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A generalised
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Abstract	<p>In this thesis a topological test for intersections between electronic potential energy surfaces constructed by Longuet-Higgins [<i>Proc. R. Soc. Lond. A</i>, 344:147-156, 1975] is generalised. The generalisation is accomplished by considering the space of complete adiabatic electronic bases as a topological space. Loops in the nuclear configuration space that map to non-trivial loops in the space of bases are shown to encircle an electronic degeneracy. It is further proved that it is not possible to make the generalised test more sensitive without using additional information. Examples from Jahn-Teller theory are presented to illustrate the test.</p>	
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A generalised topological test for intersections of molecular potential energy surfaces

Niklas Johansson

October 20, 2003

Populärvetenskaplig sammanfattning

Inom vetenskapsområden som kemi, molekylärbiologi, och materialvetenskap kan vikten av att förstå molekyler och molekylära egenskaper svårligen överskattas. Likaså är kunskap om kemiska reaktioner mellan molekyler oundgänglig i vår beskrivning av biologiska och medicinska processer.

Kvantkemin har som mål att beskriva molekyler och deras interaktioner utgående från fundamentala fysikaliska samband. Detta görs med datorberäkningar. I dessa beräkningar används oftast den *adiabatiska approximationen*. Den går ut på att man låser kärnornas läge i någon position Q , och sedan beräknar hur elektronerna beter sig runt de fixa kärnorna. Detta ger *elektroniska tillsånd* och *elektroniska energier*. Proceduren upprepas för många kärnkonfigurationer Q , exempelvis längs en reaktionskoordinat.

Den adiabatiska approximationen bryter samman runt kärnkonfigurationer där två eller flera elektroniska energier är lika. I närvaro av sådana punkter, s.k. korsningar, kan beräkningarna ge felaktiga resultat (exempelvis fel produkter i en kemisk reaktion). Därför är det viktigt att kunna hitta dessa korsningar. 1975 beskrevs ett sätt att göra detta genom att betrakta ett elektroniskt tillstånd.

I detta examensarbete har detta test generaliserats. Det bevisas att om fler tillstånd studeras kan man upptäcka fler korsningar än med det ursprungliga testet. Vidare bevisas det att det inte går att generalisera testet ytterligare.

Examensarbete 20 p, inom Molekylär bioteknikprogrammet vid Uppsala universitet

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1 Introduction

Although the concept of them is a part of our everyday life, molecules cannot be satisfactorily treated in any classical theory. They are true quantum creatures and quantum mechanics must be used to describe them. To make this description explicit is the goal of quantum chemistry. A quantum chemist uses computers to solve the quantum mechanical equations and to calculate properties of molecules. Important calculable quantities include nuclear configuration, vibrational frequencies, electron density, and electronic energies.

The computers of today are however far too slow to be able to solve the exact equations of any reasonably complicated molecular system. Therefore, even computers must use approximations. One very commonly used approximation, the *adiabatic* approximation, dates back to 1927 and the paper of Born and Oppenheimer [1]. This approximation involves the calculation of *electronic energies* that depend parametrically on the nuclear coordinates. It turns out that the approximation is valid if the nuclear configuration is such that the electronic energies are well separated. Nuclear configurations where two electronic energies are equal (i.e., the corresponding states are *degenerate*) are points where the approximation breaks down. Therefore it is of importance to be able to locate these degeneracies.

In 1975 Longuet-Higgins [2] developed a test to find certain electronic degeneracies, known as *conical intersections*, based on the behaviour of the electronic wave functions on a closed loop in the nuclear configuration space. When, almost a decade later, Berry discovered the quantum *geometric phase* [3] he realised that the condition of Longuet-Higgins' test was just the existence of a non-trivial geometric phase along the loop in the nuclear configuration space. Berry's phase, originally investigated for cyclic adiabatic quantum evolution, was soon generalised to much more general settings [4, 5, 6, 7, 8, 9].

The original idea behind the present thesis was to use the relatively recent concept of *off-diagonal* geometric phases [9] to generalise the test of Longuet-Higgins. A generalisation of the test has indeed been found, but the methods used are other than anticipated. The generalisation of Longuet-Higgins' test presented in section 4 does not involve off-diagonal geometric phases, but is based on topological methods.

The thesis is organised as follows. Section 2 deals with Berry's geometric phase. In the following section some effort is put into a review of molecular physics. The adiabatic approximation is scrutinised, and the important concept conical intersection is introduced. Section 4 begins by a description of Longuet-Higgins' test. Then, after a quick introduction to topology, the generalisation is presented, the main result being Theorem 2. To illustrate the test, we use it on some theoretical models. Lastly we prove that, without using additional information, it is impossible to generalise the test further.

Before we proceed a remark might not be out of place. This text is a thesis for the degree "Master of Science in Molecular Biotechnology Engineering". It is fair to say though, that the emphasis put on *molecular* is far greater than that put on *biotechnology*. It is nevertheless intended that a student of Molecular Biotechnology (equipped with an intermediate course in quantum mechanics) shall be able to read the thesis. It is my hope that this intention has been met at the same time that the thesis is not too lengthy for a physicist to read.

2 Geometric phase

There are two main reasons for including an introduction to quantal geometric phases in this thesis. Firstly, they appear naturally on the way towards our goal, as the topological test of Longuet-Higgins is just the existence of a non-trivial geometric phase. Secondly, the framework in which they were first described is used extensively in this work.

2.1 States, state vectors, and phases

When we study the world using physics, we usually limit ourselves to a well defined “piece” of it. This piece, e.g., a collection of nuclei and electrons, we label a *system*. In quantum mechanics systems are said to be in different *states*. A system being in a certain state is characterised by the set of values a measurement of the observable quantities might result in and the probability of obtaining these values. Two systems having the same probabilities for the same possible values for every observable are said to be in the same state.

The language used to describe states in quantum mechanics is that of state vectors. A pure state (we deal only with pure states in this thesis) is represented by a state vector $|\Psi\rangle$ in an abstract complex Hilbert space \mathcal{H} . Many vectors, namely all vectors of the form $e^{i\phi}|\Psi\rangle$, however, represent the same state as $|\Psi\rangle$. Vectors representing the same state are said to differ only in *phase*.

When can this “phase” have any significance? Well, if a quantum system is described by a linear combination of two state vectors, then the total state is dependent on the relative phase of the two vectors. As an explicit example, consider a neutron interferometer experiment. If a particle taking the upper (lower) path is described by $|0\rangle$ ($|1\rangle$), a particle in the interferometer is described by a linear combination of these kets. A phase shift $e^{i\phi}$ applied only to the lower path would change the state vector of the total system from $|\psi_1\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$ to $|\psi_2\rangle = \frac{1}{\sqrt{2}}(|0\rangle + e^{i\phi}|1\rangle)$. Note that $|\psi_1\rangle$ and $|\psi_2\rangle$ represent different states. This phase shift cannot be detected by letting a beam of neutrons simply pass through the lower path, but only by letting a beam pass through the two paths simultaneously.

All state vectors in quantum mechanics are normalised, so they are really elements of the set $\mathcal{N} \equiv \{|\Psi\rangle \in \mathcal{H} : \langle\Psi|\Psi\rangle = 1\}$. The states are elements of the *projective* Hilbert space $\mathcal{P} \equiv \mathcal{N}/\sim$, where \sim means identification of vectors differing only by a phase. Accordingly, the elements of \mathcal{P} are themselves sets of the form $[|\Psi\rangle] \equiv \{e^{i\phi}|\Psi\rangle : \phi \in [0, 2\pi]\}$. Note that neither \mathcal{N} nor \mathcal{P} is a linear space.

2.2 Geometric phase in adiabatic evolution

When Berry discovered the geometric phase [3] he considered a special type of time evolution known as *adiabatic* evolution. Consider a system described by a Hamiltonian $H(Q(t))$ depending on the parameter Q which in turn depends on time. The quantity Q might be components of a magnetic field, nuclear coordinates or something of the like. If our system initial is in an eigenstate of H the *adiabatic theorem* asserts that if H varies only slowly with time, then the system remains approximately in an eigenstate of H at all times. This

makes adiabatically evolving systems easy to deal with. The adiabatic theorem is proven in for example [10].

In the rest of this section we consider a system described by the Hamiltonian $H(Q)$. We suppose that the parameter Q varies slowly from time $t = 0$ to $t = \tau$ in such a way that $Q(0) = Q(\tau)$. We have thus traversed a loop in Q -space. This loop will be denoted Γ .

Suppose that it is possible to choose eigenvectors $|n(Q)\rangle$ of $H(Q)$ that are continuous *single valued* functions of Q along Γ . The eigenvectors fulfil

$$H(Q)|n(Q)\rangle = E_n(Q)|n(Q)\rangle. \quad (1)$$

Suppose now that the system evolves adiabatically along Γ from the initial ket $|\Psi(0)\rangle = |n(Q(0))\rangle$. After the loop has been traversed, the adiabatically evolving system has returned to its original state, but not necessarily to its original state vector, i.e., in general we have $|\Psi(\tau)\rangle = e^{i\phi}|\Psi(0)\rangle$. What phase ϕ can we expect the state vector to acquire during the motion? Well, an eigenket $|n\rangle$ of a constant Hamiltonian evolves as $|n(t)\rangle = e^{-iE_n t/\hbar}|n(0)\rangle$. A reasonable guess would thus be that our state vector evolves like

$$|\Psi(t)\rangle = e^{-\frac{i}{\hbar} \int_0^t E_n(t') dt'} |n(Q(t))\rangle. \quad (2)$$

Berry discovered that this guess is incorrect. To show this let us make the ansatz

$$|\Psi(t)\rangle = e^{i\gamma(t) - \frac{i}{\hbar} \int_0^t E_n(t') dt'} |n(Q(t))\rangle. \quad (3)$$

We aim to determine $\gamma(\tau)$. To this end we insert $|\Psi(t)\rangle$ of equation (3) into the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H(Q(t)) |\Psi(t)\rangle \quad (4)$$

and obtain

$$\dot{\gamma}(t) = i \langle n(Q(t)) | \frac{d}{dt} |n(Q(t))\rangle. \quad (5)$$

By using the chain rule we see that $\gamma(\tau)$ is given by

$$\begin{aligned} \gamma(\tau) &= i \int_0^\tau \langle n(Q(t)) | \frac{d}{dt} |n(Q(t))\rangle dt = \\ &= i \int_\Gamma \langle n(Q) | \nabla_Q |n(Q)\rangle \cdot dQ. \end{aligned} \quad (6)$$

Here ∇_Q denotes differentiation with respect to the parameters Q . Note that the last integral is taken along Γ in the parameter space. The quantity $\gamma(\tau)$ is called the *geometric phase* associated with the evolution. The name is appropriate since γ is completely independent of the dynamics of the evolution. Only the path in the parameter space (or more precisely the path in the projective Hilbert space \mathcal{P}) is needed to calculate the geometric phase. Thus we let γ_n^Γ denote the geometric phase associated with the vector $|n\rangle$ and the curve Γ . Note also that γ is real since the integrand in (6) is purely imaginary by

$$\begin{aligned} 0 &= \nabla_Q (\langle n(Q) | n(Q) \rangle) = \langle n(Q) | \nabla_Q n(Q) \rangle + \langle \nabla_Q n(Q) | n(Q) \rangle \\ &= \langle n(Q) | \nabla_Q n(Q) \rangle + \langle n(Q) | \nabla_Q n(Q) \rangle^*. \end{aligned} \quad (7)$$

After Berry's seminal work on geometric phase, a flood of papers emerged containing generalisations and theoretic explorations of the novel concept. It was shown that geometric phase is a much more general phenomenon than indicated here. We will deal nothing with these generalisations since the cyclic and adiabatic setting suits our needs perfectly, but notable contributions to the development include [4, 5, 6, 7, 8, 9].

Sometimes it is easier to use eigenkets that are *not* single valued along Γ to compute the geometric phase. Below we show how this is done. Suppose as before that we vary $Q(t)$ slowly along the closed loop Γ in Q -space. Suppose furthermore that when following an eigenket $|n(t)\rangle$ continuously we do not return to the original ket. Rather if $Q(0) = Q(\tau)$ is the starting (and ending) point of Γ , assume that we obtain

$$|n(\tau)\rangle = e^{i\phi}|n(0)\rangle. \quad (8)$$

Note that "following an eigenket" does not mean "watching the system evolve in time" but rather "choosing a theoretically computed eigenket continuously as Q varies". How do we come around this multiple valuedness? Well, we simply define new eigenkets along Γ by

$$|\tilde{n}(Q(t))\rangle \equiv e^{-if(t)}|n(t)\rangle, \quad (9)$$

where f is a differentiable function of t satisfying $f(\tau) - f(0) = \arg(\langle n(0)|n(\tau)\rangle)$. These newly defined eigenkets are single valued since

$$\langle \tilde{n}(Q(0))|\tilde{n}(Q(\tau))\rangle = e^{i(f(0)-f(\tau))}\langle n(0)|n(\tau)\rangle = 1. \quad (10)$$

Consequently we may use equation (6) to calculate the geometric phase along Γ as

$$\begin{aligned} \gamma_n^\Gamma &= i \int_0^\tau \langle \tilde{n}(Q(t))|\frac{d}{dt}|\tilde{n}(Q(t))\rangle dt = \\ &= i \int_0^\tau \langle \tilde{n}(Q(t))|\left(-i\dot{f}(t)|\tilde{n}(Q(t))\rangle + e^{-if(t)}\frac{d}{dt}|n(t)\rangle\right) dt = \\ &= \arg(\langle n(0)|n(\tau)\rangle) + i \int_0^\tau \langle n(t)|\frac{d}{dt}|n(t)\rangle dt \end{aligned} \quad (11)$$

This expression is applicable for all differentiable (but not necessarily single valued) choices of adiabatic eigenkets $|n(t)\rangle$, and serves as the definition of the geometric phase along a loop in Q -space. We emphasise that, although there are many ways of choosing eigenkets along the loop, the geometric phase defined by equation (11) is independent of this choice. This can be proved by a calculation similar to that of equation (11) showing that the geometric phases are the same for the kets $e^{i\phi(t)}|n(t)\rangle$ and $|n(t)\rangle$ where ϕ is an arbitrary function of t . This property of the geometric phase is called *gauge invariance*.

Two special cases now deserve attention. First there is the already encountered case when $|n(t)\rangle$ is single valued. The geometric phase then consists only of the second term in (11). Second, if the quantity $\langle n(t)|\frac{d}{dt}|n(t)\rangle$ vanishes along Γ the geometric phase is just $\arg(\langle n(0)|n(\tau)\rangle)$. When this is the case, the eigenket $|n(\tau)\rangle$ is called the *parallel transport* of $|n(0)\rangle$ along Γ . Kets that have continuous and everywhere real expansion coefficients with respect to a fixed basis of

\mathcal{H} are automatically parallel transported. This can be realised by noting that $\langle n(t)|\frac{d}{dt}|n(t)\rangle$ is purely imaginary by the same argument as in (7). However, if $|n(t)\rangle$ has real expansion coefficients along Γ , then we have

$$\begin{aligned}\langle n(t)|\frac{d}{dt}|n(t)\rangle &= \left(\sum_{j=1}^{\infty} a_j(t)\langle j|\right)\frac{d}{dt}\left(\sum_{i=1}^{\infty} a_i(t)|i\rangle\right) = \\ &= \sum_{i=1}^{\infty} a_i(t)\dot{a}_i(t) \in \mathbb{R}.\end{aligned}\tag{12}$$

Thus $\langle n(t)|\frac{d}{dt}|n(t)\rangle$ must vanish for real kets. We finally note that equation (11) is also valid for an open path Γ , i.e., when $|\langle n(0)|n(\tau)\rangle| \neq 1$. The corresponding γ_n^Γ is the non-cyclic adiabatic geometric phase considered in [7, 8, 11].

