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*A tribute to the memory of
Professor Couceiro da Costa*



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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 \mathbf{Q}_0 if, by so doing, any electronic degeneracy can be lifted*. In the vicinity of \mathbf{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 configurations¹. If the PES does not satisfy such a requirement (by having an extremum at \mathbf{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-

¹The 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 ($9D$) space of $G \otimes (g \oplus b)^2$ would be a mammoth task. Indeed, it is a task that we did not even complete in the $4D$ and $5D$ phase spaces of the subsystems $G \otimes g$ and $G \otimes b$.” 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 $2D$ 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

²Although 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

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

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

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

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 $\nabla_i = \nabla_{i,x}\hat{i} + \nabla_{i,y}\hat{j} + \nabla_{i,z}\hat{k}$ and $\nabla_I = \nabla_{I,x}\hat{i} + \nabla_{I,y}\hat{j} + \nabla_{I,z}\hat{k}$. Note that the potential energy $V(\mathbf{r}_e, \mathbf{r}_n)$ is assumed to be a real function³. 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:

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

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:

$$\frac{1}{\phi(t)} \frac{d\phi(t)}{dt} = -\frac{iE}{\hbar} \quad (6.4)$$

and

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

The former can be solved to yield $\phi(t) = \exp(-iEt/\hbar)$. 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

$$\tilde{\Omega}(\mathbf{r}_e, \mathbf{r}_n, t) = \Omega(\mathbf{r}_e, \mathbf{r}_n) \exp(-iEt/\hbar), \quad (6.6)$$

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:

$$\tilde{\Omega}(\mathbf{r}_e, \mathbf{r}_n, t) = \sum_i c_i \Omega_i(\mathbf{r}_e, \mathbf{r}_n) \exp(-iE_i t/\hbar) \quad (6.7)$$

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

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