground or to an adiabatic excited state depending on the region of configuration space under analysis. The above considerations seem therefore to rule out a prediction [43,44] of sign change in all states of the fivefold manifold, case $(5,0)$. As Table 6.1 shows the Baer [44] theory predicts cases $(3,2)$ and $(1,4)$, but not $(0,5)$, with similar results holding for the theory of Manolopoulos and Child [43]. Thus, none of the existing theories (including our own [48]) predicts the case $(0,5)$. Clearly, this is an issue that requires further analysis.

Table 6.1. Allowed adiabatic sign-changes at a N-fold electronic orbital degeneracy.

N	MC[a]	B[b]	this work
2	−−	−−	−−
3	+++	+++	n.o.[c]
	−+−	−+−	−+−
4	++++	++++	n.o.
	−−−−	−−−−	n.o.
	n.o.	−++−	−++−
5	−−−−−	−−−−−	n.o.
	n.o.	n.o.	−+++−
	−−−++	−−−++	n.o.
	−++++	−++++	n.o.
6	−−−−−−	−−−−−−	n.o.
	n.o.	−++++−	−++++−
	n.o.	−−−−++	n.o.
	++−−−−	++++++	n.o.

[a] D.E. Manolopolous & M.S. Child, *Phys. Rev. Lett.*, **82**, 2223 (1999).

[b] M. Baer, *Chem. Phys. Lett.*, **322**, 520 (2000).

[c] Not observed.

6.7 Is Longuet-Higgins theorem valid for any Jahn-Teller degeneracy?

It is apparent from section 6.3 that the adiabatic propagation of an electronic wave vector around a N-fold degeneracy in v-space can be associated to a $(N-1)$-angle pseudo-rotation or to a multiple-rotation in the f-space with the same dimensionality. In many cases, the rotation operator $\hat{R}_{N-1}$ yields a Π_2 path in f-space. For the twofold and threefold linear JT problems, our predictions are found to agree with those obtained from the traditional loop analysis in v-space [20, 21, 35, 136]. Not unexpectedly, perhaps, our predictions [48] do not always coincide with the ones obtained from other treatments [43, 44], nor do the latter agree amongst themselves. This may be attributed to the specific symmetry requirements involved, thus eliminating occurrences that might otherwise happen in their absence. In fact, a $(2, N-2)$ sign-change is predicted irrespective of N: only two electronic wave vectors change sign. With N=4, the

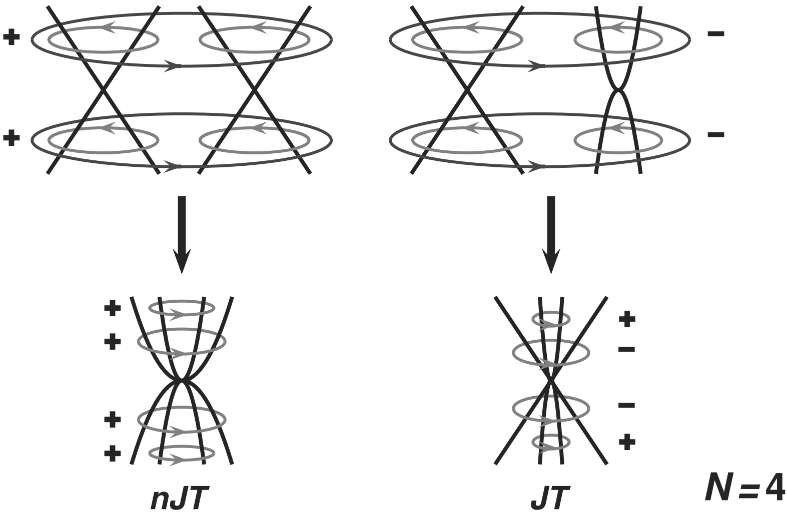

Figure 6.8. Schematic coalescence of two twofold electronic degeneracies to yield a fourfold one. For clarity, a pair of states where the sign change is not observed upon completion of a loop in v-space is indicated by two paraboloids, one up and one down, that touch tangentially (the point of contact is not necessarily an extremum). Conversely, those that change sign are indicated by a diabolo. If the two degeneracies were both of the conical type, the first LH theorem would imply that none of the four states could change sign upon adiabatic transportation of the wave function over a closed loop that encircles the two coalescing degeneracy points as this would imply an even number of conical intersections. Stated differently, only if one of the $N = 2$ coalescing degeneracies is conical can yield a single pair of sign changing states.

results from our theory then agree with one of the reported Baer's [44] solutions, but disagree with his results and the ones of Manolopoulos and Child [43] in not finding the $(4, 0)$ and $(0, 4)$ cases.