We close this section by an example of how geometric phases are calculated. Assume that the Q -space is \mathbb{R}^2 parametrised by polar coordinates ρ and θ . Suppose also that the Hilbert space is two-dimensional, and that the Hamiltonian is given by

$$H(\rho, \theta) = \begin{pmatrix} \rho \cos \theta & \rho \sin \theta \\ \rho \sin \theta & -\rho \cos \theta \end{pmatrix}.\tag{13}$$

We aim to determine the geometric phase around an arbitrary curve Γ encircling the origin once. The eigenvectors of H are given by

$$\begin{aligned}|+(\theta)\rangle &= \begin{pmatrix} \cos(\theta/2) \\ \sin(\theta/2) \end{pmatrix}, \\ |-(\theta)\rangle &= \begin{pmatrix} -\sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix}.\end{aligned}\tag{14}$$

These eigenkets are real, and thus parallel transported. Since Γ encircles the origin once we have $\theta(\tau) = \theta(0) + 2\pi$. Consequently

$$\gamma_{\pm}^\Gamma = \arg(\langle \pm(\theta(0)) | \pm(\theta(0) + 2\pi) \rangle) = \pi.\tag{15}$$

We can also perform the same calculation using the single valued eigenkets

$$\begin{aligned}|\tilde{+}(\theta)\rangle &= e^{-i\theta/2}|+(\theta)\rangle, \\ |\tilde{-}(\theta)\rangle &= e^{-i\theta/2}|-(\theta)\rangle.\end{aligned}\tag{16}$$

The geometric phase is now given, as in equation (6), by the time integral of the quantity $i\langle \tilde{\pm} | \frac{d}{dt} | \tilde{\pm} \rangle$. Remembering that θ depends on t and denoting differentiation with respect to time by a dot, we have

$$\begin{aligned}i\langle \tilde{\pm}(\theta) | \frac{d}{dt} | \tilde{\pm}(\theta) \rangle &= i\langle \tilde{\pm}(\theta) | \left(-\frac{i\dot{\theta}}{2} | \tilde{\pm}(\theta) \rangle + e^{-i\theta/2} \frac{d}{dt} | \pm(\theta) \rangle \right) = \\ &= \dot{\theta}/2,\end{aligned}\tag{17}$$

where the last equality follows since $| \pm(\theta) \rangle$ is parallel transported. The time integral of this expression is just

$$\gamma_{\pm}^\Gamma = \int_0^\tau \frac{1}{2} \dot{\theta}(t) dt = \frac{1}{2}(\theta(\tau) - \theta(0)) = \pi.\tag{18}$$

It is comforting to see that both methods work equally well. This is a concrete illustration to the gauge invariance of the geometric phase.

This simple system illustrates an important property of the geometric phase. The reader is invited to show that for an arbitrary loop Γ in the $\rho\theta$ -space, the geometric phase is $k\pi$ where k is the number of times Γ encircles the origin in the positive direction. The reason that the origin is special is that the Hamiltonian is *degenerate* at that point. Longuet-Higgins' test uses this behaviour of the geometric phase in systems with real eigenkets to detect degeneracies.

3 Quantum mechanical description of molecules

Very few problems of interest in quantum mechanics are exactly solvable¹. Even when attempting to describe atoms more complex than hydrogen one has to resort to approximations. In the description of molecules (these being obviously more complex than atoms) approximations play a crucial role. These approximations are used not only in numerical calculations, but also in theoretical explorations of molecular systems. In this section we introduce a frequently used approach to molecular physics known as *the adiabatic approximation*. It is within this basic framework most of the material of the next section is treated. We also define the terms *potential energy surface* and *conical intersection*; both concepts being very important in the sequel.

3.1 The adiabatic approximation

The adiabatic approach is described in almost any textbook on molecular theory or quantum mechanics (see for example [10, 12, 13, 14]; see also the excellent and systematic review by Longuet-Higgins [15]). The treatment of the adiabatic approximation presented here is mostly conceptual, and intended to be neither extensive nor rigorous. Before we start, a remark is in order. When we deal with molecular systems in this thesis, we always assume that we can neglect spin-orbit coupling, and that no external magnetic field is present. This implies that the Hamiltonian exhibits *time-reversal symmetry*. For an enlightening treatment of this concept, see [16]. A consequence of the time reversal symmetry is that the electronic eigenfunctions *can be chosen real*. This fact is used frequently in the following.

With this matter settled, let us turn to the main theme of this section: the description of molecules using quantum mechanics. The basic equation describing all non-relativistic quantum systems is the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle. \quad (19)$$

If this quantum system is a molecule with spin ignored, the Hamiltonian H consists of the kinetic energy of the nuclei T_N , that of the electrons T_e , and the potential energy of the electromagnetic interaction between all particles V , i.e.,

$$H = T_N + T_e + V. \quad (20)$$

T_N , T_e , and V are operators on the abstract Hilbert space \mathcal{H} in which $|\Psi(t)\rangle$ resides. The operators can be written down explicitly in the position representation. We denote the spatial coordinates of the nuclei collectively by Q , and the coordinates of the electrons by q . Thus for a molecule with N nuclei Q is a vector with $3N$ components. The explicit form for the terms in equation (20)

¹Actually this is a very vague statement. What is usually meant by “exactly solvable” is that the solutions to the differential equations can be written in terms of elementary functions (and composites of such functions), such as polynomials and exponentials.

(in the position representation and using atomic units) is

$$T_N = -\sum_{I=1}^N \frac{1}{2M_I} \nabla_I^2, \quad (21)$$

$$T_e = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2, \quad (22)$$

$$V = \sum_{i>j} \frac{1}{|q_i - q_j|} + \sum_{I>J} \frac{Z_I Z_J}{|Q_I - Q_J|} - \sum_{i,I} \frac{Z_I}{|Q_I - q_i|}, \quad (23)$$

where N_e is the number of electrons. In equations (21)–(23) capital indices denote the nuclei, and small case indices the electrons. The vectors Q_I and q_i are the spatial coordinates for nucleus I and electron i , respectively. In this notation ∇_i denotes differentiation with respect to the coordinates q_i . M_I and Z_I are the mass (in electron masses) and atomic number of nucleus I , respectively. In an attempt to simplify our notation further we redefine $Q_I \rightarrow \sqrt{2M_I}Q_I$. Equation (21) then becomes

$$T_N = \sum_{I=1}^N -\nabla_I^2 \equiv -\nabla^2. \quad (24)$$

In the rest of this section ∇ will always denote differentiation with respect to the (redefined) Q .

Basically the problem of describing a molecule is equivalent to solving equation (19). If we return to the abstract Hilbert space, the first simplification is the standard separation of the spatial and temporal variables. For stationary states this is accomplished by the ansatz $|\Psi(t)\rangle = e^{-iEt/\hbar}|\Psi\rangle$, resulting in the familiar

$$H|\Psi\rangle = E|\Psi\rangle. \quad (25)$$

The adiabatic approximation now takes advantage of the fact that the nuclei are much heavier than the electrons. The idea is to let the nuclear coordinates be fixed, and find the electronic eigenstates and corresponding energies. These energies are then used as *effective potentials* for the nuclear motion. The formal way of treating such things as “electronic eigenstates” is the following.

We consider the total Hilbert space \mathcal{H} in which $|\Psi\rangle$ lives as a tensor product between the electronic Hilbert space \mathcal{H}_e and the nuclear Hilbert space \mathcal{H}_N :

$$\mathcal{H} = \mathcal{H}_e \otimes \mathcal{H}_N. \quad (26)$$

In the position representation \mathcal{H}_e and \mathcal{H}_N are the spaces of square integrable functions of the variables q and Q , respectively. We denote these spaces by $L^2(q)$ and $L^2(Q)$. The following identifications show how abstract kets in the respective spaces are represented in the position representation:

$$\begin{aligned} |\chi\rangle \in \mathcal{H}_e &\iff \langle q|\chi\rangle \equiv \chi(q) \in L^2(q), \\ |\psi\rangle \in \mathcal{H}_N &\iff \langle Q|\psi\rangle \equiv \psi(Q) \in L^2(Q), \\ |\chi\rangle \otimes |\psi\rangle \in \mathcal{H} &\iff \langle q|\chi\rangle \langle Q|\psi\rangle = \chi(q)\psi(Q) \in L^2(q, Q), \end{aligned} \quad (27)$$

where $L^2(q, Q)$ denotes square integrable functions of the variables q and Q . If $\{|\chi_i\rangle\}$ and $\{|\psi_j\rangle\}$ are complete bases in \mathcal{H}_e and \mathcal{H}_N , respectively, a complete basis in \mathcal{H} is given by $\{|\chi_i\rangle \otimes |\psi_j\rangle\}$. We now define the electronic Hamiltonian H_e as

$$H_e(Q) \equiv T_e + V(Q). \quad (28)$$

H_e is a Q -dependent Hermitian operator on the electronic Hilbert space \mathcal{H}_e . It is the Hamiltonian of a hypothetical system, consisting of the electrons and the nuclei of the molecule with the nuclei fixed at the position Q . Let $|\chi_n(Q)\rangle$ be the eigenkets of H_e :

$$H_e(Q)|\chi_n(Q)\rangle = E_{e,n}(Q)|\chi_n(Q)\rangle. \quad (29)$$

These kets are the adiabatic electronic eigenkets. For every fixed value of the nuclear coordinates Q the set $\{|\chi_n(Q)\rangle\}$ is a complete orthonormal basis in \mathcal{H}_e . In the position representation, any function of the q -variables can be written as a linear combination of the electronic wave functions $\chi_n(q; Q) \equiv \langle q|\chi_n(Q)\rangle$. We indicate that the electronic eigenfunctions are *parametrically* dependent on Q , by separating the variables by a semicolon.

In the position representation an eigenket $|\Psi\rangle$ of the full Hamiltonian H can be expanded in these functions as

$$\langle q|\otimes\langle Q|\Psi\rangle = \Psi(q, Q) = \sum_n \chi_n(q; Q)\psi_n(Q), \quad (30)$$

for some functions $\psi_n(Q)$. For notational convenience we work in the position representation of the nuclear Hilbert space \mathcal{H}_N but in the abstract electronic Hilbert space \mathcal{H}_e , i.e., we study the quantity

$$|\Psi(Q)\rangle \equiv \langle Q|\Psi\rangle = \sum_n \psi_n(Q)|\chi_n(Q)\rangle. \quad (31)$$

The nuclear kinetic energy then assumes its familiar form (24).

Supposing that we have solved equation (29) for the electronic kets, what remains to complete the description of the molecule is to determine the functions $\psi_n(Q)$. To find an equation satisfied by the $\psi_n(Q)$, the expansion of equation (31) is inserted into (25). We obtain

$$\begin{aligned} H(Q)|\Psi(Q)\rangle &= (T_N + H_e) \sum_n \psi_n(Q)|\chi_n(Q)\rangle = \\ &= \sum_n \left(T_N \left(\psi_n(Q)|\chi_n(Q)\rangle \right) + \psi_n(Q)E_{e,n}(Q)|\chi_n(Q)\rangle \right) \\ &= E|\Psi(Q)\rangle. \end{aligned} \quad (32)$$

Since $T_N = -\nabla^2$, evaluation of the first term under the summation sign yields

$$\begin{aligned} T_N \left(\psi_n(Q)|\chi_n(Q)\rangle \right) &= -\nabla \cdot \left(|\chi_n\rangle \nabla \psi_n(Q) + \psi_n(Q) \nabla |\chi_n\rangle \right) = \\ &= -|\chi_n\rangle \nabla^2 \psi_n(Q) - 2(\nabla |\chi_n\rangle) \cdot (\nabla \psi_n(Q)) - \psi_n(Q) \nabla^2 |\chi_n\rangle, \end{aligned} \quad (33)$$

where we for convenience have dropped the argument in $|\chi_n(Q)\rangle$. Denoting an electronic matrix element $\langle\chi_m|A|\chi_n\rangle$ by A_{mn} , we get from equation (32) with the aid of equation (33)

$$\begin{aligned} E\psi_m(Q) &= \langle\chi_m|H|\Psi(Q)\rangle = \\ &= \sum_n \left(-\delta_{mn}\nabla^2\psi_n(Q) - 2\nabla_{mn}(Q) \cdot (\nabla\psi_n(Q)) \right. \\ &\quad \left. - \psi_n(Q)\nabla_{mn}^2(Q) + \psi_n(Q)E_{e,n}(Q)\delta_{mn} \right), \end{aligned} \quad (34)$$

where δ_{mn} is the Kronecker symbol. The matrix elements $\nabla_{mn}(Q)$ and $\nabla_{mn}^2(Q)$ are Q -dependent, but from now on the argument will be dropped for simplicity. If we suppose that it suffices to use a finite number r of electronic eigenkets, this can be written in matrix notation as

$$\left(-\nabla^2 - 2[\nabla_{mn}] \cdot \nabla - [\nabla_{mn}^2] + \text{diag}(E_{e,n}) \right) \begin{pmatrix} \psi_1(Q) \\ \vdots \\ \psi_r(Q) \end{pmatrix} = E \begin{pmatrix} \psi_1(Q) \\ \vdots \\ \psi_r(Q) \end{pmatrix}, \quad (35)$$

where the matrices $[\nabla_{mn}]$ and $[\nabla_{mn}^2]$ are given by

$$[\nabla_{mn}] = \begin{pmatrix} \nabla_{11} & \cdots & \nabla_{1r} \\ \vdots & \ddots & \vdots \\ \nabla_{r1} & \cdots & \nabla_{rr} \end{pmatrix}, \quad (36)$$

$$[\nabla_{mn}^2] = \begin{pmatrix} \nabla_{11}^2 & \cdots & \nabla_{1r}^2 \\ \vdots & \ddots & \vdots \\ \nabla_{r1}^2 & \cdots & \nabla_{rr}^2 \end{pmatrix}. \quad (37)$$

These matrices are ordinary Q -dependent numerical matrices. If they are non-zero, equation (35) is a system of coupled differential equations for the functions $\psi_n(Q)$, containing differential operators of first and second order in the Q . In the simplest form of the adiabatic approximation one *neglects these two matrices*. This neglect greatly simplifies the problem. The matrix equation (35) is then

$$\left(-\nabla^2 + \begin{pmatrix} E_{e,1} & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & E_{e,r} \end{pmatrix} \right) \begin{pmatrix} \psi_1(Q) \\ \vdots \\ \psi_r(Q) \end{pmatrix} \approx E \begin{pmatrix} \psi_1(Q) \\ \vdots \\ \psi_r(Q) \end{pmatrix}. \quad (38)$$

That is, we have r (one for each electronic state) *uncoupled* differential equations of the form

$$(-\nabla^2 + E_{e,n}(Q))\psi_n(Q) \approx E\psi_n(Q). \quad (39)$$

For each n , this is just the Schrödinger equation for a number of nuclei moving in the potential $E_{e,n}(Q)$.

The eigenstates in the adiabatic approximation are, as is apparent from (38), of the form

$$|\Psi_n(Q)\rangle \approx \psi_n(Q)|\chi_n(Q)\rangle, \quad (40)$$

where $\psi_n(Q)$ solves (39), and $|\chi_n(Q)\rangle$ solves (29). Thus the problem of solving equation (25) has been reduced to solving the two simpler equations (29) and (39). Equation (29) yields the electronic eigenstates and the energies $E_{e,n}(Q)$ acting as effective potentials in (39). This is the essence of the adiabatic approximation. As the nuclei slowly move around in the potential $E_{e,n}(Q)$, the electrons immediately adapt, and remain in the eigenstate $|\chi_n(Q)\rangle$. The name adiabatic approximation is indeed appropriate (cf. section 2). Neglecting external effects, $E_{e,n}(Q)$ is independent of translational and rotational motions of the molecule. For a non-linear molecule, one therefore often regards $E_{e,n}(Q)$ as a real valued function of $3N - 6$ coordinates. (For a linear molecule the number of coordinates is $3N - 5$.) This function is called a *potential energy surface*. Geometrically (for a non-linear molecule) it is a $(3N - 6)$ -dimensional hypersurface in a $(3N - 5)$ -dimensional space.

This concludes our introduction to the adiabatic approximation. A question which we have not touched at all is when the approximation is valid. When we in the next subsection investigate this, we will come one step further on our way towards the aim of this thesis. Namely, we will run into the conical intersections.

