Astérisque

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Astérisque, tome 210 (1992), p. 115-134

<http://www.numdam.org/item?id=AST_1992__210__115_0>

Classification and Normal Forms for Quantum Mechanical Eigenvalue Crossings

George A. Hagedorn

In the study of molecular dynamics, it is often useful to consider the quantum mechanics of the electrons with the nuclei in fixed positions. When this is done, the positions of the nuclei are described by a nuclear configuration vector $X \in \mathbb{R}^n$, and the Hamiltonian for the electrons is a self-adjoint operator-valued function $h(X)$ of the nuclear configurations. A discrete eigenvalue $E(X)$ of $h(X)$ is called an electron energy level.

Electron energy levels play a major role in the time–dependent Born–Oppenheimer approximation [1,2]. In this approximation the electrons propagate adiabatically and the nuclei obey a semiclassical approximation. In this context, adiabatic means that if the electrons are initially in an eigenstate associated with a level $E(X)$, then at a later time, they will be again be found in an eigenstate associated with $E(X)$. The eigenvalue $E(X)$ also acts an effective potential for the semiclassical propagation of the nuclei.

This approximation breaks down when the electron energy level $E(X)$ crosses any other part of the spectrum of $h(X)$, and the simplest such breakdown occurs when $E(X)$ crosses another eigenvalue of $h(X)$. In this paper we describe the first step in the study of what happens when a Born–Oppenheimer state encounters such a crossing. This first step is the classification of generic minimal degeneracy quantum eigenvalue crossings and determination of normal forms for $h(X)$ near each type of crossing. The various different types of crossings arise from different symmetry situations. We prove below that eleven distinct situations can occur.

* Partially supported by National Science Foundation Grant DMS–9001635.

Throughout the paper we assume $h(X)$ is a C^2 function of $X \in \mathbb{R}^n$ in the sense that its resolvent is C^2. In the various different situations, we assume the dimension n of the nuclear configuration space is large enough so that the appropriate type of crossing can occur generically. We show below that in each generic crossing situation, the two eigenvalues coincide on a submanifold Γ of some specific codimension. If n is less than this codimension, then that type of crossing generically does not occur.

We let G denote the symmetry group of $h(X)$. That is, G is the group of all unitary and antiunitary operators that are X–independent in some representation of the electronic Hilbert space, and that commute with all the operators $h(X)$. We let H denote the subgroup of unitary elements of G, and note that antiunitary elements of G reverse time.

Since the product of unitary and antiunitary operators is antiunitary, there are clearly two cases: Either $G = H$ or H is a subgroup of G of index 2.

When $G = H$, standard group representation theory applies, and each distinct eigenvalue of $h(X)$ is associated with a unique representation of G. Minimal multiplicity eigenvalues correspond to 1–dimensional representations, and if two simple eigenvalues $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ cross, then there are two possiblilities:

Type A Crossings: The two irreducible representations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are not unitarily equivalent to one another.

Type B Crossings: The two irreducible representations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are unitarily equivalent to one another.

When H is a subgroup of index 2, standard group representation theory does not apply. Instead of representations, the basic objects of interest are called corepresentations. A general theory of corepresentations was first developed by Wigner [6]. A more modern, non–basis–dependent treatment can be found in [5]. This general theory shows that any corepresentation can be decomposed as a direct sum of irreducible corepresentations. Furthermore, there are three distinct types of irreducible corepresentations which are called Types *I, II, and III.*

To describe these three types, we first note that G can be decomposed as $G = H \cup \mathcal{K}H$, where $\mathcal{K}$ is an arbitrary, but fixed, antiunitary element of G. Then, if U is an irreducible corepresentation of G, we let U_H denote the restriction of U to H. Then the three types are described as follows [5]:

Type I Corepresentations: U_H is an irreducible representation.

Type II Corepresentations: U_H decomposes into a direct sum of two equivalent irreducible representations, $U_H = D \oplus D$. Furthermore, U may be cast in the form
$U(h) = \begin{pmatrix} D(h) & 0 \\ 0 & D(h) \end{pmatrix}$, $U(\mathcal{K}) = \begin{pmatrix} 0 & -K \\ K & 0 \end{pmatrix}$, and $U(\mathcal{K}h) = U(\mathcal{K})\, U(h)$, for all $h \in H$. Here K is an antiunitary operator that satisfies $K^2 = -D(\mathcal{K}^2)$ and $K\, D(\mathcal{K}^{-1}h\mathcal{K})\, K^{-1} = D(h)$ for all $h \in H$.

Type III Corepresentations: U_H decomposes into a direct sum of two inequivalent irreducible representations, $U_H = D \oplus C$. Furthermore, U may be cast in the form
$U(h) = \begin{pmatrix} D(h) & 0 \\ 0 & C(h) \end{pmatrix}$, $U(a) = \begin{pmatrix} 0 & D(\mathcal{K}^2)K^{-1} \\ K & 0 \end{pmatrix}$, and $U(\mathcal{K}h) = U(\mathcal{K})\, U(h)$, for all $h \in H$. Here $K : \mathcal{H}_D \to \mathcal{H}_C$ is an antiunitary operator that satisfies $K\, D(\mathcal{K}^{-1}h\mathcal{K})\, K^{-1} = C(h)$ for all $h \in H$.

When $G \neq H$, each distinct eigenvalue of $h(X)$ is associated with a unique corepresentation of G. From the structure theory outlined above, it is clear that minimal multiplicity eigenvalues associated with Type I corepresentations have multiplicity 1. Minimal multiplicity eigenvalues associated with Type II or Type III corepresentations have multiplicity 2. In the minimal multiplicity situations, the antiunitary operators K that occur in Type II corepresentations map a one dimensional space to itself. A simple calculation shows that such operators satisfy $K^2 = 1$. Thus, in the minimal multiplicity situation, K is a conjugation, and $D(\mathcal{K}^2) = -1$.

This structure theory of corepresentations shows that if two minimal multiplicity eigenvalues $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ cross, then there are nine possiblilities:

Type C Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both of Type I, but are not unitarily equivalent to one another. Both eigenvalues have multiplicity 1 away from the crossing.

Type D Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both of Type *II*, but are not unitarily equivalent to one another. Both eigenvalues have multiplicity 2 away from the crossing.

Type E Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both of Type *III*, but are not unitarily equivalent to one another. Both eigenvalues have multiplicity 2 away from the crossing.

Type F Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are of Types *I* and *II*. Away from the crossing, the eigenvalue associated with the Type *I* corepresentation has multiplicity 1 and the other eigenvalue has multiplicity 2 away from the crossing.

Type G Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are of Types *I* and *III*. Away from the crossing, the eigenvalue associated with the Type *I* corepresentation has simple multiplicity and the other eigenvalue has multiplicity 2.

Type H Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are of Types *II* and *III*. Both eigenvalues have multiplicity 2 away from the crossing.

Type I Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both of Type *I* and are unitarily equivalent to one another. Both eigenvalues are multiplicity 1 away from the crossing.

Type J Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both of Type *II* and are unitarily equivalent to one another. Both eigenvalues are multiplicity 2 away from the crossing.

Type K Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both of Type *III* and are unitarily equivalent to one another. Both eigenvalues are multiplicity 2 away from the crossing.

REMARK: One can easily find simple quantum systems that provide examples of the various types of crossings.

We now turn to the detailed structure of the electron Hamiltonian function