An attempt to rationalize the above discrepancies is made in Figure 6.8, where a (high-N) fold degeneracy is viewed as the coalescence of two (low-N) fold ones, specialized to $N = 4$. The approach [48] stands therefore on the assumption that both the low- and (high-N)-fold degeneracies can occur along the same locus, which should generally be valid on symmetry grounds. The argument is then akin to that of viewing, *e.g.*, an $e \oplus t_2$ problem as a fivefold degenerate vibration for identical coupling parameters. Note that a pair of states where a sign change is not observed upon completion of a loop in v-space (a Δ-path) is indicated by two paraboloids, one up and one down, touching tangentially (not necessarily an extremum, and hence should not be confused with a pseudo-JT situation [11, 13]). Conversely, the ones that change sign (Π_2-type) are indicated by a diabolo. Clearly, the LH theorem imposes that only one of the $N=2$ coalescing degeneracies may be conical leading to a single pair of sign changing states.

The question then arises: since an odd number of two-state conical intersections is involved in a sixfold degeneracy, does the argumentation of the previous paragraph imply the existence of the $(0, 6)$ case? As sketched in Figure 6.9, the answer will be negative. In fact, the $N=6$ case may also be viewed as a coalescence of $N=4$ and $N=2$ degeneracies. Because the LH theorem has been shown to apply to $N=4$, only one of those coalescing degeneracies can be of the conical type, leading again to just one pair of states subject to the GP effect. Since there is no reason of principle for one of the above two schemes to prevail over the other, the maximum number of sign-changing states common to both interpretations is two, *i.e.*, the $(2, 4)$ case. As Table 6.1 shows Baer's theory [44] additionally predicts the cases $(6, 0)$, $(4, 2)$ and $(0, 6)$, while the only predictions from the Manolopoulos-Child [43] theory are $(4, 2)$ and $(0, 6)$. By an extension of the above argument, one is led to conclude that only one pair of sign changing states is observable for any arbitrary N-fold degeneracy [19, 45, 48]. Note that the odd-N state cases pose no problem, since only a single sign-unchanging state needs to be added to the closest even-N state problem. Thus, the intriguing question urges of whether the LH theorem applies to arbitrary N-fold degeneracies.

To get additional physical insight into the above question, consider a JT problem where more than a pair of adiabatic states is assumed to change sign upon parallel transportation along a closed path around the locus of degeneracy. For example, assume that the case $(4, 0)$ behaves that way, with Ψ_i ($i=1-4$) denoting such states. Since they are degenerate in the vicinity of the seam, a solution of the SE would also be $\Psi = \sum_{i=1}^{N} C_i \Psi_i$. Recalling now that opposing wave vectors in a ray represent a unique physical state [129], all Ψ_i must change