3.2 Validity of the adiabatic approximation

The way of arriving at the adiabatic approximation outlined above is in fact not the usual way. (Actually we have not “arrived” at it at all, we have only stated it.) In standard treatments the starting point is equation (40). The ket $\psi_n(Q)|\chi_n(Q)\rangle$ is used as a trial ket, applying the variational method. This approach, leading basically to (39), can be found in [15]. We will not present it here, but this method puts the approximation on somewhat more solid ground by showing that the error in $|\Psi_n(Q)\rangle$ is proportional to the third power of the small parameter $\kappa \sim (m_e/M_N)^{1/4}$, where M_N is a typical nuclear mass [10]. In the derivation of (39) by the variational method it is of importance that the electronic kets are *non-degenerate*. Below we show why this is necessary.

Consider the elements of the matrices $[\nabla_{mn}]$ and $[\nabla_{mn}^2]$. We aim to determine when they can be considered small. We write the elements of $[\nabla_{mn}^2]$ in terms of the elements of $[\nabla_{mn}]$:

$$\begin{aligned}
\nabla_{mn}^2 &= \langle \chi_m | \nabla^2 | \chi_n \rangle = \langle \chi_m | \nabla \cdot \left(\sum_i |\chi_i\rangle \langle \chi_i | \nabla | \chi_n \rangle \right) \\
&= \langle \chi_m | \left(\sum_i (\nabla |\chi_i\rangle) \cdot (\langle \chi_i | \nabla | \chi_n \rangle) + |\chi_i\rangle \nabla \cdot \langle \chi_i | \nabla | \chi_n \rangle \right) \rangle = \\
&= \sum_i \left((\langle \chi_m | \nabla | \chi_i \rangle) \cdot (\langle \chi_i | \nabla | \chi_n \rangle) + \langle \chi_m | \chi_i \rangle \nabla \cdot \langle \chi_i | \nabla | \chi_n \rangle \right) = \\
&= \sum_i \nabla_{mi} \cdot \nabla_{in} + \nabla \cdot \nabla_{mn}.
\end{aligned} \tag{41}$$

In the above calculation the orthogonality of the $|\chi_n\rangle$ was used. First, we see that $[\nabla_{mn}^2]$ is just the square of $[\nabla_{mn}]$, plus the divergence of it. Secondly, note that the diagonal terms of $[\nabla_{mn}]$ always vanish, since

$$\nabla_{nn} = \langle \chi_n | \nabla | \chi_n \rangle = \nabla \cdot (\langle \chi_n | \chi_n \rangle) - \langle \nabla \chi_n | \chi_n \rangle = -\nabla_{nn}. \tag{42}$$

It is important to realise that the last equality requires both reality and normalisation of $|\chi_n\rangle$. Consequently both matrices are negligible *whenever the off-diagonal terms ∇_{mn} are small and slowly varying*.

Next we derive an expression for these terms that gives a clue as to when they are small, and, more importantly for the present work, shows dramatically when they are not. Consider equation (29) for $|\chi_n\rangle$. If we differentiate it with respect to Q we obtain

$$(T_e + V(Q) - E_{e,n}(Q))\nabla|\chi_n\rangle = -\nabla(V(Q) - E_{e,n}(Q))|\chi_n\rangle. \quad (43)$$

The operator $T_e + V(Q) - E_{e,n}(Q)$ lacks an inverse at $|\chi_n\rangle$ and at kets degenerate with it. However, at kets orthogonal to these, the inverse is defined, and we may write

$$\nabla|\chi_n(Q)\rangle = -(T_e + V(Q) - E_{e,n}(Q))^{-1} \nabla(V(Q) - E_{e,n}(Q))|\chi_n(Q)\rangle, \quad (44)$$

and, consequently,

$$\begin{aligned} \nabla_{mn} &= -\langle\chi_m|(T_e + V(Q) - E_{e,n}(Q))^{-1} \nabla(V(Q) - E_{e,n}(Q))|\chi_n\rangle = \\ &= -\langle\chi_m|\frac{1}{E_{e,m}(Q) - E_{e,n}(Q)}\nabla(V(Q) - E_{e,n}(Q))|\chi_n\rangle = \\ &= -\frac{\langle\chi_m|\nabla V(Q)|\chi_n\rangle}{E_{e,m} - E_{e,n}}, \end{aligned} \quad (45)$$

where the last equality holds since $E_{e,n}(Q)$ is independent of the q . The necessity of requiring non-degeneracy of the electronic kets in the adiabatic approximation is now painfully obvious. Since $\langle\chi_m|\nabla V(Q)|\chi_n\rangle$ is non-vanishing in general, the matrix elements ∇_{mn} diverge to infinity at a degeneracy between electronic levels m and n . Conversely one can loosely claim that the adiabatic approximation is valid when the electronic energies are well separated. Naturally this claim can be more firmly justified, but this will not be a concern of ours.

The points in Q -space where the electronic states are degenerate are exactly the points where the potential energy surfaces cross. If the energy difference $\Delta E(Q) = E_{e,n}(Q) - E_{e,m}(Q)$ between the states vanishes linearly in at least one direction in the nuclear configuration space, such a crossing is termed a *conical intersection*. It is illuminating to explain this terminology. Note first that linear vanishing of the energy difference implies that the potential energy surfaces are non-differentiable at the conical intersection. To see this, consider a crossing between the electronic levels 1 and 2. Remember that if a differentiable function goes linearly to zero, it also takes on negative values. Thus if $E_{e,1}(Q)$ and $E_{e,2}(Q)$ are differentiable, then $\Delta E(Q) = E_{e,2}(Q) - E_{e,1}(Q)$ is negative for some Q near the conical intersection. This is however impossible, since the states are ordered according to increasing energy! The reader may at this point object, that this non-differentiability is merely an artefact due to inadequate labelling of the states. This is however the case *only if the Q -space is one dimensional* (see Figure 1). To see that this does not hold in higher dimensions, consider the following example. Suppose that both the electronic ket space and the parametric Q -space are two-dimensional. Let X and Y be coordinates of the Q -space. Suppose furthermore that the electronic Hamiltonian has the simple form

$$H_e(X, Y) = \begin{pmatrix} X & Y \\ Y & -X \end{pmatrix}. \quad (46)$$

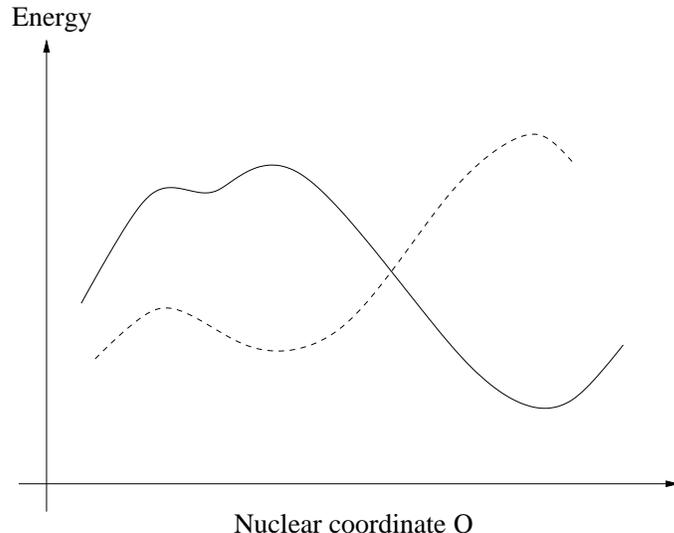


Figure 1: Energy levels of a hypothetical molecule with one-dimensional nuclear configuration space. The eigenvalues are differentiable at the degeneracy if the state corresponding to the dashed line is taken as state 1, and the one corresponding to the solid line as state 2. If they are labelled according to increasing energy, however, they are not differentiable.

Note that the matrix elements are everywhere continuous and differentiable. The energy eigenvalues are obtained as

$$E_{\pm}(X, Y) = \pm\sqrt{X^2 + Y^2} = \pm R, \quad (47)$$

where R is the usual radial coordinate in the XY -plane. The surfaces described by $E_{\pm}(X, Y)$ are nothing but cones emanating in opposite directions from their common vertex at the origin (see Figure 2). It is impossible to define two smooth potential energy surfaces that describe this system. The “cone” in the conical intersection is very real (and pointy!) although the Hamiltonian is well-behaved. An important observation that can be intuitively understood by considering this simple example concerns how frequent conical intersections are. In order for a real 2×2 symmetric matrix to have degenerate eigenvalues, two conditions must be fulfilled. The diagonal elements must be equal, and the (always coinciding) off-diagonal elements must vanish. The set of points in Q -space where the matrix is degenerate is thus subject to two constraints. Consequently, in general this set has co-dimension² 2. This statement holds also for more complicated Hamiltonians [2].

If intersections are so common (the subset of them having co-dimension 2), they should be abundant in any system having three or more degrees of freedom (e.g., in any molecule consisting of more than two atoms). Is the adiabatic approximation then applicable at all for such systems? The answer to this is in fact yes. The only occasion when the conical intersections are important is when they are located where the function $\psi_n(Q)$ has appreciable amplitude.

²The co-dimension of an m -dimensional subset of an n -dimensional space is defined as $n - m$.

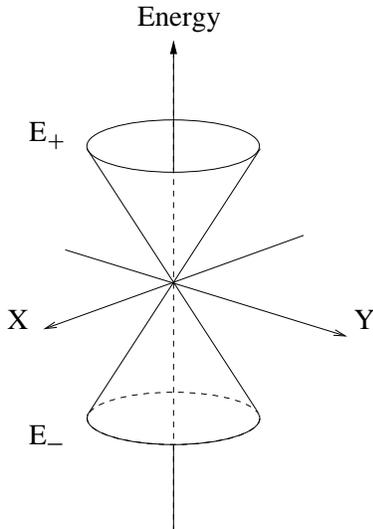


Figure 2: Potential energy surfaces shaped as cones. The non-differentiability is not removable by a relabelling of the states.

Thus far we have shown that the adiabatic approximation, one of the fundamentals of molecular theory, breaks down near intersections of the electronic potential energy surfaces. We have also agreed on calling the intersections conical if the energy difference is linearly vanishing. To be fully equipped, as far as molecular theory is concerned, we must also learn how to analyse the electronic eigenkets near a conical intersection. To conclude this subsection some effort is put into this issue.

Suppose that we are considering a region in the nuclear configuration space, where the electronic states 1 to s are nearly degenerate, but well separated from all other electronic states. Let Q_0 be a suitable point in this region. If $1 \leq n \leq s$, we have by the above discussion that the matrix elements ∇_{mn} are small for $m > s$. Thus for an arbitrary point Q in the region

$$\begin{aligned} \langle \chi_m(Q_0) | \chi_n(Q) \rangle &\approx \langle \chi_m(Q_0) | \left(|\chi_n(Q_0)\rangle + (Q - Q_0) \cdot \nabla |\chi_n(Q_0)\rangle \right) \rangle \\ &= 0 + (Q - Q_0) \cdot \nabla_{mn}(Q_0) \approx 0. \end{aligned} \quad (48)$$

Consequently

$$\begin{aligned} |\chi_n(Q)\rangle &= \sum_{i=1}^{\infty} |\chi_i(Q_0)\rangle \langle \chi_i(Q_0) | \chi_n(Q) \rangle \approx \\ &\approx \sum_{i=1}^s |\chi_i(Q_0)\rangle \langle \chi_i(Q_0) | \chi_n(Q) \rangle. \end{aligned} \quad (49)$$

That is, the electronic eigenket can to a good approximation be written as a linear combination of the (energetically close) eigenkets *at a fixed point* Q_0 . The s expansion coefficients $\chi_i(Q) \equiv \langle \chi_i(Q_0) | \chi(Q) \rangle$, for an arbitrary element $|\chi\rangle \in \mathcal{H}_e$ can be considered components of a real s -dimensional vector. By using

equation (29) we find the eigenvalue equation fulfilled by the vectors representing electronic eigenkets:

$$\begin{pmatrix} \langle 1|H_e|1\rangle & \dots & \langle 1|H_e|s\rangle \\ \vdots & \ddots & \vdots \\ \langle s|H_e|1\rangle & \dots & \langle s|H_e|s\rangle \end{pmatrix} \begin{pmatrix} \chi_1^{(n)}(Q) \\ \vdots \\ \chi_s^{(n)}(Q) \end{pmatrix} = E_{e,n}(Q) \begin{pmatrix} \chi_1^{(n)}(Q) \\ \vdots \\ \chi_s^{(n)}(Q) \end{pmatrix}, \quad (50)$$

where the quantities $\chi_i^{(n)}(Q) \equiv \langle \chi_i(Q_0) | \chi_n(Q) \rangle$ are the expansion coefficients of the electronic eigenket $|\chi_n(Q)\rangle$. In the above equation the matrix elements of H_e are taken with respect to the fixed eigenkets, i.e.,

$$\langle i|H_e|j\rangle \equiv \langle \chi_i(Q_0) | H_e | \chi_j(Q_0) \rangle. \quad (51)$$

The matrix elements are, however, still functions of Q , since H_e depends on Q . Within the framework above we analyse electronic eigenkets near conical intersections. Suitable forms of the matrix Hamiltonian in equation (50) are taken from the literature.

It is important to emphasise at this point, that we have done nothing to solve the problem of the adiabatic breakdown near the degeneracy. We merely found a convenient way to describe the electronic states. It is often the case, however, that the adiabatic approach is applicable even if there is a degeneracy at a “reasonable” nuclear configuration. The reason for this was explained Jahn and Teller, who in 1937 proved a remarkable theorem which states that at a symmetry dictated electronic degeneracy in any non-linear molecule, there is always at least one coordinate in which the degeneracy is broken linearly [17]. The intersection is thus conical, meaning that the point of degeneracy *cannot be the equilibrium conformation*. The electronic potential energy surfaces for such a case are pictured in Figure 3. If this effect is large enough, the stable nuclear configuration, down in the valley of Figure 3, will be such that the degeneracy is lifted, and the adiabatic approximation valid. An interesting consequence of this effect is that molecules, naively expected to be symmetrical, can fail to be so because of an electronic degeneracy at the symmetric configuration. A common way to investigate a molecule possessing an s -fold degeneracy at Q_0 is thus to assume a strong symmetry breaking, and make the ansatz

$$|\Psi(Q)\rangle \approx \sum_{i=1}^s a_i(Q) |i\rangle, \quad (52)$$

where $|i\rangle \equiv |\chi_i(Q_0)\rangle$ are independent of Q . Then, by the use of equation (25), we obtain

$$\left(-\nabla^2 + \begin{pmatrix} \langle 1|H_e|1\rangle & \dots & \langle 1|H_e|s\rangle \\ \vdots & \ddots & \vdots \\ \langle s|H_e|1\rangle & \dots & \langle s|H_e|s\rangle \end{pmatrix} \right) \begin{pmatrix} a_1(Q) \\ \vdots \\ a_s(Q) \end{pmatrix} = E \begin{pmatrix} a_1(Q) \\ \vdots \\ a_s(Q) \end{pmatrix}. \quad (53)$$

The adiabatic approximation now consists of writing

$$\begin{pmatrix} a_1(Q) \\ \vdots \\ a_s(Q) \end{pmatrix} \approx \psi_n(Q) \begin{pmatrix} \chi_1^{(n)}(Q) \\ \vdots \\ \chi_s^{(n)}(Q) \end{pmatrix}, \quad (54)$$

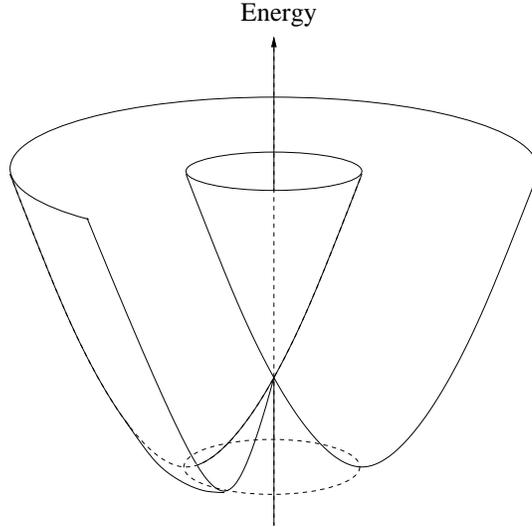


Figure 3: Potential energy surfaces for a simple Jahn–Teller system. The lower surface has been cut open to enhance visibility. Note that there is a double cone at the intersection. The stable nuclear conformation is down in the valley (dashed).

where the vector $(\chi_1^{(n)}(Q), \dots, \chi_s^{(n)}(Q))$ is a solution of (50), and $\psi(Q)$ solves

$$(-\nabla^2 + E_{e,n}(Q)) \psi_n(Q) = E \psi_n(Q). \quad (55)$$

Equation (50) thus plays the role of equation (29) and equation (55) is the counterpart of equation (39). This procedure is called the *crude* adiabatic approximation, and is a common starting point when considering Jahn–Teller systems. With this we are sufficiently familiar with molecular theory to begin our study of the topological aspects of conical intersections.

