

Theoretical Studies of Internal Rotation for an Asymmetric Top

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Abstract

For internal rotation in 3-fold tops, the internal axis system (IAS) has been a great convenience because the vibrational angular momentum is constant and is directed along a single axis. A procedure for finding an IAS for the general asymmetric top-asymmetric frame case is given. This procedure is an existence proof that such an axis system can be found. Once the IAS is found, details will be given on how the Mathieu equation can be solved and how the results can be described as a Fourier series. A useful alternative to the IAS is an axis system obtained by rotating away from the IAS by a constant amount (independent of the torsional angle) so as to position the frame in a more convenient orientation. For this rotated internal axis system (RIAS), a Mathieu equation can also be used as a basis except that the kinetic energy for the Mathieu solution only contains contributions from the a component of the vibrational angular momentum. Expectation values for other operators including contributions from the b component of the vibrational angular momentum are deferred to the full diagonalization of the rotation-vibration Hamiltonian.

I. INTRODUCTION

The choice of rotating axes in the presence of large amplitude vibrational motions has a significant influence on the ease of understanding the vibration-rotation spectra. In an earlier paper [1], the effects of a change of axis system on expressions for the rotation-vibration Hamiltonian were derived. The Hamiltonian can be written in the form

$$H = p^T G p - p^T G C^T P - P^T C G p + P^T C G C^T P + P^T \mu P + V, \quad (1)$$

where p is a vector of N_v vibrational momenta, P is the rotational angular momentum vector, G is the inverse mass of the vibration (a $N_v \times N_v$ matrix), C is the vibrational angular momentum coupling coefficient (a $3 \times N_v$ matrix), μ is the inverse of the moment of inertia tensor, and V is the sum of the potential energy and pseudo potential terms depending on the determinant of G and μ . For non-periodic large amplitude motions, a reduced axis system (RAS) can be found that minimizes vibrational angular momentum. It was recognized that periodic motions, such as encountered in molecules with internal rotation, presented special problems because the vibrational angular momentum cannot be forced to zero by an appropriate choice of axis system.

For internal rotation in 3-fold tops, the internal axis system (IAS) has been a great convenience because the vibrational angular momentum (with $N_v = 1$) for the internal rotation coordinate τ is constant, i. e. independent of τ , and is directed along a single axis [2]. In such a single top system, the axis of K quantization can be chosen to be along along this axis and the Mattheiu equation can be solved as a function of K using the G and V dependent parts of Eq. (1). In the usual notation of internal rotation, the matrix element of G corresponding to the internal rotation is called F and the corresponding matrix element of C is called ρ . In the early literature, an additional non-periodic transformation is performed to make all the elements of C equal to zero. In a subsequent application of Floquet's theorem, the Hamiltonian is transformed back into a form where the boundary conditions are periodic. While this is a useful set of transformations for solving a differential equation, it has little utility when solving the Hamiltonian using matrix methods since the matrix Hamiltonian is identical to the case where C is constant and directed along a single axis. However, it is still frequently useful to use the periodic symmetries of the Mattheiu equation to expand the energy (or individual elements of the Hamiltonian) in a Fourier series in $2\pi(\rho K - \sigma)/3$.

A detailed prescription for finding the IAS has not been developed for the case when neither the internal rotation top or the molecular frame have any symmetry. In the more general case, it would be useful if an IAS existed in which C is constant and directed along a single axis, Liu and Quade have used an approximate IAS in which the zero-order Fourier coefficient of C is made zero by a non-periodic coordinate transformation, but the higher Fourier coefficients of C are not zeroed by the transformation [3]. In the next section, an algorithm for finding an IAS will be given in which all higher Fourier coefficients of C can be made zero. Since this algorithm will always converge to an IAS, the algorithm constitutes a proof that the IAS exists. The use of Fourier series will be then briefly be discussed.

This K dependent basis obtained from the Mattheiu equation can be used to solve the full J and K dependent Hamiltonian in several ways. In the internal axis method (IAM), as described by Woods [4], the molecular axes of the Hamiltonian are not coincident

with the axis of quantization for the Mathieu equation, and the Mathieu energies are transformed to the molecular axes using the Wigner D operators. With this approach, the K quantum number in the Mathieu energies is merely a parameter which is not related to the K quantum number labeling rotational basis functions, except through the Wigner D operators. An alternative approach, which has also been designated as an IAM or the rho axis method [5], is to use the IAS as the molecular axis system and to use the Mathieu eigenfunctions as the rotational basis. This second approach will not work generally for multiple internal rotors, and has the added disadvantage that the expectation values of the inverse inertial tensor, μ , are not diagonal. Nonetheless, this approach is appealing for its simplicity and has been used extensively [6].