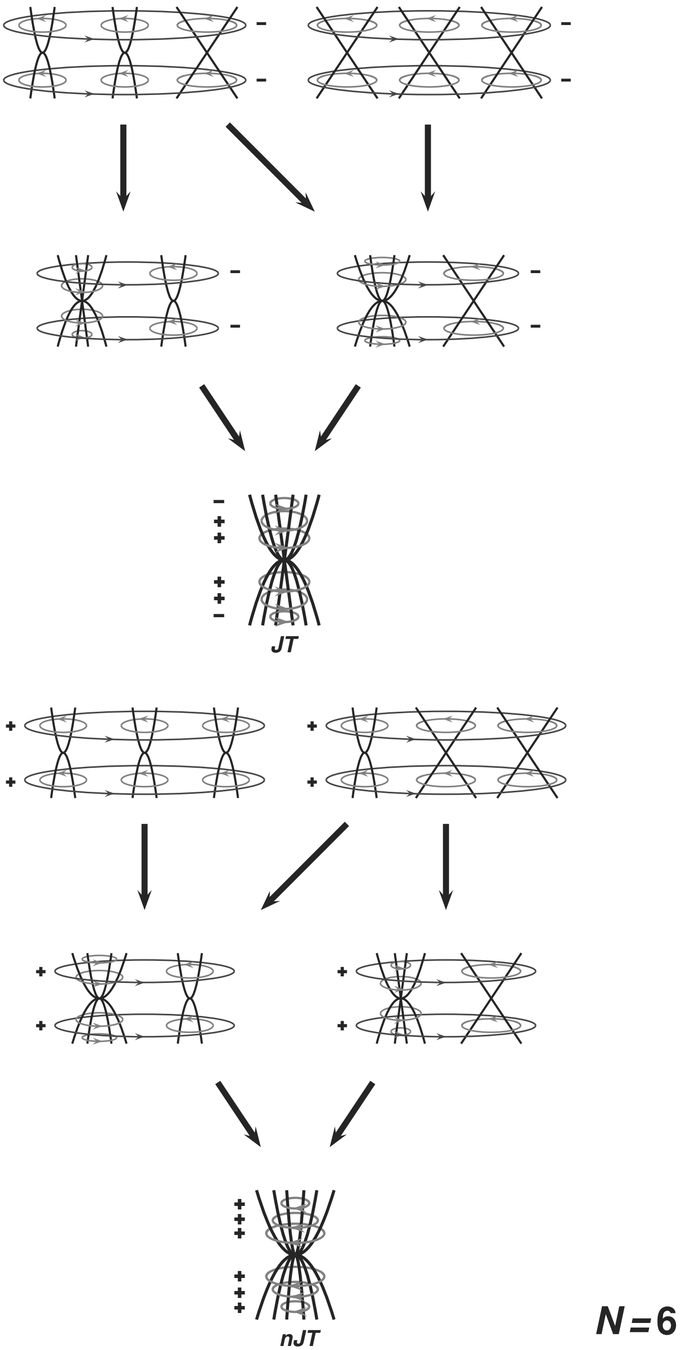

Figure 6.9. Schematic coalescence of low-order degeneracies in the configuration space of the JT system to form a sixfold electronic degeneracy.

sign simultaneously during the parallel transportation of Ψ along the loop. Since this must be further warranted for any loop, only by accident could it happen unless all pairs are identical. Stated differently, only one pair of adiabatic states can change sign. The above can be summarized in the following [48] (extended Longuet-Higgins) 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 v-space along a loop that encircles the degeneracy point.* The method of *reductio ad absurdum* will be employed for the demonstration. Assume then that M such pairs show a sign change. Clearly, M cannot be even an even number as this would imply a loop encircling an even number of twofold degeneracies (conical intersections), thence violating the first LH theorem. If M is odd, then let us isolate arbitrarily one pair of states that shows such a sign change. The remaining $M-1$ pairs would then form a manifold with an even number of twofold conical intersections. This cannot be allowed since, as noted above, it would violate the first LH theorem. Thus, none of the $2M-2$ states can change sign upon completing a loop around the crossing point: only one pair (the isolated one) can show such a sign change. *QED*

6.8 Does a general relation between the geometrical phase and mixing angles exist?

For the $2D$ Hilbert space, we have shown that by writing a single complex wave function in terms of the two real ones, Eq. (6.68), a relation can be obtained between the geometrical phase and the mixing angle. Specifically, the angle $\gamma(\mathbf{r}_n) = \tilde{\gamma}/2$ that diagonalizes the potential matrix (mixing angle) has been shown to be identical to ATD angle, $\alpha(\mathbf{r}_n)$ [41], and GP, $A(\mathbf{r}_n)$ [40], at least up to a constant term that has no physical significance. The process of building the single-valued complex function for the above $O(2)$ case suggests therefore the following generalized expression for the O(N) case:

$$\tilde{\Psi} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \exp\left[\frac{2(n-1)\pi\iota}{N}\right] \Psi_n \tag{6.80}$$