4 Topological detection of intersections

It should from the preceding section be clear why it is of importance to understand and be able to locate conical intersections: *they are points where the adiabatic approximation breaks down*. In this section we set out to generalise a method to find conical intersections that has been known for almost 30 years. The method was originally discovered by Longuet-Higgins in 1975 [2]. Thus, albeit a very concrete manifestation of the concept of geometric phase, this test preceded Berry’s pivotal work [3] almost by a decade. To arrive at the starting point of the present work we summarise the original method developed by Longuet-Higgins. Then follows a (non-rigorous) overview of some topological prerequisites. We then briefly return to the original method, now with topological eyes, after which we are ready to state and prove the promised generalisation. We close the section by exemplifying how the test is employed, and by some further theoretical explorations of it.

4.1 The work of Longuet-Higgins

In the 1970’s there was some debate whether the so-called non-crossing rule for diatomic molecules carries over to the polyatomic case [2, 18, 19, 20, 21, 22]. The non-crossing rule states that it is a rare event for potential energy surfaces to intersect. That this is the case for diatomic molecules comes as no surprise to us, since the Q -space for such a molecule is one-dimensional³, i.e., there are no subsets of co-dimension 2. Longuet-Higgins determined once and for all where the truth lies by (among other things) constructing the aforementioned test, and by applying it to a simple tri-atomic system to prove the existence of a crossing of the potential energy surfaces.

The argument of Longuet-Higgins begins by noting that the electronic eigenkets, in our notation $|\chi_n(Q)\rangle$, are only parametrically dependent on the Q . This means that the electronic eigenkets can in fact have discontinuities in the Q -space. For this to occur however, there must be a degeneracy at the discontinuity. (To see this, note that by continuity of the Hamiltonian, the limit of the jumping eigenket taken along any path to the discontinuity, is an eigenket at the discontinuity.)

Consider now a simply connected (two-dimensional) surface S in Q -space (which is basically \mathbb{R}^{3N-6}) bounded by the closed curve Γ , along which there are no electronic degeneracies. The electronic eigenket corresponding to one of the eigenvalues is then well-defined *up to a sign* all along the path. (We are still assuming time reversal invariance, so that $\chi_n(q; Q)$ can be chosen real, giving only two possible choices for $|\chi_n(Q)\rangle$.) As we move along Γ , we can (since there are no degeneracies along Γ) see to it that $|\chi_n(Q)\rangle$ varies continuously. When we come back to the starting point, however, there is no guarantee that we arrive at the original ket. We might very well have picked up a minus sign along the way. This is exactly the statement that the geometric phase factor γ_n^Γ can take the values ± 1 , (since real and differentiable kets are automatically parallel transported). The values ± 1 are also the only possibilities. The theorem of Longuet-Higgins is now the following.

³Note that this implies that the curves of Figure 1 should never have crossed in the first place!

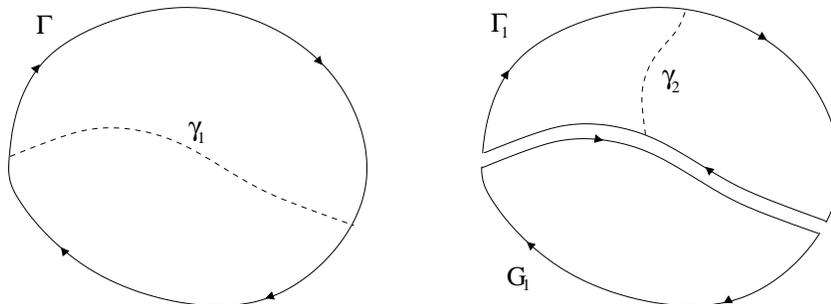


Figure 4: The loops in the nuclear configuration space considered in the proof of Theorem 1.

Theorem 1 (Longuet-Higgins). *Let S be a simply connected surface in the nuclear configuration space. Let S be bounded by the closed loop Γ . If the electronic eigenket $|\chi(Q)\rangle$ changes sign when continuously transported around Γ , then there is a point on S where $|\chi(Q)\rangle$ becomes degenerate with another electronic state.*

The proof of this theorem given below, is the original one given by Longuet-Higgins in 1975.

Proof. It is clear from the above considerations that the closed loops in Q -space can be divided into those along which $|\chi(Q)\rangle$ returns to the original ket, and those producing a sign change. Suppose now that the conditions of the theorem hold and that $|\chi(Q)\rangle$ is non-degenerate on S . Then it is also continuous everywhere in S . Let the curve γ_1 , going from one point on Γ to another point on Γ , lie completely in S . Denote by Γ_1 and G_1 the thus created loops. (See Figure 4.) Then either Γ_1 or G_1 is sign reversing. (If both were sign preserving then, contrary to assumption, Γ too would be sign preserving by the continuity of $|\chi(Q)\rangle$.) Choose the sign reversing loop (suppose it is Γ_1) and bisect it by γ_2 lying in S . This again produces one (smaller) sign reversing loop. In this way we may continue to create an arbitrarily small loop, around which $|\chi(Q)\rangle$ changes sign. The point to which these loops converge is a point of discontinuity of $|\chi(Q)\rangle$, since an infinitesimal change in Q leads to a finite change in the eigenket. Consequently $|\chi(Q)\rangle$ is discontinuous and the assumption of non-degeneracy is false. \square

This theorem makes it possible to detect the presence of a degeneracy by examining one electronic eigenket on a loop in the nuclear configuration space⁴. In this way conical intersections have been found by *ab initio* calculations in both LiNaK [23] and ozone [24]. It is noteworthy that the sign change implies a degeneracy on *any* surface bounded by Γ . This in particular implies that the set of degeneracy points has co-dimension of at most two.

The test described above was by Longuet-Higgins himself called a *topological* test. What then, is topological about it? One answer is that the sign reversal property is not affected by continuous deformations of the loop Γ (as long as the degeneracy remains inside of course!). However, there are subtler points which

⁴“from purely circumstantial evidence” as humorously put by Longuet-Higgins.

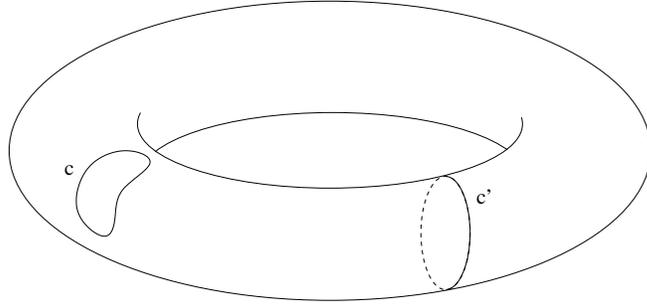


Figure 5: Loops on the torus. c is trivial, but c' is not.

we will examine carefully later on (subsections 4.3 and 4.4). In doing so our understanding of the topological nature of the test will develop and deepen. This analysis will also suggest the generalisation of the test presented in subsection 4.4.

4.2 Topology for beginners

This subsection is intended to give readers not familiar with topology a fair chance to grasp the main ideas in the remainder of this section. Stringency and rigour will be set aside for analogies and intuition. It is very likely therefore that some concepts will seem strange, and some theorems seem unbelievable. I apologise in advance for this, and refer the unsatisfied reader to ordinary textbook treatments of topology. An excellent, easy-to-read yet thorough, introduction to the subject is found in [25]. Also, topology is a *much* wider area than indicated here. Only what is absolutely essential to the present work is included.

Topology is roughly the study of geometric properties that do not change under continuous deformations. (A doughnut remains a doughnut even if you accidentally sat on it.) A topologist would (contrary to a geometer) consider a sphere and an ellipsoid equivalent. Also would he or she claim that a rubber band being stretched is the same object all the way until it breaks.

The basic objects in topology, such as doughnuts and rubber bands, are called *topological spaces*. The doughnut, or rather the surface of it, is called the torus and the (infinitely thin) rubber band is called the one-dimensional sphere (or the circle). They are denoted T^2 and S^1 respectively. For our purposes we may think of topological spaces as smooth subsets of \mathbb{R}^d .

Equipped with topological spaces one defines what it means for a mapping between two such spaces to be continuous. This definition generalises the usual concept of continuity, so we use our intuition and think of it as “close points map to close points”. If there exists a one-to-one correspondence between two spaces that is continuous *in both directions*, then the spaces are considered equivalent or *homeomorphic*. A *curve* in a topological space X is just a continuous mapping c from the interval $[0,1]$ to X . A curve will be called a *loop* if it starts and ends at the same point, i.e., if $c(0) = c(1)$. A loop can equivalently be viewed as a continuous mapping from the unit circle S^1 to X . Consider loops on the torus. There are obviously different kinds of them. Two possibilities are shown in Figure 5. The loop c sits nicely and trivially at the side of the torus. Someone might place a rubber band like that. The loop c' , however, is a completely

different creature. To arrange a rubber band in that way, one would have to tear it apart, place it, and glue the ends back together. Furthermore we see that it is possible to “gradually shrink” the loop c to a point. This is impossible with c' (at least if we are to stay on the torus, i.e., on the surface of the doughnut).

To distinguish between these types of curves we say that c is *trivial* or *contractible*. More formally, if c is a loop in the topological space X , c is trivial if there exists a *continuous* map $K : S^1 \times [0, 1] \rightarrow X$, such that

$$K(t, 0) = c(t) \text{ and } K(t, 1) = x_0 \in X. \quad (56)$$

The variable t is an element of S^1 performing a complete turn. For each ϵ_0 the function $H(t, \epsilon_0)$ represents a loop in X . This family of loops represents, as ϵ_0 goes from 0 to 1, a continuous deformation of c to the single point x_0 . The function H is called a *homotopy* between c and x_0 . If every loop in a topological space is trivial, the space is said to be *simply connected*. Properties such as triviality of loops and simply connectedness are *invariant* under homeomorphisms, and thus considered to be *topological* properties. (The same loops are non-trivial in the doughnut you sat on, as in the one left on the table.)

We are now in a position to prove a lemma that will be vital in the following.

Lemma 1. *Let X and Y be topological spaces. Let X be simply connected. If c is a loop in X , and if $F : X \rightarrow Y$ is continuous, then $F(c)$ is a trivial loop in Y .*

Proof. Let K be a homotopy between c and $x_0 \in X$. Then $L \equiv F \circ K$ is continuous as it is a composite of continuous maps. Furthermore

$$L(t, 0) = F(c(t)) \text{ and } L(t, 1) = F(x_0) \in Y. \quad (57)$$

Thus, L is a homotopy between $F(c)$ and $F(x_0)$. Consequently $F(c)$ is trivial. \square

We now turn to some examples of topological spaces, and their properties. We will also discuss two new concepts that arise naturally when defining projective spaces.

Examples.

1. The simplest space containing non-trivial loops is the already encountered S^1 . We think of it as the unit circle in \mathbb{R}^2 . As such, it is parametrised by the polar angle ϕ . A closed loop can be viewed as a continuous map ϕ from $[0, 1]$ to \mathbb{R} , such that $\phi(1) = \phi(0) + 2k\pi$, k being any integer. If k equals zero, the loop is trivial, otherwise it is not.
2. The n -dimensional sphere S^n is (as a subset of \mathbb{R}^{n+1}) the set $S^n = \{x \in \mathbb{R}^{n+1} : \|x\| = 1\}$. For $n \geq 2$, S^n is simply connected.
3. Let $SO(n)$ denote the set of (real) orthogonal $n \times n$ matrices whose determinant is unity. This is the *special orthogonal group*, which can be considered as a topological space. Its elements are rotations in \mathbb{R}^n . If the requirement of unit determinant is removed, the space is called $O(n)$. $O(n)$ is homeomorphic to two disjoint copies of $SO(n)$, corresponding to matrices with determinant $+1$, and matrices with determinant -1 , respectively.

4. Consider S^n . We define the *real projective space* of dimension n to be the set of all *pairs of mutually antipodal points* on S^n . This space is denoted \mathbb{RP}^n . An element of \mathbb{RP}^n is thus a two-element set $\{x, -x\} \equiv [x]$, where x is in \mathbb{R}^{n+1} and $\|x\| = 1$. Note that the ordering of x and $-x$ is inessential (the expression appearing in the definition is “pair”, not “ordered pair”). The notation $[x]$ is to be read as “the equivalence class of x ”, meaning simply the element of \mathbb{RP}^n to which x belongs. This space will show up naturally in our description of quantum systems exhibiting time reversal symmetry. (It also happens to be of tremendous interest in geometry.) Apart from pairs of antipodal points on S^n , \mathbb{RP}^n can also be viewed as the set of lines in \mathbb{R}^{n+1} that goes through the origin. Such a line defines a unique pair of antipodal points and vice versa.

It is not immediately obvious to see whether or not there are non-trivial loops in spaces such as \mathbb{RP}^n or $SO(n)$. A useful tool for determining such things is the concept *covering space*. Y is called a covering space of X if there is a map $p : Y \rightarrow X$, called a *covering map*, which is continuous, onto, and fulfils a couple of other criteria. We do not discuss the remaining criteria for being a covering map here, even if they are important. Instead we take the somewhat naive point of view that a covering space locally is a number of copies of the space in question. Suppose for instance that we are studying \mathbb{RP}^2 . There is a very natural map p from S^2 to \mathbb{RP}^2 defined by

$$p(x) = [x]. \tag{58}$$

Each point in S^2 is mapped to its equivalence class. This map fulfils all the criteria that characterise a covering map. S^2 is thus a covering space of \mathbb{RP}^2 . Every (sufficiently small) subset of \mathbb{RP}^2 is represented by two disjoint subsets in S^2 . A covering space of the topological space X that is simply connected is called the⁵ *universal covering space* of X .

Now let Y be a covering space of X , with covering map p . Two facts will be of importance to us. We state them as lemmas. The first is just a (weaker) version of Lemma 54.1 on page 342 in [25].

Lemma 2. *Let c be a loop in X such that $c(0) = x_0$. If $p(y_0) = x_0$, then there is a uniquely defined curve (not necessarily a loop!) \tilde{c} , called the lift of c , in Y which is such that $\tilde{c}(0) = y_0$ and $p(\tilde{c}) = c$.*

The second lemma, which follows fairly directly as a corollary of Theorem 54.3 on page 344 in [25] is the following.

Lemma 3. *Let Y be a covering space of X . If c is a trivial loop in X then the lift \tilde{c} of c is a trivial loop in Y .*

These statements we just take as God-given. They give us a possibility to find non-trivial loops in for example \mathbb{RP}^n . Consider Figure 6. The curve c in \mathbb{RP}^2 that lifts to \tilde{c} is a loop since \tilde{c} starts and ends at antipodal points on S^2 . However, \tilde{c} is not a loop in S^2 , so c is non-trivial by Lemma 3. Apparently, there are non-trivial loops in \mathbb{RP}^2 . A peculiar thing about the loop c , is that if we go around it twice, the resulting loop $2c$ is trivial. The reason for this is

⁵If a universal covering space of X exists, it is unique. Hence it is common to write *the* universal covering space of X .