In many situations, the requirement that the IAS axis be the axis of K quantization is inconvenient. A useful alternative to the IAS is an axis system obtained by rotating away from the IAS by a constant amount (independent of the torsional angle) so as to position the frame in a more convenient orientation. For this rotated internal axis system (RIAS), a Mathieu equation can also be used as a basis except that the kinetic energy for the Mathieu solution only contains contributions from the a component of the vibrational angular momentum. Discussion of use of the RIAS will be given below.

In the past there have been a number of alternative approaches for the case when neither the top or the frame have any symmetry. One approach is to use an axis system, such as the principal axis system, which simplifies some other part of the rotational Hamiltonian but leaves all projections of C non-zero and a function of the vibrational coordinate [7]. A second approach is to use a more optimum axis system but to use only a $K = 0$ basis. Such approaches work best in the limit of high barriers and low vibration state, but have diminished utility when the torsional barrier is lower or when higher torsional states need to be considered. The methods outlined in this paper allow all Coriolis effects to be included in the basis functions and should be helpful in a wider variety of situations.

II. FINDING THE IAS

Before describing how to find the IAS, it is useful to describe the effect of a rotation on C when $N_v = 1$. For a rotation around the z axis,

$$\begin{aligned} C'_x &= C_x \cos \phi + C_y \sin \phi \\ C'_y &= C_y \cos \phi - C_x \sin \phi \\ C'_z &= C_z + d\phi/d\tau \end{aligned} \tag{2}$$

where τ is the internal rotation angle. Because C_z is modified by such a τ -dependent transformation, the general solution to find the IAS involves three non-linear ordinary differential equations in two angular unknowns with periodic boundary conditions in τ . While numerical techniques exist for solving such differential equations, it is not obvious that the solution exists or is unique. However, there is a simpler algorithm that converges rapidly to a solution.

Before we start the solution, assume that the three components of C have been calculated for a set of equally spaced τ values in an arbitrary axis frame. A frame that is fixed with respect to a set of three atoms in the molecule is convenient, since the coordinate derivatives

with respect to τ required to calculate C and G can be easily found. To facilitate calculation of derivatives and integrals, the C will be expanded in a Fourier series in τ . This series is rapidly convergent since the structure can usually be expressed as a very low-order series. It is preferable if τ is sampled with an odd number of points so that the real and imaginary parts of the highest-order Fourier coefficient are both defined.

The following three steps in the algorithm are applied iteratively until C_z is not a function of τ and all C_x and C_y are zero:

(1) Find a τ -independent coordinate transformation that takes the *average* values of C and transforms them to the new z axis. This can be done by rotating by ϕ around the z axis to make \overline{C}_x zero, followed by rotating by θ around the x axis to make \overline{C}_y zero. The phase of both rotations will be chosen such that the cosine is positive. For n-fold tops with $n > 2$, this step is all that is needed to find the IAS because C will be constant and independent of τ . The transformation in this step will reduce the average value of $C_x^2 + C_y^2$.

(2) Find a rotation ϕ around the z axis such that the resulting C'_z is constant. If C_{zk} is the k-th Fourier coefficient of C_z , then

$$\phi = -m\tau - \sum_{k=1}^N \text{Re} [C_{zk} \exp(ik\tau)/ik], \quad (3)$$

where m is the nearest integer to C_{z0} . The values of ϕ are then used to transform C_x and C_y . The new constant value of C_z is $p = C_{z0} - m$ and has a magnitude $\leq 1/2$. The transformation in this step leaves $C_x^2 + C_y^2$ invariant.

(3) Two rotations are applied: first a rotation of α around x, followed by a rotation of β around y. The size of these rotations is chosen to make C'_x and C'_y zero to first order in α and β . Because C_z is a constant at this point, Fourier coefficients of different order do not mix. The expressions for the Fourier coefficients for α and β in terms of the coefficients of C_x and C_y are

$$\begin{aligned} \alpha &= \sum_{k=0}^N \text{Re} \left[\frac{ikC_{xk} + \rho C_{yk}}{-\rho^2 - k^2 + \epsilon} \exp(ik\tau) \right]_1 \\ \beta &= \sum_{k=0}^N \text{Re} \left[\frac{ikC_{yk} - \rho C_{xk}}{\rho^2 - k^2 + \epsilon} \exp(ik\tau) \right]_1 \end{aligned} \quad (4)$$

where ϵ is a small number, e.g. 10^{-10} , used to prevent divergence for $k=0$ when p is very small. Values of α and β are obtained for each sample point in τ . If any α or β is greater than $\delta = 0.125$ in magnitude, then all α and β are scaled so that the maximum magnitude is δ . The Fourier series in α and β are then used to obtain $d\alpha/d\tau$ and $d\beta/d\tau$ and C is transformed using Eq. (2) with cyclic permutation of the axes and with α and β substituted for ϕ . The transformations in this step will reduce the average value of $C_x^2 + C_y^2$, even when α and β are constrained by δ . The higher-order effects of these transformations are to create small non-zero values for \overline{C}_x and \overline{C}_y . In addition, C_z will no longer be constant.

