Generating symmetry-adapted bases for non-Abelian point groups to be used in vibronic coupling Hamiltonians

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ABSTRACT

The vibronic coupling Hamiltonian is a standard model used to describe the potential energy surfaces of systems in which non-adiabatic coupling is a key feature. This includes Jahn–Teller and Renner–Teller systems. The model approximates diabatic potential energy functions as polynomials expanded about a point of high symmetry. One must ensure the model Hamiltonian belongs to the totally symmetric irreducible representation of this point group. Here, a simple approach is presented to generate functions that form a basis for totally symmetric irreducible representations of non-Abelian groups and apply it to $D_{\infty h}$ (2D) and $\mathbf{O}$ (3D). For the $\mathbf{O}$ group, the use of a well known basis-generating operator is also required. The functions generated for $D_{\infty h}$ are then used to construct a ten state, four coordinate model of acetylene. The calculated absorption spectrum is compared to the experimental spectrum to serve as a validation of the approach.

1. Introduction

For decades, vibronic coupling models [1–4] have served as bridges connecting nuclear dynamics studies with the static studies of electronic structure calculations [5]. The vibronic coupling model is a simple polynomial expansion of diabatic potential energy surfaces and couplings. The expansion coefficients are chosen so that the eigenvalues of the potential operator map on to the adiabatic potential surfaces. This diabatisation by ansatz circumvents many of the problems of describing non-adiabatic systems. It is also the inspiration for a diabatisation scheme that is used in modern, direct-dynamic methods that include non-adiabatic effects [6]. For a model Hamiltonian to correctly approximate the eigenvectors of the true Hamiltonian it has to span the totally symmetric irreducible representation (IrRep) of the point groups the molecule belongs to, at the appropriate symmetric geometries [7]. In recent times, many articles have demonstrated the advantages of using symmetry when constructing analytic model potentials [8–12], most often in the context of permutation-inversion groups [13].

Vibronic coupling Hamiltonians predominantly use a Taylor expansion of the nuclear coordinates that suitably represent the (quasi)-diabatic electronic potential operator elements around the point of high symmetry. Quasi-diabatic states conserve the property of having slowly varying potential energy [14], thereby requiring few, low-order polynomial terms to converge its Taylor series in some pertinent region of interest.

Generally, electronic excited states at point-symmetric nuclear configurations will form a bases for an IrRep of the point group the molecule belongs to. By choosing coordinates that also form a basis for IrReps, symmetry allows us to determine whether a given monomial term is allowed in some element or whether monomials across different elements share coefficients. A textbook example are the linear terms in the $E \otimes \varepsilon$ Jahn–Teller diabatic model describing E degenerate states with a branching space along ε degenerate modes. The symmetry of this system dictates that the linear coupling and gradient should share the same coefficient, correctly resulting in the well-known "mexican hat" adiabatic potential. When constructing such models, one must always ensure such relationships are maintained, since these ensure the symmetry of the system is kept. It is therefore most convenient to work with a symmetry-adapted basis of matrices which obey the desired symmetry considerations. This is especially relevant in the case of non-Abelian groups, since it is there we find situations like the one just described.

In this paper, we present approaches for generating such diabatic matrices that form bases for totally symmetric IrReps, starting from functions representing electronic states and nuclear coordinates which transform as known IrReps of the group for which the matrix representations for the operations are known. We generate matrices for the $\mathbf{O}$ and $D_{\infty h}$ point groups and provide all the polynomial expansions representing nuclear coordinates

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(up to fourth and sixth order respectively) and states for many of the IrReps of each group.

Molecules that belong to either of these groups will exhibit Jahn–Teller and Renner–Teller effects respectively and are archetypal examples of the breakdown of the Born–Oppenheimer approximation. The Jahn–Teller (JT) effect occurs when a molecule in a high-symmetry configuration has degenerate electronic states. Vibronic coupling between these states along degenerate nuclear coordinates form a conical intersection at the high symmetry point, stabilising the system away from it and thus lowering the symmetry of the system. The Renner–Teller (RT) effect is a special case that happens in linear molecules. Due to symmetry considerations a glancing intersection rather than a conical intersection is formed [4].

Cederbaum et al. were the first to study the form of vibronic Hamiltonian of linear systems for interacting degenerate and non-degenerate electronic states to different orders and their effects on resulting spectra [1,15]. To generate the $D_{\infty h}$ Hamiltonian, we followed a similar approach to Viel and Eisfeld [16], who generated matrices up to sixth order for $E \otimes e$ Jahn–Teller Hamiltonians. They used them to fit to the $^2E'$ anharmonic surfaces along twofold e' stretches of NO_3 obtained from *ab initio* MR-SDCI calculations. They compared results of several diabatic potential models, one of which includes extra *ad hoc* functions that do not obey the C_3 requirements. They warn over the use of such *ad hoc* functions, showing they can result in wavefunctions with different expectation values, population transfer and autocorrelation values to those models obeying the C_3 requirements. That work was followed by the generation of bases properly describing pseudo Jahn–Teller (pJT) coupling between E degenerate states to nondegenerate A states [11]. They tested them on the pJT coupling between the ground state $^2A_2''$ and exited $^2E'$ states along the twofold e bending mode surfaces of cation NH_3^+ obtained from *ab initio* MRCI calculations. A large decrease in fitting error was obtained as higher order terms were included.