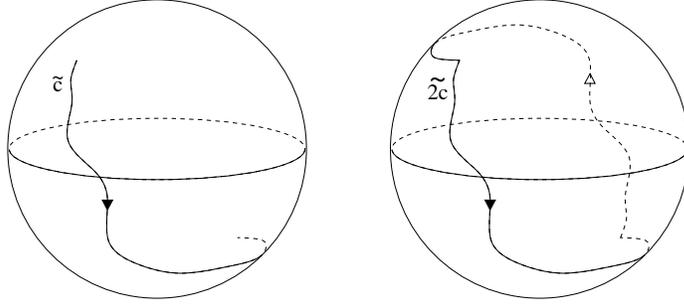


Figure 6: Lifts of the loops c and $2c$ in $\mathbb{R}P^2$ to the covering space S^2 .

that the lift $\tilde{2c}$ is trivial. The fact that a loop which lifts to a trivial loop itself is trivial, is not an implication of Lemma 3, but rather of Lemma 1.

To conclude this subsection, we familiarise ourselves with the two simplest special orthogonal groups $SO(2)$ and $SO(3)$. The first of these are rotations in \mathbb{R}^2 . The elements of $SO(2)$ are thus all of the form

$$\begin{pmatrix} \cos \phi & -\sin \phi \\ \sin \phi & \cos \phi \end{pmatrix}. \quad (59)$$

$SO(2)$ is parametrised by the angle of rotation ϕ . For each element in $SO(2)$, there is a corresponding element in S^1 . This correspondence is a homeomorphism, and consequently $SO(2)$ and S^1 are equivalent from a topological point of view.

Similarly $SO(3)$ is homeomorphic to $\mathbb{R}P^3$. To make this statement plausible consider the quaternion representation of a three-dimensional rotation. Here a rotation is represented by an element on $S^3 \subset \mathbb{R}^4$. A rotation by the angle θ around the unit vector \mathbf{v} is represented by

$$q(\mathbf{v}, \theta) = (\cos(\theta/2), \mathbf{v} \sin(\theta/2)) \in S^3. \quad (60)$$

If we let \mathbf{v} take any value on S^2 and θ go from zero to 2π then every point on S^3 is represented once by q . However, each rotation is represented twice, since the rotation described by $\tilde{\mathbf{v}} = -\mathbf{v}$ and $\tilde{\theta} = 2\pi - \theta$ is the same transformation as the one described by \mathbf{v} and θ . The fact that $q(\tilde{\mathbf{v}}, \tilde{\theta}) = -q(\mathbf{v}, \theta)$ shows that antipodal points represent the same rotation. Thus $SO(3)$ is “ S^3 with antipodal points identified”, i.e., $\mathbb{R}P^3$. $\mathbb{R}P^3$, and therefore also $SO(3)$, is subject to the same peculiarity as $\mathbb{R}P^2$. If a non-contractible loop is followed twice, the result is contractible. This is illustrated by the famous coffee-cup trick. Take a coffee-cup (preferably empty) and put in your right palm. Rotate it around a vertical axis (pointing upwards). Let it pass under your armpit and elbow, until it has performed a complete turn. Your arm, now almost painfully twisted, shows that this loop is non-trivial. Now let your elbow slide over your head, and gently let the cup pass behind it. Note that this makes the cup turn *in the same direction as before*. Finally hold your unwound arm before you. The cup has now completed two turns, and the fact that your arm is not twisted is a manifestation that the loop is trivial.

By this curiosity we end our detour into the rich field of topology and turn back up on the main road of this thesis.

4.3 The work of Longuet-Higgins revisited

Equipped with the tools of the preceding subsection, we return to the topological test of Longuet-Higgins. We consider the surface S bounded by Γ as a topological space. This space is simply connected. (Remember that S is required to be simply connected in Theorem 1.) The loop Γ in it is thus homotopic to a point.

We also wish to view the set of electronic kets as a topological space. In doing this we assume that it suffices to consider a subspace of finite dimension n (say) of the Hilbert space \mathcal{H} . An arbitrary ket can then be viewed as an element of \mathbb{C}^n . We know, however, that it by time reversal (TR) symmetry is possible to choose the electronic eigenkets real. This means that by a suitable choice of basis $\{\hat{\mathbf{e}}_1, \dots, \hat{\mathbf{e}}_n\}$ in \mathbb{C}^n , the allowed electronic eigenkets are of the form

$$|\chi\rangle = \lambda \sum_{i=1}^n \chi_i \hat{\mathbf{e}}_i, \tag{61}$$

where χ_1, \dots, χ_n are real and λ is a complex number. Denote the subset of \mathbb{C}^n consisting of the kets of equation (61) by \mathcal{H}_{TR} . This set is independent of the explicit choice of suitable basis $\{\hat{\mathbf{e}}_1, \dots, \hat{\mathbf{e}}_n\}$, since it is just all permitted eigenkets. Furthermore, denote the kets of \mathcal{H}_{TR} with strictly real coefficient (i.e., with $\lambda \in \mathbb{R}$) by \mathcal{RH} . This subset (which depends on the basis) is not a complex subspace of \mathbb{C}^n . It is, however, an n -dimensional real subspace of \mathbb{C}^n if the latter is identified with \mathbb{R}^{2n} . Thus we consider \mathcal{RH} to be just \mathbb{R}^n . The space of real normalised kets we denote by \mathcal{RN} . As a topological space it is identified with the set of unit vectors in \mathbb{R}^n , i.e., the $(n-1)$ -dimensional sphere S^{n-1} . The states that are compatible with the time reversal symmetry are represented by normalised electronic eigenkets of the form (61). Kets differing only in λ represent the same state. We denote the set of allowed states, which is a subset of \mathcal{P} , by \mathcal{P}_{TR} . Topologically \mathcal{P}_{TR} is $\mathcal{RN} = S^{n-1}$ with antipodal points identified, i.e., \mathbb{RP}^{n-1} . \mathcal{RN} is thus a covering space of \mathcal{P}_{TR} . We can now use Lemma 1 to construct another proof of Theorem 1 as follows.

Suppose that the real ket $|\chi(Q)\rangle \in \mathcal{RN}$ changes sign when continuously transported around Γ at the same time that it is non-degenerate in S . Its corresponding element in \mathcal{P}_{TR} is then everywhere uniquely defined on S and is a continuous function of Q . We thus have a continuous map F from S to \mathcal{P}_{TR} that takes $Q \in S$ to $F(Q) = [|\chi(Q)\rangle] = \{|\chi(Q)\rangle, -|\chi(Q)\rangle\} \in \mathcal{P}_{TR}$. By Lemma 1, Γ must map to a trivial loop in \mathcal{P}_{TR} . Lemma 3, however, implies that this is not the case since $F(\Gamma)$ lifts to an open curve in \mathcal{RN} . The theorem follows by contradiction.

The theorem apparently follows from the fact that the loop in the nuclear configuration space maps to a *non-trivial* loop in \mathcal{P}_{TR} . We note that the possibility to choose real kets is still needed in the proof. The reason for this is that the projection of \mathcal{N} onto \mathcal{P} fails to be a covering map. (Technically the preimage of an open set $U \subset \mathcal{P}$ fails to be the disjoint union of open sets $V_\alpha \subset \mathcal{N}$ such that the restriction of p to V_α is a homeomorphism onto U .)

At this point it is relevant to ask whether there might be other curves in \mathcal{RN} than the open ones that project to non-trivial curves in \mathcal{P}_{TR} , and thus also imply a degeneracy somewhere on S . This question will be considered in the following subsection.

4.4 A generalised topological test for intersections

Below we use the machinery of topology to generalise the test of Longuet-Higgins. However, even if all the necessary concepts have been introduced, the generalisation is not stated and proved directly. It makes the line of thought more clear, I hope, to approach it in the way it was discovered. Maybe, when the results are at last stated mathematically, they will also be more transparent if we have this background. Thus, we begin by considering a system that is relatively easy to analyse.

4.4.1 The two-level case

Our starting point is the simplest non-trivial Jahn–Teller system. In this system a doubly degenerate electronic state (labelled E) and a likewise doubly degenerate vibrational mode (e) interact. Thus, both the crude adiabatic electronic Hilbert space and the nuclear configuration space are two-dimensional. This system is called $E \otimes e$, and has been studied extensively in the literature [26, 27, 28, 29, 30]. The crude adiabatic approach is used in [26]. The basis vectors $|\chi_1(Q_0)\rangle$ and $|\chi_2(Q_0)\rangle$ (which, from now on will be denoted $|\chi_1\rangle$ and $|\chi_2\rangle$) are chosen at the degeneracy, which without loss of generality can be assumed to be located at the origin. Polar coordinates ρ and θ are used to parametrise the Q -space. Equation (53) then reads [26]

$$\left(-\nabla^2 + \begin{pmatrix} \frac{1}{2}\rho^2 & k\rho e^{-i\theta} + \frac{1}{2}g\rho^2 e^{2i\theta} \\ k\rho e^{i\theta} + \frac{1}{2}g\rho^2 e^{-2i\theta} & \frac{1}{2}\rho^2 \end{pmatrix} \right) \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}. \quad (62)$$

The matrix Hamiltonian of this equation exhibits time-reversal symmetry even if it is not explicit (the matrix elements being complex). As we shall see, however, there is a unitary transformation of the basis $\{|\chi_1\rangle, |\chi_2\rangle\}$ that yields real matrix elements, and consequently real eigenkets.

The adiabatic potential energy surfaces are obtained as eigenvalues of the electronic Hamiltonian. In this two-dimensional case, to find them amounts to nothing more than solving a second order algebraic equation, yielding

$$E_{\pm} = \frac{1}{2}\rho^2 \pm \sqrt{k^2\rho^2 + kg\rho^3 \cos 3\theta + \frac{1}{4}g^2\rho^4}. \quad (63)$$

Note that there is a degeneracy at the origin, but also three extra degeneracies at $\rho = 2k/g$ and $\theta = \pi/3, \pi,$ and $5\pi/3$. All these intersections are conical, except if $k = 0$. In this case the potential energy surfaces are two co-axial parabolas that gently touch at the origin. This type of intersection is called *glancing* or *osculating*. Thus, either we have multiple conical intersections or a single glancing one.

The adiabatic eigenkets are the eigenvectors of the electronic Hamiltonian:

$$\begin{aligned} |+\rangle &= \frac{1}{\sqrt{2}}(e^{-i\alpha/2}|\chi_1\rangle + e^{i\alpha/2}|\chi_2\rangle), \\ |-\rangle &= \frac{i}{\sqrt{2}}(-e^{-i\alpha/2}|\chi_1\rangle + e^{i\alpha/2}|\chi_2\rangle). \end{aligned} \quad (64)$$

The real parameter α is just the phase of the lower off-diagonal element of the electronic Hamiltonian, i.e., $\alpha = \arg(k\rho e^{i\theta} + \frac{1}{2}g\rho^2 e^{-2i\theta})$. A unitary transformation of the crude adiabatic basis gives us the real expansion coefficients whose existence is guaranteed by the time-reversal invariance. They read

$$\begin{aligned} |+\rangle &= \cos(\alpha/2)|1\rangle + \sin(\alpha/2)|2\rangle, \\ |-\rangle &= -\sin(\alpha/2)|1\rangle + \cos(\alpha/2)|2\rangle, \end{aligned} \quad (65)$$

where $|1\rangle \equiv \frac{1}{\sqrt{2}}(|\chi_1\rangle + |\chi_2\rangle)$ and $|2\rangle \equiv \frac{i}{\sqrt{2}}(-|\chi_1\rangle + |\chi_2\rangle)$.

We study two limits of this system. Suppose first that we are on a circular loop, Γ_1 in the nuclear configuration space, described by $\rho = \rho_1 \ll 2k/g$, and θ ranging from 0 to 2π . Γ_1 encircles the degeneracy at the origin, but not the other three. We have

$$\alpha = \arg(k\rho_1 e^{i\theta} + \frac{1}{2}g\rho_1^2 e^{-2i\theta}) \approx \arg(k\rho_1 e^{i\theta}) = \theta. \quad (66)$$

The eigenvectors are therefore approximately given by

$$\begin{aligned} |+(\theta)\rangle &\approx \cos(\theta/2)|1\rangle + \sin(\theta/2)|2\rangle, \\ |-(\theta)\rangle &\approx -\sin(\theta/2)|1\rangle + \cos(\theta/2)|2\rangle. \end{aligned} \quad (67)$$

As θ goes from 0 to 2π we see that both eigenkets change sign. Their geometric phase factors along Γ_1 are both -1 , and a quantum chemist using the topological test of Longuet-Higgins would find the degeneracy at the origin by considering the computed electronic eigenkets on this loop.

In the language of subsection 4.3, the analysis is the following. We can view the real part of the Hilbert space \mathcal{RH} in which $|+\rangle$ and $|-\rangle$ live, as \mathbb{R}^2 , by letting the basis $\{|1\rangle, |2\rangle\}$ be the standard basis in \mathbb{R}^2 . The eigenkets are normalised, and thus lie on the unit circle, S^1 , which corresponds to \mathcal{RN} . As Γ_1 is traversed, each eigenket represents a closed loop in \mathcal{PTR} , which in this example is \mathbb{RP}^1 ⁶. The lift of this loop into S^1 is open, however, since $|-(2\pi)\rangle = -|-(0)\rangle$, so the loop in \mathcal{PTR} must be non-trivial by Lemma 3. This implies the degeneracy by Lemma 1.

Now picture a second quantum chemist, determining the electronic eigenkets on a loop Γ_2 , where θ still goes from 0 to 2π , but with $\rho = \rho_2 \gg 2k/g$. This loop encircles all four electronic degeneracies. The approximation of (66) must now be changed to

$$\alpha = \arg(k\rho_2 e^{i\theta} + \frac{1}{2}g\rho_2^2 e^{-2i\theta}) \approx \arg(\frac{1}{2}g\rho_2^2 e^{-2i\theta}) = -2\theta. \quad (68)$$

Our approximate adiabatic eigenkets are now instead

$$\begin{aligned} |+(\theta)\rangle &\approx \cos\theta|1\rangle - \sin\theta|2\rangle, \\ |-(\theta)\rangle &\approx \sin\theta|1\rangle + \cos\theta|2\rangle. \end{aligned} \quad (69)$$

These eigenkets *do not* change sign as the loop is traversed. Consequently our second quantum chemist would fail to detect the degeneracies using the test of Longuet-Higgins.

⁶ \mathbb{RP}^1 is actually also S^1 !

Let us however not despair, but examine the kets of (69) more carefully. Note first that along any loop, the corresponding eigenkets must perform a certain number of half-turns, in order to return to the original element in \mathcal{P}_{TR} . Along Γ_2 , the eigenkets, viewed as elements of \mathbb{R}^2 , make a complete clockwise turn around the unit circle, i.e., two half-turns. Suppose now that we gradually shrink Γ_2 . If the eigenvectors are continuous in the interior of the loop we still obtain a complete clockwise turn. (A jump from a clockwise turn to another number of half-turns, would require a discontinuous jump in the eigenvectors.) So either we encounter a degeneracy as we contract the loop, or we obtain an arbitrary small loop along which the eigenkets make a complete turn. But the point to which this loop converges, must be a point of degeneracy, since an infinitesimal displacement in Q -space gives a finite change in the kets at this point! This means that we *can* in fact draw the conclusion that Γ_2 encircles at least one degeneracy based on the behaviour of the eigenkets along it⁷.

All this is of course easily analysed by topological methods. The loop traversed in $\mathcal{P}_{TR} = \mathbb{R}\mathbb{P}^1$ is lifted to a non-trivial loop in $\mathcal{RN} = S^1$. Thus the loop in \mathcal{P}_{TR} is non-trivial, and there must be a degeneracy somewhere inside the loop.

Excited by this apparent success in finding a generalisation for the two-level case, we immediately move on to the n -dimensional case, only to be utterly disappointed.