Since Eq. (4) makes C_x and C_y zero to first order in the rotation angles, the average value of $C_x^2 + C_y^2$ becomes smaller quadratically with each iteration. Usually, only 4 iterations are needed to reduce this average to 10^{-12} . Therefore, the convergence properties assure that the IAS exists. The precision of the transformations used to find the IAS is primarily limited

by the use of Fourier series to perform the integration and differentiation of the rotations. In practice, 19 sample points ($N = 9$) gives results accurate to 10^{-7} .

When the IAS has been found, it may be convenient to perform an additional rotation about the z axis with $\phi = m\tau$, where m is the nearest integer to $(p - \rho)$ and ρ is the value of ρ from the first iteration. This extra rotation will preserve the original frame and axis identities. If this final rotation is not made, the final value of p will have a magnitude $\leq 1/2$. Finally, if the resulting p is negative, it can be made positive by rotating around the x or y axis by π .

III. FOURIER SERIES

Having found an IAS, it is now possible to solve a Mathieu equation of the form

$$H = (p - \rho K)F(p - \rho K) + v. \quad (5)$$

Note that both F and V can be periodic functions of τ , but p is a constant. Eq. (5) can be solved by matrix methods using a free rotor basis, $\exp(im\tau)$, for each desired value of ρK . If there is n -fold symmetry to both F and V , then the non-zero matrix elements of H will connect basis functions with Δm equal to a multiple of n . In addition, the Hamiltonian is invariant under the transformation $m \rightarrow m - m_0$ and $\rho K \rightarrow \rho K - m_0$, where m_0 is a multiple of n . An elegant way of articulating this transformation symmetry is to express the eigenvalues as a Fourier series in $2\pi(\rho K - \sigma)/n$, where $\sigma = 0, 1, \dots, n-1$. The eigenvectors can also be expressed in a similar series, except for a phase factor that need not be periodic. For simplicity, assume that F and V are even functions of τ so that the Hamiltonian matrix in the free rotor basis is real. If the Hamiltonian is real, the eigenvectors can be chosen to have a phase that makes them real.

When calculating expectation values for operators that change K , e.g. $P_a D_{ab} P_b$, the phases of the eigenvectors need to be selected carefully so that such expectation values do not change sign abruptly with small changes in ρK . A simple phase choice that generally produces well-behaved expectation values is to multiply the eigenvector $|v, \sigma, \rho K\rangle$ by ± 1 so that the overlap $\langle v, \sigma, \sigma | v, \sigma, \rho K \rangle$ is positive.

Then, using the example of the D_{ab} operator,

$$\begin{aligned} \langle v', \sigma, K' | D_{ab} (P_a P_b + P_b P_a) | v'', \sigma, K'' \rangle &= i^A \langle K' | P_a P_b + P_b P_a | K'' \rangle \\ &\times \text{Re} \sum_k \langle v' | D_{ab} | v'' \rangle_k \exp \left[\frac{2\pi i k}{n} \left(P \frac{K' + K''}{2} - \sigma \right) \right] \end{aligned} \quad (6)$$

where the Fourier coefficients, $\langle v' | D_{ab} | v'' \rangle_k$, are obtained by evaluating

$$\begin{aligned} \frac{i^{-A}}{2} \left[\langle v', 0, \rho(K - \frac{1}{2}) | D_{ab} | v'', 0, \rho(K + \frac{1}{2}) \rangle \right. \\ \left. + (-1)^A \langle v', 0, \rho(K + \frac{1}{2}) | D_{ab} | v'', 0, \rho(K - \frac{1}{2}) \rangle \right] \end{aligned} \quad (7)$$

at equally spaced intervals in ρK between $-n/2$ and $n/2$. If the operator is a cosine series in τ , $A = 0$, while if it is a sine series, then $A = 1$. If the operator is a combination of even

and odd contributions, then the even and odd parts should be calculated separately. This phase convention is used to make (7) real and to make (6) Hermitian. This example can be applied to any other $\Delta K = \pm q$ operator by replacing $K \pm 1/2$ with $K \pm q/2$ in (7). It can also be applied to transition dipoles or hyperfine components by replacing $P_a P_b$ with an appropriate direction cosine operator. Note that in all cases, the explicit rotational operator (such as $P_a P_b$) is not included in the calculation of the Fourier series, even though its matrix elements are K dependent.