Recalling now that

$$\tilde{\Psi} = \exp[\imath A(\mathbf{r}_n)]\Psi \tag{6.81}$$

one obtains upon use of Eq. (6.77) and evaluation of $\langle\tilde{\Psi}|\nabla\tilde{\Psi}\rangle$,

$$\nabla A(\mathbf{r}_n) = -\frac{1}{\sqrt{N}}\left[\nabla\xi_{12} + \sum_{n=1}^{N-2} c_{n,n+1}\nabla\xi_{n+1,n+2} - \prod_{n=1}^{N-2} s_{n,n+1}\nabla\xi_{N-1,N}\right] \tag{6.82}$$

Specializing for the N=3 case, one gets

$$\nabla A(\mathbf{R}) = -\frac{1}{\sqrt{3}}\left[\nabla\xi_{12} + (\cos\xi_{12} - \sin\xi_{12})\nabla\xi_{23}\right] \tag{6.83}$$

which provides an explicit relation between the GP angle and the mixing angles $\xi_{12}(\mathbf{r}_n)$ and $\xi_{23}(\mathbf{r}_n)$. Corresponding expressions can be obtained for other Lie groups, in all cases involving $\nabla A(\mathbf{R})$ and the gradient of each of the $N-1$ mixing angles. The problem lies therefore on the capability to reduce the Hamiltonian to a single SE as done on section 6.6.1 for the $e \otimes E$ problem. This would not only simplify considerably the generalized BO formulation recently suggested [141, 142] for the three-state problem but provide a generalization to higher-degeneracies. In this regard, the most convenient formulation appears to be the one of Eq. (6.37), where the nuclear wave functions are treated as real and a vector potential appears in the Hamiltonian. In this case, $\nabla A(\mathbf{R})$ can be replaced there to solve the dynamics problem in terms of the mixing angles. Alternatively, one may think of following the argumentation above and treat a N-fold degeneracy as a succession of $\left(\begin{array}{c} N \\ 2 \end{array}\right)$ twofold degeneracies solved step-by-step as done by Longuet-Higgins [*i.e.*, via repeated use of hybrid wave functions in Eq. (6.68)]. In this case the answer to the above question should be also affirmative. Research along these lines is currently in progress in our Group.

6.9 Concluding remarks

We have given a perspective on the BO approximation and several related issues: separation of the electronic and nuclear motions, coupled-channel treatment, scaling properties, validity, and diabatic states. Furthermore, considerable emphasis has been put on the need for its generalization such as to account for the topological implications in systems with degeneracies of the conical type, due to the separation of the electronic (fast) and nuclear (slow) degrees of freedom. Without hoping for convenience at a balanced coverage of the topic, the analysis has been carried by specializing on the work developed in recent years by the author and his collaborators while providing references to other published material. Beyond well known studies on two-fold degeneracies, recent developments on the theme of high electronic degeneracies occurring for Jahn-Teller systems have been also surveyed. In particular, a theory recently proposed by the author [19, 45, 48] that avoids altogether the solution of the dynamics problem by making instead use of symmetry invariants has been reviewed in some detail. How to bring it into the realm of quantum dynamics by generalizing the procedure utilized to decouple the two-state problem into two one-state ones with the help of GP is a promising issue that warrants a future reanalysis of this topic.

Note added in proof

After completing this work, Generalized Born-Oppenheimer equations including the geometrical phase effect have been derived for three- and four-fold electronic manifolds in Jahn-Teller systems near the degeneracy seam [143]. The theory shows unprecedented simplicity while being readily extendable to N-fold systems of arbitrary dimension. In addition, an application to a model threefold system has been reported [143], and the results compared with Born-Oppenheimer (geometrical phase ignored), extended Born-Oppenheimer [141], and coupled three-state calculations [144].

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tract No. 21790/08/NL/HE.

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