4.4.2 The n -level case

Suppose we are interested in a molecular system described in the crude adiabatic approximation by an $n \times n$ matrix Hamiltonian H_e exhibiting time reversal invariance. Let H_e be continuously dependent on the nuclear coordinates and let S be a simply connected surface in the nuclear configuration space \mathbb{R}^d . Assume that S is bounded by the closed loop Γ along which H_e is non-degenerate. Just as in subsection 4.3, the space \mathcal{RH} of real electronic state vectors is \mathbb{R}^n . The normalised real eigenkets of H_e are unit vectors in \mathbb{R}^n , i.e., elements of $\mathcal{RN} = S^{n-1}$. Antipodal points on S^{n-1} represent the same state, so the space \mathcal{P}_{TR} of time reversal compatible states is our familiar $\mathbb{R}\mathbb{P}^{n-1}$.

Longuet-Higgins' test now takes advantage of the fact that if one of the eigenkets, chosen continuously along the loop Γ , represents an open curve in \mathcal{RN} , then there must be a degeneracy inside Γ . We would like to use that a degeneracy is likewise implied, if the eigenket represents a *non-trivial loop* in \mathcal{RN} . This went well in the case $n = 2$ as we saw above. We should not be surprised by this since for this simple case $\mathcal{RN} = S^1$, which is full of non-trivial loops. In the case $n > 2$, however, $\mathcal{RN} = S^{n-1}$ is *simply connected*⁸. We are

⁷This behaviour is somewhat similar to the phase effects studied by Bhandari in [31]. Suppose one would distort the present loop in the Hilbert space so as to avoid that $|\pm(\theta)\rangle$ gets orthogonal to $|\pm(0)\rangle$ for some θ . (This cannot be done without violating the time-reversal symmetry) Then the geometric phase, if chosen continuously, would go from 0 to 2π along the loop, in line with Bhandari's "non-modular" phase. There are, however, fundamental differences since Bhandari considers the *change* in the geometric phase along a curve, and not the actual geometric phase.

⁸It is this difference between two and higher dimensions that let particles living in a two-dimensional world obey "arbitrary" statistics, while particles living in three or more dimensions are confined to being either fermions or bosons. Particles having this statistical freedom are called anyons [32, 33].

thus confronted with the unpleasant fact that there are no non-trivial loops in \mathcal{RN} . The original test of Longuet-Higgins already finds every non-trivial loop in \mathcal{P}_{TR} .

Before we decide to break down and cry, however, let us investigate whether it is possible to extract some additional information if we consider, not a single eigenket along the loop, but a complete set of them. The n real eigenkets of H_e , call them $|\chi_i\rangle$, form a continuously varying orthonormal basis of \mathbb{R}^n all along Γ . If we could consider such bases as elements of some topological space, the bases along Γ would trace out a loop in that space. If this loop is non-trivial we expect that this would imply the presence of a degeneracy. We write the n eigenkets, as the columns of a $n \times n$ matrix, F :

$$F(t) = \begin{pmatrix} \langle 1|\chi_1(t)\rangle & \dots & \langle 1|\chi_n(t)\rangle \\ \vdots & \ddots & \vdots \\ \langle n|\chi_1(t)\rangle & \dots & \langle n|\chi_n(t)\rangle \end{pmatrix}, \quad (70)$$

where $\{|1\rangle, \dots, |n\rangle\}$ is a fixed basis of \mathcal{H} giving real expansion coefficients $\langle i|\chi_j(t)\rangle$, and t parametrises the loop Γ . The matrix $F(t)$ is orthogonal, i.e., it is an element of $O(n)$. We hope that this space can play the role of \mathcal{RN} .

If $O(n)$ corresponds to our covering space \mathcal{RN} , what then corresponds to the space $\mathcal{P}_{TR} = \mathbb{RP}^{n-1}$? Well, each vector $|\chi_i(t)\rangle$ is defined only up to its sign. If we have decided upon an ordering of the states (e.g., according to increasing energy), we consequently have 2^n possible choices of $F(t)$ at each point t . The space that corresponds to \mathbb{RP}^{n-1} in this case is thus $O(n)$ with two matrices identified *if their columns are identical or differing by an overall sign*. Let us call this space $OP(n)$.

Our objective, thus, is to study a loop in $OP(n)$ by considering a lift of it to the covering space $O(n)$. It suffices, however, to consider lifts to $SO(n)$, since any lift of a loop from $OP(n)$ to $O(n)$ starting in one of the disjoint subsets of $O(n)$, will stay in that subset. In other words, if we require the kets to be continuous around Γ , it suffices to fix the determinant of F to $+1$ at the starting point for it to be $+1$ on all Γ . (With topological glasses on, $SO(n)$ is also a covering space of $OP(n)$.)

We can thus reason in the following way. If the Hamiltonian H_e is non-degenerate in S , then the eigenkets can be chosen continuous on S . Therefore the matrix $F(t)$ can also be taken as continuous (and with determinant $+1$). Consequently $F(t)$ must (by Lemma 1) trace out a trivial loop in $SO(n)$. The cases when $F(t)$ traces out an open curve (i.e, when some columns change sign⁹) are taken care of by Longuet-Higgins' test. We can however also say that if $F(t)$ represents a *non-trivial* loop in $SO(n)$, then there is a degeneracy in S .

The crucial question is now if there are any non-trivial loops in $SO(n)$. As already indicated, this is indeed the case. For each $n \geq 3$ there is one class of non-trivial loops in $SO(n)$. The loops become trivial when traversed twice.

Note that for $n = 2$ we get exactly the test we already found for this case. $SO(2)$ is just S^1 . It provides no extra information to monitor two orthogonal and positively oriented vectors in \mathbb{R}^2 . The first uniquely determines the second.

We now aim to state the test as a theorem. The already believing reader, can just jump to 4.4.3 for an example of how the test can be used. We begin

⁹As a consequence of the fact that continuous transport of the eigenkets keeps $F(t)$ in $SO(n)$, it is always an even number of columns that change sign.

by noting, just as Longuet-Higgins did, that if there are no degeneracies of H_e on a curve, then the eigenvectors can be chosen continuously along that curve. Furthermore, in the theorem of Longuet-Higgins it is implicit that if there are no degeneracies on S , then continuous transport of one eigenvector from one point to another is *independent of path*. To see this suppose that the eigenvector \mathbf{v} is transported to \mathbf{w} along γ_1 , and to $-\mathbf{w}$ along γ_2 , γ_1 and γ_2 being two curves in S having the same starting and ending points. ($\pm\mathbf{w}$ are the only possible outcomes, since the eigenvector is non-degenerate.) Then if \mathbf{w} were transported along the loop $-\gamma_1 + \gamma_2$, it would change sign. This would imply a degeneracy, i.e., a contradiction to the non-degeneracy assumption.

Thus, if H_e is non-degenerate on S , the eigenvectors of each eigenvalue of H_e represent two globally defined continuous n -dimensional vector fields on S differing only by sign. The following lemma is now obvious.

Lemma 4. *Suppose there are no degeneracies of H_e on S . The normalised eigenvectors of H_e then defines 2^n globally defined (on S) continuous $O(n)$ -valued functions of the form (70). These differ only by the sign of the columns.*

Proof. Just use the continuous eigenvectors as columns. Continuity follows from that of the eigenvectors. \square

Note that half of the maps of Lemma 4 are maps to $SO(n)$, and that the map is completely determined as soon as the value at a single point is chosen. As soon as F is fixed, then for any two points x_0 and x_1 in S , $F(x_1)$ is the continuous transport of $F(x_0)$ to x_1 along any curve between the points, lying completely in S . We now state and prove the main theorem.

Theorem 2. *Suppose we choose a complete and positively oriented set of eigenkets of H_e at the starting point of Γ . Let these be continuously transported around Γ . This defines a curve in $SO(n)$ by equation (70). If this curve is a non-trivial loop, then there is a degeneracy somewhere on S .*

Proof. Suppose H_e is non-degenerate on S . Then by Lemma 4 the map F is continuous on all S . The continuously transported eigenkets are the image of Γ under F . They consequently must represent a loop. (Thus far this is basically the *reductio ad absurdum* of Longuet-Higgins.) This loop is trivial as a consequence of Lemma 1, and the theorem follows by contradiction. \square

In proving the theorem we, as the reader doubtlessly realised, avoided any use of the covering space relation between $OP(n)$ and $SO(n)$. This was done simply because it works, and since it makes the logic clearer for the non-topologist. However, the language of covering spaces makes the topological nature of the Longuet-Higgins test clearer. It also reveals the relation between the original test and the present generalisation. Hence it was included in this thesis.

It is worth noting that although the analysis above is carried out for molecular systems, the results immediately apply to a general matrix Hamiltonian H_e obeying time reversal symmetry.

4.4.3 To use the test

In order to find conical intersections by the above test, we certainly need to be able to determine whether a given loop in $SO(n)$ is trivial or not. This can

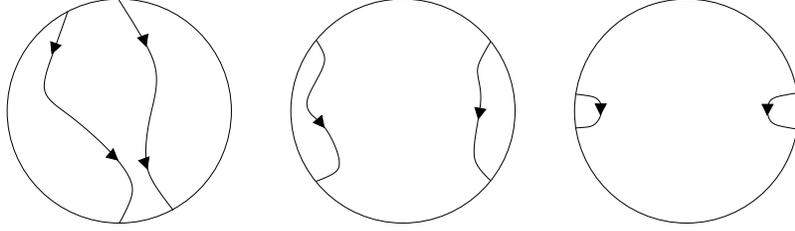


Figure 7: Contraction of a loop in \mathbb{RP}^3 .

in principle be done for all n , but we are particularly interested in the cases $2 \leq n \leq 5$, since the number of electronic states needed to describe typical Jahn–Teller systems is five or less. We begin with the two simplest cases. These are familiar spaces, and relatively easy to analyse.

If $n = 2$ everything is actually quite easy. $SO(2)$ is just S^1 , and we can calculate the angle ϕ of equation (59), and see to it that it is continuous along the loop. Then $\phi_{end} = \phi_{start} + 2k\pi$. The loop is trivial if and only if $k = 0$.

The case $n = 3$ is a little bit more complicated. We use a representation of $SO(3) = \mathbb{RP}^3$ that we have not seen before. By the axis-angle representation of three-dimensional rotations $SO(3)$ is homeomorphic to the closed ball in three dimensions with antipodal points on its surface identified. A rotation by the angle ϕ around the unit vector $\hat{\mathbf{v}}$ is represented by the point $\phi\hat{\mathbf{v}}$ in three-space. We let $\hat{\mathbf{v}}$ take any value on S^2 , and $0 \leq \phi \leq \pi$. Thus the rotations are represented by elements of the closed ball of radius π , i.e., $B^3(\pi)$. Antipodal points on the surface must, however, be identified, since a rotation by π is the same transformation regardless of whether the axis of rotation is $\hat{\mathbf{v}}$ or $-\hat{\mathbf{v}}$. Any loop in $SO(3)$ is represented by a curve in $B^3(\pi)$ which must intersect the boundary of the ball an even number of times, $2k$. (We count going out at one point, and entering at the antipodal as two intersections.) If $2k$ is divisible by four, the loop is trivial. Otherwise it is not. Figure 7 gives a picture of how a loop intersecting the boundary four times can be contracted to a point¹⁰. Note that a point at which the curve in $B^3(\pi)$ gently touches the boundary must be counted four times: two enterings, and two exits. In practice, suppose that we are given a number of matrices,

$$F(t) = \begin{pmatrix} F_{11}(t) & F_{12}(t) & F_{13}(t) \\ F_{21}(t) & F_{22}(t) & F_{23}(t) \\ F_{31}(t) & F_{32}(t) & F_{33}(t) \end{pmatrix}, \quad (71)$$

representing a loop in $SO(3)$. To determine whether the loop is trivial, one would first calculate the corresponding angle and axis for every t :

$$\phi(t) = \arccos\left(\frac{1}{2}(\text{Tr}F(t) - 1)\right), \quad (72)$$

$$\hat{\mathbf{v}}(t) = \frac{(F_{32}(t) - F_{23}(t), F_{13}(t) - F_{31}(t), F_{21}(t) - F_{12}(t))}{\|(F_{32}(t) - F_{23}(t), F_{13}(t) - F_{31}(t), F_{21}(t) - F_{12}(t))\|}. \quad (73)$$

For the derivation of these formulae note first that the trace of a matrix is independent of basis, and with the rotation axis as one of the basis vectors

¹⁰The reader is invited to do a similar analysis for the coffee-cup trick.

we have $\text{Tr}F(t) = 1 + 2 \cos \phi(t)$. This yields equation (72). Secondly, note that the rotation vector before normalisation is the dual pseudovector of the antisymmetric matrix $F(t) - F(t)^T$. It thus transforms as a pseudovector (see for example [34] pages 140–141). In a basis with one basis vector chosen parallel to the rotation axis, so that the rotation angle is less than or equal to π , $\hat{\mathbf{v}}$ is this vector.

To determine if the loop is trivial, the only remaining work is to count the number of times ϕ passes π accompanied by an abrupt sign change in $\hat{\mathbf{v}}$. Each such passing corresponds to two intersections with the boundary of the ball. If ϕ passes π without the sign change in $\hat{\mathbf{v}}$, the curve touches the boundary at this point. The following example illustrates the procedure.

We consider the Jahn–Teller system denoted $T \otimes \tau_2$. In this system the electronic degeneracy is three-fold, and the nuclear configuration space is three-dimensional. The crude adiabatic equation describing this system (i.e., equation (53) for the system) is [35]

$$\left(-\frac{1}{2}\nabla^2 + \frac{1}{2}R^2 + K \begin{pmatrix} 0 & -Z & -Y \\ -Z & 0 & -X \\ -Y & -X & 0 \end{pmatrix} \right) \begin{pmatrix} a_1(\mathbf{R}) \\ a_2(\mathbf{R}) \\ a_3(\mathbf{R}) \end{pmatrix} = E \begin{pmatrix} a_1(\mathbf{R}) \\ a_2(\mathbf{R}) \\ a_3(\mathbf{R}) \end{pmatrix}. \quad (74)$$

In (74) $\mathbf{R} = (X, Y, Z)$ parametrises the nuclear configuration space. The electronic Hamiltonian is the matrix of this equation plus the diagonal contribution $\frac{1}{2}R^2$ which guarantees the existence of bound states. The electronic energies are just the \mathbf{R} -dependent eigenvalues of the electronic Hamiltonian. These are given by

$$E_e(\mathbf{R}) = \frac{1}{2}R^2 + \Lambda, \quad (75)$$

where Λ denotes one of the roots of the secular equation of the matrix in (74):

$$\Lambda^3 - K^2 R^2 \Lambda + 2K^3 XYZ = 0. \quad (76)$$

Solving this cubic equation by standard methods shows that the potential energy surfaces intersect at all points of the form

$$\frac{R}{\sqrt{3}}(\mp 1, \mp 1, \mp 1) \quad \frac{R}{\sqrt{3}}(\mp 1, \pm 1, \pm 1) \quad \frac{R}{\sqrt{3}}(\pm 1, \mp 1, \pm 1) \quad \frac{R}{\sqrt{3}}(\pm 1, \pm 1, \mp 1), \quad (77)$$

where R takes only positive values. Using the upper signs, the points of (77) represent intersections of the two lowest potential energy surfaces. The two highest electronic energies are degenerate at points described by the lower signs. These latter points also happen to be minima for the lowest potential energy surface. At the origin, where the eight rays of degeneracy meet (and nowhere else), there is a three-fold degeneracy.