The choice used here for the Fourier series assures that the operators are Hermitian and that the Fourier coefficients reflect the symmetry of the Hamiltonian. Operators that are even in τ will have a cosine series for $v' = v''$, while operators that are odd in τ will be zero for $v' = v''$. Matrix elements that are off-diagonal in v will be represented by either a sine or cosine series, based on whether the wave functions at $\rho K = \sigma$ are even or odd functions of r .

The importance of the Fourier series expansion of energies and other operators is that the Mattheu basis need not be recalculated for every value of K . In addition, the Fourier expansion shows the periodic nature of the dependence of these operators on K , which can be important in understanding the spectrum. An important aspect of these Fourier series is that they converge rapidly even for moderate barriers to internal rotation and that the convergence improves with increasing barrier height.

IV. USES OF AN ALTERNATIVE AXIS SYSTEM

When there are several large amplitude vibrational motions a molecule, it is often inconvenient to use the IAS. For example, if a molecule has two or more internal rotors, the IAS for the two rotations will not usually coincide. Even if the second vibration is non-periodic, maintaining the IAS over the motion of the second vibration will lead to large vibrational angular momentum for the second vibration. An alternative is to use the formalism of Woods [4] with a more convenient axis system. A second simpler alternative is to apply a fixed rotation from the IAS that is independent of the internal rotation coordinate. This new axis system will be called the rotated internal axis system (RIAS). The effect of this rotation will be to create new constant values of $\rho_b = C_y$ and $\rho_c = C_x$. For simplicity in the following discussion, assume that $\rho_c = 0$, although extension to the general case is straightforward. The parts of the Hamiltonian including these new terms will be excluded from the Mattheu basis function calculation, but will be included in the final solution of the full Hamiltonian.

The solution of the Mattheu equation is identical to the IAS except that $\rho = \rho_a = C_z$. The Fourier series of most expectation values can also be calculated using the IAS procedure, using ρ_a in the Fourier series. However, care has to be taken with the new terms that involve p , because the expectation value of p is not periodic. Fortunately, the quantity $(p - \rho_a K)$ is periodic and the Hamiltonian can be written in the form

$$H = H^0 + H' + \rho_b^2 F P_b^2 + P^T \mu P \quad (8)$$

$$H^0 = (p - \rho_a K) F (p - \rho_a K) + V \quad (9)$$

$$H' = -\rho_b P_b F (p - \rho_a K) - (p - \rho_a K) F \rho_b P_b \quad (10)$$

where H^0 is the Hamiltonian used to calculate the Mathieu basis. The expectation values of H' can be calculated using Eq. (6) with appropriate substitution of operators. Since F is an even function and since the matrix elements of p are real, the matrix elements of H' are real and $A = 0$. For $v' = v''$, H' will be sine series, since p is odd in τ . Such matrix elements become quite small as the barrier height is increased, but are not zero. For matrix elements of H' that connect vibrational states with different parity in τ at $\rho K = \sigma$, the Fourier expansion will be cosine series. Such matrix elements can be quite substantial even as the barrier height is increased.

The effect of the linear P_b terms on the final Hamiltonian are significant, but generally benign. Usually the matrix elements of H' couple states that are well separated in energy relative to the size of the interaction. This RIAS approach has been used successfully to fit the spectrum of dimethyl ether [8], in which the b axis is aligned with the 2-fold axis of symmetry. The approach can also be useful in heavy frame molecules where it is convenient to make the RIAS coincident with an axis system that makes the inertial tensor diagonal for one reference structure. For example, OH internal rotation in ethanol can be treated in a RIAS for which the inertial axis system is diagonal for the trans conformer. Because the frame is so heavy with respect to the H atom in the top, the inertial tensor is almost diagonal for the gauche conformers as well. Nonetheless, the presence of these $P_a P_b$ terms has a significant effect on the gauche states and on the interaction between the tram and gauche states. In addition, the IAS for the methyl internal rotation can be converted to a RIAS that is coincident with that for the OH torsion.

V. CONCLUSIONS

The techniques that were formerly available symmetric internal rotors are now available for the general case of an internal rotor with both an asymmetric top and an asymmetric frame. Specifically, a procedure now exists for finding an axis system in which the vibrational angular momentum is constant and directed along a single axis. The significance of the IAS is that a Mathieu basis can be used that diagonalizes all the parts of the Hamiltonian associated with the internal rotation problem and that exhibits all the periodic symmetry in $\rho K - \sigma$. A calculation approach has also been outlined for situations where it is not convenient to have all the vibrational angular momentum aligned with the axis of K quantization.

The approaches developed here should be very useful for a variety of internal rotation problems including analysis of the spectra of molecules with partially deuterated methyl groups and molecules with intrinsically asymmetric internal rotation such as alcohols.

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