For the **O** group, although the form of the 3D Jahn–Teller Hamiltonian had been known since the first half of last century [17] and later for all IrReps of the group [18], it has been only recently that Opalka and Domcke used invariance theory to generate higher-order expansions as bases for the E and T_2 IrReps [12,19]. Here we used a basis generating operator, devised by Wigner, Lowdin and Shapiro, amongst others [20] to generate Hamiltonians for degenerate states and coordinates of A_1, E and T_1 symmetry. This is a well known method for generating symmetry-adapted functions and only briefly presented here.

1.1. Basis generating operator

A given function from a set of n_ν orthonormal basis functions $f_1^\nu, f_2^\nu, f_3^\nu, \ldots, f_{n_\nu}^\nu$ spanning the space of IrRep ν in a group with k classes, under a given transformation operation $\mathbf{O}_R$ corresponding to the symmetry operator $\mathbf{R}$ of the group, must satisfy:

$$\mathbf{O}_R f_q^\nu = \sum_{p=1}^{n_\nu} D_{pq}^\nu(R) f_p^\nu \quad q = 1, 2, \ldots n_\nu, \quad \nu = 1, 2, \ldots k \quad (1)$$

where $D_{pq}^\nu(R)$ is the matrix representation of the transformation operation operator $\mathbf{O}_R$ on IrRep ν. Operating further on the above expression by the sum of all operations $\mathbf{O}_R$ of some arbitrary IrRep μ of the group $\sum_R D_{ij}^\mu(R)$ we get:

$$\sum_R D_{ij}^\mu(R) \cdot \mathbf{O}_R f_q^\nu = \sum_{p=1}^{n_\nu} \sum_R D_{ij}^\mu(R) \cdot D_{pq}^\nu(R) f_p^\nu$$
$$= (g/n_\mu) \delta_{\nu\mu} \delta_{jq} f_i^\nu \quad (2)$$

owing to the great orthogonality theorem:

$$\sum_R D_{ij}^\mu(R) D_{pq}^\nu(R)^* = (g/n_\mu) \delta_{\nu\mu} \delta_{ip} \delta_{jq} \quad (3)$$

where g is the order of the group. In other words, operating with $\sum_R D_{ij}^\mu(R) \cdot \mathbf{O}_R$ on a basis function f_q^ν will generate another basis function f_i^ν of the same IrRep or else annihilate the function (if $\nu \neq \mu$).

A second operator can be constructed by choosing $i = j$ and summing over j:

$$\sum_i^{n_\mu} \sum_R D_{ii}^\mu(R) \cdot \mathbf{O}_R = \sum_R \chi^\mu(R) \cdot \mathbf{O}_R = \mathbf{P}^\mu \quad (4)$$

This operator $\mathbf{P}^\mu$ has the property of annihilating any function that does not belong to the μth IrRep space, or else project out any function which does. With both these operators it is therefore possible, starting with an arbitrary function within the μth space (called a generator of expansion), to generate the complete set of orthonormal functions belonging to this IrRep. To generate the totally symmetric IrReps of the group, it is therefore only necessary to utilise the latter operator.

To generate all polynomials described here we used the open-source mathematics software SAGE [21].

2. Generating symmetry-adapted basis

2.1. $D_{\infty h}$ Renner–Teller symmetry-adapted basis

There are an infinite number of possible gerade/ungerade E_n IrReps indexed by n where $\alpha = \frac{\pi}{n}$, α being the angle of the C_α rotation required to interchange any two real basis functions forming a twofold degenerate representation of this group.

The dominant contribution of the first few singlet excited states of organic molecules tend to be from functions with low orbital angular momentum. For linear organic molecules we therefore expect that the low singlet states, being formed from π and σ functions built of $l = 2p$ functions would result in electronic states forming a basis for low n representations. Similarly, it is rare to find a full orthonormal set of coordinates with high n index number for small molecules (for example, normal coordinates do not exceed Π symmetry [7]).

Given these considerations, we will restrict the construction of symmetry-adapted bases of matrices by solely using functions that form a basis for $\Sigma^{+/-}$, $\Pi_{u/g}$ and $\Delta_{u/g}$ IrReps (A_n and E_n for $n = 1, 2$) to represent diabatic states and only $\Pi_{u/g}$ functions to represent nuclear coordinates.

The resulting matrices were used to construct a 10-state 4-dimensional diabatic model in the subspace of $\Pi_{u/g}$ coordinates exhibiting Renner–Teller coupling. Theoretical absorption spectra were calculated which compare well to experimental one, validating the use of the bases generated (Section 3).

Herzig and Altmann have published the most comprehensive book of point group tables to date [22]. One can use spherical harmonic functions as a basis to form a representation of any point group. They provide the matrix representations of the $\Pi_{g/u}$ and $\Delta_{u/g}$ IrReps for all the operations of the group, in the complex symmetrised spherical harmonic basis:

$$\begin{aligned}
\Pi_u &:= (\Pi_u^+, \Pi_u^-) = \langle Y_1^1, Y_1^{-1} | \\
\Pi_g &:= (\Pi_g^+, \Pi_g^-) = \langle Y_2^1, -Y_2^{-1} | \\
\Delta_g &:= (\Delta_g^+, \Delta_g^-) = \langle Y_2^2, Y_2^{-2} | \\
\Delta_u &:= (\Delta_u^+, \Delta_u^-) = \langle Y_3^2, -Y_3^{-2} |
\end{aligned} \quad (5)$$

where Y_l^m are the ortho-normalised spherical harmonics using the Condon–Shortley phase convention [22] (the $D_{\infty h}$ tables can be