In [35] the electronic eigenket corresponding to the lowest potential energy surface is considered. It is shown that continuous transport along any one of its degeneracies produce a sign change of the ket. On the other hand transport around *two* degeneracies makes the ket return to its original value. We are interested in finding a loop in the nuclear configuration space encircling degeneracies without producing any sign changes at all. Let Γ be given by

$$\begin{aligned} X &= R \cos \theta, \\ Y &= R \sin \theta, \\ Z &= 0, \end{aligned} \quad (78)$$

where $R > 0$ and θ as usual runs from 0 to 2π . The loop Γ encircles, depending on which surface we consider bounded by it, four double or one triple degeneracy. The electronic eigenkets along Γ are eigenvectors of the matrix¹¹

$$KR \begin{pmatrix} 0 & 0 & -\sin \theta \\ 0 & 0 & -\cos \theta \\ -\sin \theta & -\cos \theta & 0 \end{pmatrix}. \quad (79)$$

The eigenvalues are 0 and $\pm KR$, and correspond to the eigenvectors

$$\begin{aligned} |1(\theta)\rangle &= \frac{1}{\sqrt{2}}(\sin \theta, \cos \theta, 1), \\ |2(\theta)\rangle &= (\cos \theta, -\sin \theta, 0), \\ |3(\theta)\rangle &= \frac{1}{\sqrt{2}}(\sin \theta, \cos \theta, -1). \end{aligned} \quad (80)$$

None of the eigenvectors changes sign upon transport around Γ . This means that the test of Longuet-Higgins will not find the degeneracies. Interestingly, this is true for an arbitrarily small loop of this form. To use the test derived in this section we first construct the matrix F , which simply has the vectors of (80) as columns:

$$F(\theta) = \begin{pmatrix} \frac{1}{\sqrt{2}} \sin \theta & \cos \theta & \frac{1}{\sqrt{2}} \sin \theta \\ \frac{1}{\sqrt{2}} \cos \theta & -\sin \theta & \frac{1}{\sqrt{2}} \cos \theta \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix}. \quad (81)$$

We next look for the values of θ for which $F(\theta)$ represents a rotation by the angle π . By equation (72) this is equivalent to the trace of F being -1 . This gives us

$$0 = \text{Tr}F(\theta) + 1 = \frac{1}{\sqrt{2}}(\sin \theta - 1) - (\sin \theta - 1) = \frac{1 - \sqrt{2}}{\sqrt{2}}(\sin \theta - 1). \quad (82)$$

Thus the angle of rotation is π if and only if $\theta = \pi/2$, i.e., at one point along Γ . It now remains to see if the rotation vector changes sign at $\theta = \pi/2$. This is indeed the case. The vector is

$$\hat{\mathbf{v}} = \frac{1}{N}(-\cos \theta, \sin \theta - 1, (1 - \sqrt{2}) \cos \theta), \quad (83)$$

where N is a (positive) constant of normalisation. The first and third component change sign as θ passes $\pi/2$. The second component does not change sign, but this is simply because it is zero at $\theta = \pi/2$. (This is because $\sin(\theta) - 1$ tends quadratically to zero, while N tends to zero linearly.) A graph showing the components of $\hat{\mathbf{v}}$ and the rotation angle ϕ along Γ appears in Figure 8.

Thus we know how to use the test in cases where the dimensionality of the Hilbert space is two or three. We deal with the cases $n = 4$ and $n = 5$ by reducing them to the three-dimensional case. This makes the procedure somewhat lengthy, but a simple and directly applicable criterion does not seem to exist.

¹¹Remember that the eigenspaces of two matrices are identical if they differ only by a multiple of the identity matrix.

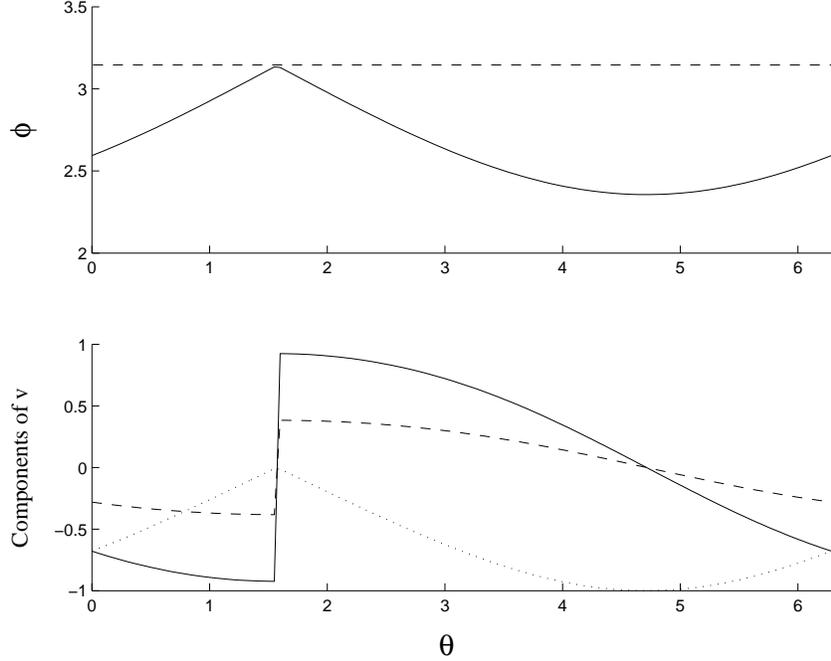


Figure 8: Components of $\hat{\mathbf{v}}$ and rotation angle ϕ as Γ is traversed. Note that ϕ is equal to π once, and that $\hat{\mathbf{v}}$ changes sign at that point.

Let us first consider the $n = 4$ case. Suppose that we are presented with a loop in $SO(4)$ represented by the matrices

$$F(t) = \begin{pmatrix} F_{11}(t) & F_{12}(t) & F_{13}(t) & F_{14}(t) \\ F_{21}(t) & F_{22}(t) & F_{23}(t) & F_{24}(t) \\ F_{31}(t) & F_{32}(t) & F_{33}(t) & F_{34}(t) \\ F_{41}(t) & F_{42}(t) & F_{43}(t) & F_{44}(t) \end{pmatrix}. \quad (84)$$

The first column of $F(t)$, $\mathbf{F}(t) \equiv (F_{11}(t), F_{21}(t), F_{31}(t), F_{41}(t))$ then represents a continuously varying element in S^3 . Now define the matrix

$$T(\mathbf{F}) = \begin{pmatrix} F_{11}(t) & F_{21}(t) & F_{31}(t) & F_{41}(t) \\ -F_{21}(t) & F_{11}(t) & -F_{41}(t) & F_{31}(t) \\ -F_{31}(t) & F_{41}(t) & F_{11}(t) & -F_{21}(t) \\ -F_{41}(t) & -F_{31}(t) & F_{21}(t) & F_{11}(t) \end{pmatrix}. \quad (85)$$

The matrix $T(\mathbf{F})$ is orthogonal as the reader may verify by calculating the scalar product between its columns. It is also a continuous function of the element $\mathbf{F} \in S^3$. This has two implications. First, $T(\mathbf{F})$ is an element of $SO(4)$ since it can be continuously connected to the identity matrix (corresponding to $\mathbf{F} = (1, 0, 0, 0) \in S^3$). Secondly the loop $T(t) \equiv T(\mathbf{F}(t))$ must by Lemma 1 represent a trivial loop in $SO(4)$ since S^3 is a simply connected space. We consider now the loop in $SO(4)$ given by $T(t)F(t)$. Since matrix multiplication is continuous and since $T(t)$ can be continuously deformed to any element (the identity, say) in $SO(4)$, the loop given by $T(t)F(t)$ is non-trivial exactly when

$F(t)$ is. However, the loop $T(t)F(t)$ is simpler than the loop $F(t)$. Carrying out the matrix multiplication yields (using the orthogonality of $F(t)$)

$$T(t)F(t) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & A_{11}(t) & A_{12}(t) & A_{13}(t) \\ 0 & A_{21}(t) & A_{22}(t) & A_{23}(t) \\ 0 & A_{31}(t) & A_{32}(t) & A_{33}(t) \end{pmatrix}. \quad (86)$$

It turns out that the loop $T(t)F(t)$ is trivial if and only if the thus defined loop

$$A(t) = \begin{pmatrix} A_{11}(t) & A_{12}(t) & A_{13}(t) \\ A_{21}(t) & A_{22}(t) & A_{23}(t) \\ A_{31}(t) & A_{32}(t) & A_{33}(t) \end{pmatrix} \quad (87)$$

in $SO(3)$ is trivial. By this construction we may use our method developed for $SO(3)$ to determine whether a loop in $SO(4)$ is trivial or not. We use the following example as an illustration.

Consider the $G \otimes g$ Jahn-Teller system. In this system both the electronic Hilbert space and the nuclear coordinate space are four-dimensional. The coupling matrix (i.e., the crude adiabatic Hamiltonian minus the diagonal quadratic contribution) is [36]

$$H_e^G = \begin{pmatrix} -Q_3 & -Q_4 & -Q_1 + Q_3 & -Q_2 - Q_4 \\ -Q_4 & Q_3 & Q_2 - Q_4 & -Q_1 - Q_3 \\ -Q_1 + Q_3 & Q_2 - Q_4 & Q_1 & -Q_2 \\ -Q_2 - Q_4 & -Q_1 - Q_3 & -Q_2 & -Q_1 \end{pmatrix}, \quad (88)$$

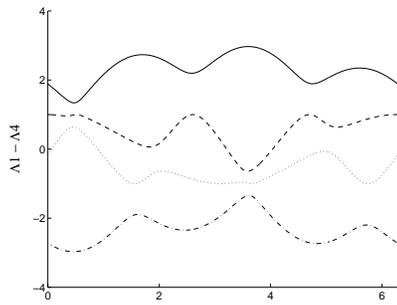
where the Q_i (which, in the parameters of equation (A2) in [36], are defined as $Q_i = \sqrt{2}k_g^G qg_i$) are the vibrational coordinates. The adiabatic electronic eigenkets are eigenvectors of this matrix. Let the loop Γ in the nuclear configuration space be given by

$$\begin{aligned} Q_1 &= \cos \theta, \\ Q_2 &= \sin \theta, \\ Q_3 &= \sin \theta, \\ Q_4 &= \cos \theta, \end{aligned} \quad (89)$$

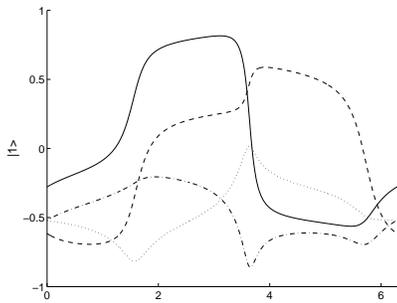
where θ goes from 0 to π . This loop certainly encircles at least the degeneracy at $Q_i = 0$. For $i = 1, \dots, 4$ we use numerical methods to determine the eigenvectors $|i(\theta)\rangle$ and the eigenvalues $\Lambda_i(\theta)$ on Γ . The results are presented in Figure 9.

Note that there is no degeneracy along Γ , and that none of the eigenvectors changes sign. This means that the test of Longuet-Higgins would not imply that Γ encircles a degeneracy. We now explicitly construct the matrices $F(\theta)$ (with the components of $|i(\theta)\rangle$ as i :th column) and $T(|1(\theta)\rangle)$. Matrix multiplication along the loop produces the loop $A(\theta)$ of equation (87). The rotation angle and axis of $A(\theta)$ (as determined by equations (72) and (73)) are plotted in Figure 10. Note that there is only one point where the rotation angle is π , and that the rotation vector changes sign abruptly there. Thus the generalised test implies a degeneracy.

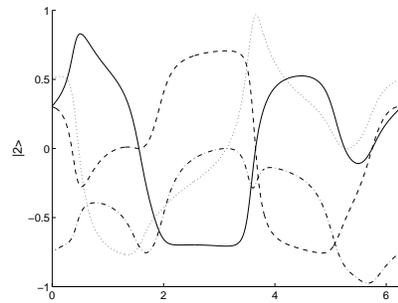
Now we turn to the five-dimensional case, which is a little tricky to handle. Below we outline a possible approach, but do not consider any specific example.



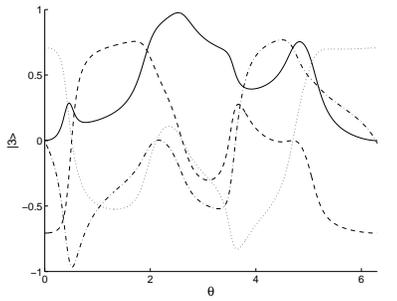
(a)



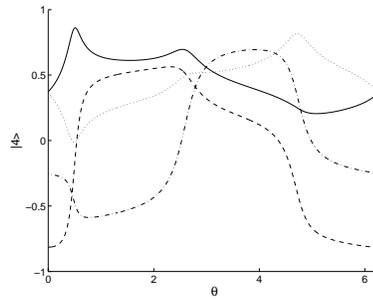
(b)



(c)



(d)



(e)

Figure 9: Eigenvalues (a) and eigenvectors (b–e) of the matrix Hamiltonian H_e^G along Γ . The four components of the eigenvectors are plotted separately. There is no θ for which two eigenvalues coincide. Furthermore the eigenvectors $|1\rangle - |4\rangle$ all return to their original value when the loop is traversed.

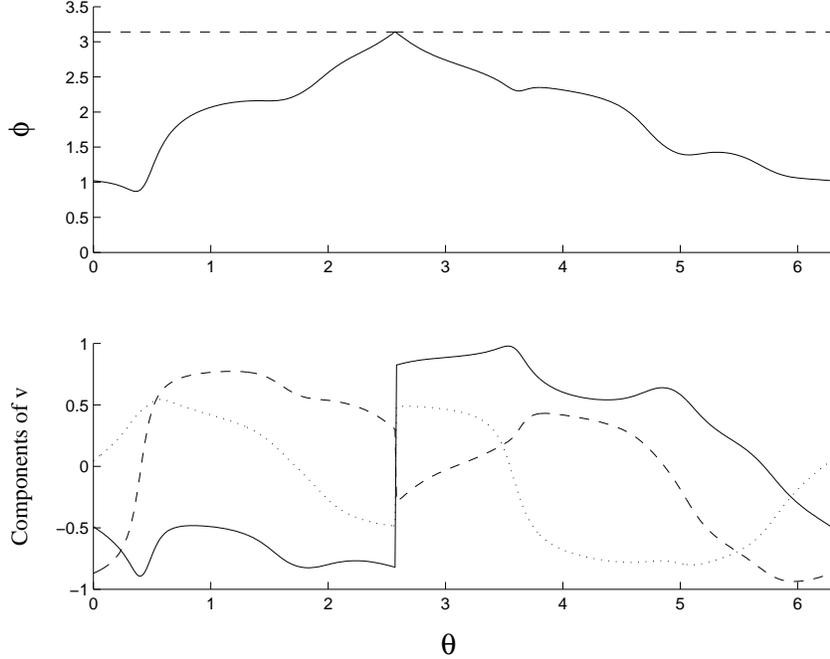


Figure 10: Rotation angle ϕ and axis \hat{v} of the numerically computed matrix $A(\theta)$ as functions of θ .

Suppose that $F(t)$ represents a loop in $SO(5)$ as t goes from 0 to 1. Any matrix in $SO(5)$ has at least one eigenvector with eigenvalue $+1$. Let the eigenvector with eigenvalue $+1$ of $F(t)$ be denoted $\hat{e}(t)$, and suppose that it is uniquely defined (up to sign) for all t . Assume that we for each t can continuously choose an orthogonal matrix $B(t)$, which satisfies $B(1) = B(0)$ and has $\hat{e}(t)$ as its first column. Then the matrix $B^T(t)F(t)B(t)$ is block diagonal:

$$B^T(t)F(t)B(t) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & A_{11}(t) & A_{12}(t) & A_{13}(t) & A_{14}(t) \\ 0 & A_{21}(t) & A_{22}(t) & A_{23}(t) & A_{24}(t) \\ 0 & A_{31}(t) & A_{32}(t) & A_{33}(t) & A_{34}(t) \\ 0 & A_{41}(t) & A_{42}(t) & A_{43}(t) & A_{44}(t) \end{pmatrix}. \quad (90)$$

The matrix $A(t) = (A_{ij}(t))$ represents a loop in $SO(4)$. The loop $F(t)$ is trivial exactly when the loop $A(t)$ is. This means that we are done, since we already know how to handle loops in $SO(4)$. Thus, as soon as we learn how to choose the matrix $B(t)$, we have a triviality criterion for loops in $SO(5)$.

First we need to find out whether it is reasonable to assume that $\hat{e}(t)$ is uniquely defined for all t . An eigenvector is uniquely defined (up to sign) whenever it is non-degenerate. We do not consider the details here, but it can be shown that the set $D = \{R \in SO(5) : R \text{ has } +1 \text{ as a degenerate eigenvalue}\}$ has co-dimension 3 in $SO(5)$. Thus the assumption of non-degeneracy is quite innocent. If $F(t)$ happens to be degenerate for some t we can try to remove the degeneracy by multiplying the whole loop by some constant matrix $M \in SO(5)$.

Secondly we must consider the possibility that the vector $\hat{\mathbf{e}}(t)$ changes sign along the loop, i.e., that $\hat{\mathbf{e}}(1) = -\hat{\mathbf{e}}(0)$. If this happens it turns out that the loop we are considering must be non-trivial. To see this note that a trivial loop can always be contracted to a point not lying in D and *without crossing any point in D* . This is true since the co-dimension of D is 3. But if we contract a sign reversing loop in this way, it will remain sign reversing, and the point to which it converges must thus be a point of degeneracy. Hence we have a contradiction, and thus any sign reversing loop must be non-trivial.

If we are not so lucky that the vector $\hat{\mathbf{e}}(t)$ changes sign as the loop is traversed, how do we proceed to choose the matrix $B(t)$? Well, we need four unit vectors $\hat{\mathbf{v}}_1(t), \dots, \hat{\mathbf{v}}_4(t)$ in \mathbb{R}^5 to serve as columns of $B(t)$. They have to be pairwise orthogonal and orthogonal to $\hat{\mathbf{e}}(t)$. Furthermore, we need the $\hat{\mathbf{v}}_i(t)$ to be continuous along the loop, and to fulfil $\hat{\mathbf{v}}_i(1) = \hat{\mathbf{v}}_i(0)$. One way of doing this is to choose three fixed linearly independent vectors $\hat{\mathbf{w}}_1, \hat{\mathbf{w}}_2$, and $\hat{\mathbf{w}}_3$ in such a way that $\hat{\mathbf{e}}(t)$ never lies in the linear subspace $\text{span}(\hat{\mathbf{w}}_1, \hat{\mathbf{w}}_2, \hat{\mathbf{w}}_3)$ spanned by the vectors. (It is quite unlikely that a curve in \mathbb{R}^5 intersects a certain three-dimensional subspace.) The Gram–Schmidt orthogonalisation procedure applied on the list $(\hat{\mathbf{e}}(t), \hat{\mathbf{w}}_1, \hat{\mathbf{w}}_2, \hat{\mathbf{w}}_3)$ produces an orthonormal list $(\hat{\mathbf{e}}(t), \hat{\mathbf{v}}_1(t), \hat{\mathbf{v}}_2(t), \hat{\mathbf{v}}_3(t))$. The vector $\hat{\mathbf{v}}_4(t)$ is now uniquely determined as the vector completing the list to a positively oriented orthonormal basis. This construction gives continuous $\hat{\mathbf{v}}_i$ since the Gram–Schmidt procedure is continuous as long as the vectors are linearly independent. With these vectors we can construct our desired $B(t)$, and thus block-diagonalise $F(t)$. The reduction from $SO(5)$ to $SO(4)$ can be summarised as follows:

1. See to it that $F(t)$ has a non-degenerate eigenvector $\hat{\mathbf{e}}(t)$ corresponding to the eigenvalue $+1$ along the loop.
2. Check if $\hat{\mathbf{e}}(t)$ changes sign when chosen continuously along the loop. If it does the loop is non-trivial.
3. If $\hat{\mathbf{e}}(t)$ returns to its original value, choose $\hat{\mathbf{w}}_1, \hat{\mathbf{w}}_2$, and $\hat{\mathbf{w}}_3$. Perform the orthogonalisation procedure to obtain the $\hat{\mathbf{v}}_i(t)$.
4. Construct the matrix $B(t)$ with columns $(\hat{\mathbf{e}}(t), \hat{\mathbf{v}}_1(t), \dots, \hat{\mathbf{v}}_4(t))$.
5. Compute $B^T(t)F(t)B(t)$ to obtain the loop $A(t)$ in $SO(4)$.

With this our discussion of the explicit use of the test ends. It is worth noting as a concluding remark that there is a method of determining whether a loop in $SO(n)$ is trivial or not that works for all n . It is possible to lift the loop to the universal covering space of $SO(n)$, which is called $Spin(n)$. To do this is, however, far from easy. The principle is described in for example [37], pages 270–274.

4.4.4 Is there a better topological test?

A natural question to ask, now when we have succeeded in generalising a test for finding intersections, is whether it is possible to generalise it even further. It is not hard to find examples of Hamiltonians that exhibit degeneracies which the generalised test fails to detect, so perhaps there is room for improvement.

Below we show that if the only information we have about the Hamiltonian H_e is that it is continuous in the nuclear configuration space, and if we are only

allowed to consider electronic eigenkets on a (sufficiently simple) loop in this space, then the above test is in some sense optimal.

To make this statement more precise we proceed in two steps. Assume that we consider a closed loop Γ in the nuclear configuration space \mathbb{R}^d . We study the eigenvectors of H_e , a real continuous symmetric $n \times n$ matrix which is non-degenerate along the loop. Suppose that the curve in $SO(n)$ corresponding to the eigenvectors of H_e is a trivial loop (i.e., that the generalised test does not imply a degeneracy).

First we show that if Γ is such that there is a surface S bounded by it which is homeomorphic to the unit disc B^2 , then we can, under the above conditions, construct a Hamiltonian, continuous and non-degenerate on all S , giving exactly the prescribed eigenvectors on Γ . This proves that there is no test implying degeneracies on *every* surface bounded by Γ .

However, it might be possible to find a test that implies a degeneracy *somewhere*, e.g., at a single point, in the nuclear configuration space. In the case of a sufficiently simple Γ this is, however, relatively easily proven to be impossible. The proof consists of constructing a Hamiltonian continuous and non-degenerate *everywhere* in the nuclear configuration space, giving the prescribed eigenvalues and eigenvectors on Γ . Since there is a non-degenerate Hamiltonian having the observed eigenvectors, there is no way of concluding that there is a degeneracy!

We now turn to the proof of these claims, beginning by the following two lemmas.

Lemma 5. *For every ON-basis $F = \{\hat{\mathbf{e}}_1, \dots, \hat{\mathbf{e}}_n\}$ of \mathbb{R}^n and every set of real numbers $\Lambda = \{\lambda_1 < \dots < \lambda_n\}$, there is exactly one real symmetric matrix $M(F, \Lambda)$ having F as eigenvectors and Λ as corresponding eigenvalues. If Λ and F are continuous functions, so is $M(F, \Lambda)$.*

Proof. We construct the desired matrix as a product of three matrices: one matrix with the eigenvectors as columns, one diagonal matrix whose elements are the eigenvalues, and one matrix with the eigenvectors as rows:

$$M(F, \Lambda) = \begin{pmatrix} | & \dots & | \\ \hat{\mathbf{e}}_1 & \dots & \hat{\mathbf{e}}_n \\ | & \dots & | \end{pmatrix} \begin{pmatrix} \lambda_1 & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & \lambda_n \end{pmatrix} \begin{pmatrix} - & \hat{\mathbf{e}}_1 & - \\ \vdots & \vdots & \vdots \\ - & \hat{\mathbf{e}}_n & - \end{pmatrix}. \quad (91)$$

Continuity is immediate from this construction, and uniqueness follows since a linear map (and thus a matrix) is completely specified by its values on a basis of the space. \square

The next lemma states that the eigenvalues of H_e on Γ can be continuously extended to a surface homeomorphic to B^2 preserving the non-degeneracy.

Lemma 6. *Let S be a surface homeomorphic to B^2 , bounded by the loop Γ . Let $\lambda_1, \dots, \lambda_n$ be continuous real-valued functions on Γ ordered as $\lambda_1(g) < \lambda_2(g) < \dots < \lambda_n(g)$ for all $g \in \Gamma$. These functions can then be extended to continuous functions $\hat{\lambda}_i : S \rightarrow \mathbb{R}$ defined on all S and satisfying $\hat{\lambda}_1(s) < \hat{\lambda}_2(s) < \dots < \hat{\lambda}_n(s)$ for all $s \in S$.*

Proof. Let G be a homeomorphism from S to B^2 . Let B^2 be parametrised by $r \in [0, 1]$ and $t \in S^1$. r is the usual radial coordinate, and t is viewed as a unit vector in \mathbb{R}^2 . Any point in $B^2 \subset \mathbb{R}^2$ is of the form rt . For every $s \in S$

the corresponding point in B^2 is $G(s) = r(s)t(s)$. The thus defined function $r : S \rightarrow [0, 1]$ is continuous since by the triangle inequality

$$|r(s + \delta) - r(s)| = \left| \|G(s + \delta)\| - \|G(s)\| \right| \leq \|G(s + \delta) - G(s)\|. \quad (92)$$

The function $t : S \rightarrow S^1$ is continuous everywhere except possibly at the point $s_0 \in S$ that is mapped to the origin by G :

$$\begin{aligned} \|t(s + \delta) - t(s)\| &= \frac{1}{r(s)} \left\| \frac{r(s)}{r(s + \delta)} G(s + \delta) - G(s) \right\| = \\ &\leq \frac{1}{r(s)} \left\{ \|G(s + \delta) - G(s)\| + \left| \frac{r(s)}{r(s + \delta)} - 1 \right| \|G(s + \delta)\| \right\}. \end{aligned} \quad (93)$$

Unless $r(s) = 0$ this expression goes to zero when δ does. Γ is parametrised by t as $\Gamma(t) = G^{-1}(t)$. Let A_i be any real numbers satisfying $A_1 < A_2 < \dots < A_n$. Define

$$\hat{\lambda}_i(s) \equiv r(s)\lambda_i(\Gamma(t(s))) + (1 - r(s))A_i. \quad (94)$$

These functions are continuous on $S \setminus \{s_0\}$ as they are composites of continuous functions there. At s_0 we use that the functions λ_i are bounded. (They are continuous functions on a compact set.) Suppose $|\lambda_i(g)| \leq M$ for all i and g . If we for simplicity let $r_\delta \equiv r(s_0 + \delta)$ and $t_\delta \equiv t(s_0 + \delta)$ we have

$$\begin{aligned} |\hat{\lambda}_i(s_0 + \delta) - \hat{\lambda}_i(s_0)| &= |r_\delta \lambda_i(\Gamma(t_\delta)) - r_\delta A_i| \leq |r_\delta \lambda_i(\Gamma(t_\delta))| + |r_\delta A_i| \leq \\ &\leq r_\delta (M + |A_i|). \end{aligned} \quad (95)$$

Since r_δ tends to zero when δ tends to zero, continuity at s_0 follows. Furthermore it is apparent from equation (94) that the $\hat{\lambda}_i$ satisfy the same ordering property as the λ_i . \square

We now prove that we can extend not only the eigenvalues, but also the eigenvectors continuously to S . Then by the use of Lemma 5 we automatically have an extension of H_e . This means that no test can imply a degeneracy on every surface bounded by Γ only by considering the eigenvectors on Γ .

Theorem 3. *Let S be a surface homeomorphic to B^2 bounded by the closed loop Γ . Suppose that the eigenvectors of H_e are non-degenerate along Γ and represent a trivial loop in $SO(n)$. Then there is a continuous non-degenerate extension \hat{H}_e of H_e defined on all S .*

Proof. The eigenvalues of H_e can by Lemma 6 be continuously extended to S in such a way that the non-degeneracy is preserved. Call this extension $\Lambda(s)$. We show that the same is true for the eigenvectors, which we as a curve in $SO(n)$ denote by F . Let, as in the proof of Lemma 6, G be a homeomorphism from S to B^2 , and let $G(s) = r(s)t(s)$. Let furthermore $K : S^1 \times [0, 1] \rightarrow SO(n)$ be a homotopy between F and a point R_0 in $SO(n)$:

$$\begin{aligned} K(t, 0) &= F(t), \\ K(t, 1) &= R_0 \in SO(n), \end{aligned} \quad (96)$$

where t parametrises Γ as it goes around S^1 . Now for each $s \in S$ define

$$F(s) \equiv K(t(s), 1 - r(s)). \quad (97)$$

The function F defined in this way is continuous on $S \setminus \{s_0\}$ since it is a composite of continuous functions there. To prove continuity at s_0 we note that (using the same notation as in the proof of Lemma 6)

$$\begin{aligned} \|F(s_0 + \delta) - R_0\| &= \|K(t_\delta, 1 - r_\delta) - R_0\| \leq \\ &\leq \sup\{\|K(t, 1 - r_\delta) - R_0\| : t \in S^1\}. \end{aligned} \quad (98)$$

Since K is a continuous function on a compact subset of \mathbb{R}^2 it is also uniformly continuous. This means that for every $\epsilon > 0$ there is a $\delta > 0$ so that for any two points x_1 and x_2 in $S^1 \times [0, 1]$ we have $\|x_2 - x_1\| < \delta \Rightarrow \|K(x_2) - K(x_1)\| < \epsilon$. Specifically for every $\epsilon > 0$ there is (since $r(s)$ is everywhere continuous) a $\delta > 0$ so that for every $t \in S^1$ we have $\|K(t, 1 - r_\delta) - R_0\| < \epsilon$. The supremum of equation (98) thus goes to zero as δ does. Consequently F is a continuous extension of the eigenvectors. To obtain the desired extension of H_e just put $\hat{H}_e(s) \equiv M(F(s), \Lambda(s))$, which is continuous by Lemma 5. \square

It is important to realise that S must be homeomorphic to B^2 for the theorem to be true. As an example, for a surface bounded by a self-intersecting loop the theorem is not applicable. Even if such a loop maps to a trivial loop in $SO(n)$, it is possible that one of the loops emanating from the intersection does not. This would (by our new test) mean that the Hamiltonian cannot be continuously extended to a surface bounded by this ‘‘subloop’’.

Thus far we know that any test considering eigenkets on a loop Γ which is the boundary of a surface S homeomorphic to B^2 can never do better than our test in implying a degeneracy on every surface bounded by the loop. If we sharpen the restrictions on Γ we can show that no test can do better than ours in implying a degeneracy *anywhere*. The stronger we choose the conditions on Γ , the easier the proof. Below we follow the path of least resistance.

Theorem 4. *Let Γ be a circle in \mathbb{R}^d . Suppose that the eigenvectors of H_e are non-degenerate along Γ and represent a trivial loop in $SO(n)$. Then there is a continuous non-degenerate extension \hat{H}_e of H_e defined on all \mathbb{R}^d .*

Proof. Suppose without loss of generality that Γ lies in the Q_1Q_2 -plane with its center at the origin. Choose cylindrical polar coordinates $\rho, \phi, Q_3, \dots, Q_d$ so that Γ is given by $\rho = \rho_0$. Choose as S the disc $\rho \leq \rho_0$ in the Q_1Q_2 -plane. Theorem 3 is applicable, so there is a continuous extension $\tilde{H}_e(\rho, \phi)$ to S . Define

$$\hat{H}_e(\rho, \phi, Q_3, \dots, Q_d) \equiv \begin{cases} \tilde{H}_e(\rho, \phi) & \text{if } \rho \leq \rho_0 \\ \tilde{H}_e(\rho_0, \phi) & \text{if } \rho > \rho_0 \end{cases}. \quad (99)$$

\hat{H}_e defined in this way is continuous and non-degenerate in all \mathbb{R}^d . \square

This theorem concludes our investigation of how general the test is.

5 Summary

In this thesis we note that the crude adiabatic electronic eigenkets of a molecular system exhibiting time reversal invariance can collectively be regarded as an element of $SO(n)$. When taken around a loop Γ in the nuclear configuration space the corresponding elements can trace out a trivial loop, a non-trivial loop, or an open curve in $SO(n)$. The open curves imply (by the theorem of Longuet-Higgins) a degeneracy on every surface bounded by Γ . We have shown that also the non-trivial loops imply a degeneracy on every surface. This new test is the main result of the thesis. Both the open curves and the non-trivial loops project down to non-trivial loops in the space $OP(n)$, defined as $SO(n)$ with two elements identified if their columns are pairwise identical or differ only by sign. The test can in this way be interpreted as an immediate generalisation of Longuet-Higgins' test. We also show that the test cannot be generalised further, and present theoretical examples where the generalised test works, but the old test fails.

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