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POLYAD: Predicting and Fitting Mixed Vibrational States to a Multi-Resonant Hamiltonian

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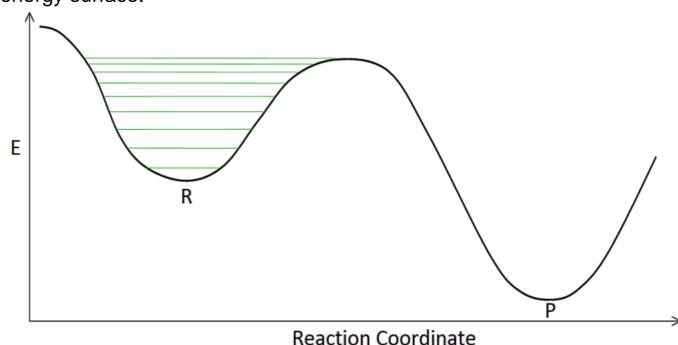
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Polyad: Predicting and fitting mixed vibrational states to a multi-resonant Hamiltonian

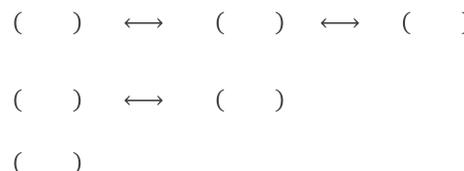Joshua A. Kammeraad and William F. Polik*, Department of Chemistry, Hope College, Holland, MI 49423

Introduction

Reaction coordinate diagrams are a common way of representing potential energy as a function of molecular geometry as a reaction proceeds from reactants to products. They are a simplification of the potential energy surface, as they represent all geometry changes along a single coordinate. The actual potential energy surface is a mathematical function of energy versus molecular geometry that cannot be measured directly. However, vibrational quantum states can be spectroscopically observed that characterize the potential energy surface. A goal of this research is to relate vibrational energy levels to the potential energy surface.

Harmonic Oscillator Model

The simplest model for a potential energy surface near the minimum is the harmonic oscillator model. The mathematical form of this surface is a parabola which gives rise to equally spaced energy levels. The energy levels associated with this surface are simple to characterize algebraically.

Anharmonic Oscillator Model

A more realistic potential energy surface accounts for molecular dissociation. As the potential energy surface becomes wider than a parabola, the energy levels become more closely spaced. The anharmonic model adds terms which correct for these changes in spacing of energy levels.
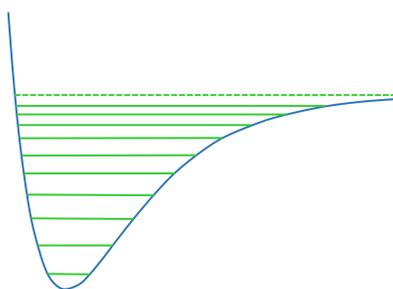
Polyatomic Model

The harmonic and anharmonic models are one-dimensional but can be easily generalized to multiple dimensions by adding the energy contribution of each dimension. This is necessary to describe the vibrational potential energy surface for a polyatomic N-atom molecule which has 3N-6 vibrational dimensions or modes. For example, water has 3 atoms so it has 3(3)-6=3 vibrational modes.
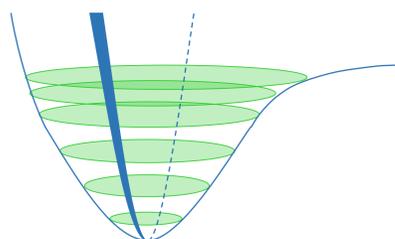
Resonance

When more than one vibrational mode exists, resonance allows energy to be transferred among the different modes. Resonances can be very significant when the oscillators are nearly degenerate, meaning that they have similar frequencies and thus energies. Enrico Fermi discovered in 1931 that resonance applied to molecular vibrations while studying CO_2 when he found a resonance between one quantum of symmetric stretch and two quanta of symmetric bend.
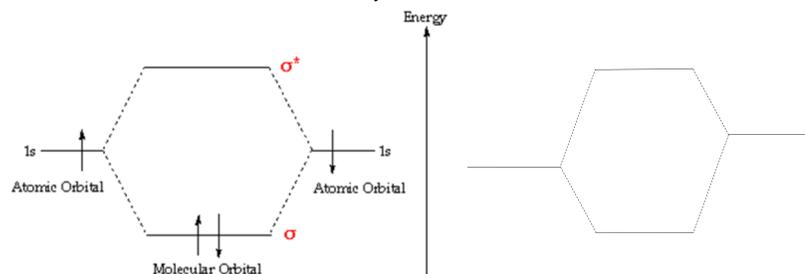
Polyads

A set of states that mutually interact through resonances is called a polyad. Multiple resonances lead to a network of interacting states that all have similar energies. When considering molecules with more atoms and states with more quanta, polyads can become quite large.
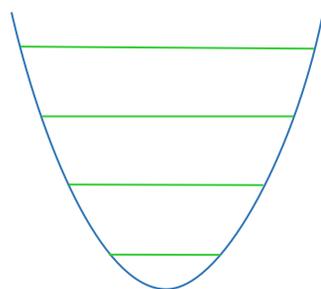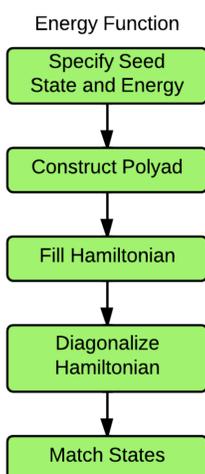
Energy Levels Mixing and Shifting

States with similar energies such as those within the same polyad mix and their energy levels shift. A well-known example is when atomic orbitals mix to form bonding and antibonding molecular orbitals, which have energies that are shifted from the atomic orbital energies. The same mathematics describes mixing and shifting of nearly degenerate vibrational states such as those found by Fermi in CO_2.

Polyad Computer Program

Polyad is a computer program that implements the multi-resonant Hamiltonian model, which incorporates significant resonances directly and approximates other interactions using second order perturbation theory. It connects theory to experiment by predicting energy levels within a user-defined energy range from spectroscopic constants, fitting spectroscopic constants to a set of spectroscopic data, and assessing agreement between a computed model and a spectrum.
The program flow of Polyad begins with reading the model file containing spectroscopic constants and their initial values.

Program Overview

Read Model → Fit, Assess → Read Data → Assess → Fix All Parameters
Read Data → Fit → Fit Data
Predict
Fit Data → Output Fit → Calculate All States

Energy Function

Specify Seed State and Energy → Construct Polyad → Fill Hamiltonian → Diagonalize Hamiltonian → Match States

If fitting or assessing a data file containing observed energy levels, the model parameter values are optimized to fit the data, and files are printed displaying different aspects of the fit. All parameters are fixed when assessing so that the fit simply compares model to data. A listing of all states and their theoretical energy levels can also be printed.
The key to all of Polyad's capabilities is the ability to calculate the energy level associated with a given quantum state, taking into account mixing and shifting. This is done by the Energy function, which begins with a seed quantum state and its observed energy from the spectroscopic data file. The function constructs the polyad of states that contains the seed state and calculates values to fill the Hamiltonian (energy) matrix. This matrix is then diagonalized, which is a mathematical way of incorporating mixing and shifting. The diagonalized Hamiltonian contains observable states and energies, of which one is matched to the seed state and its energy.
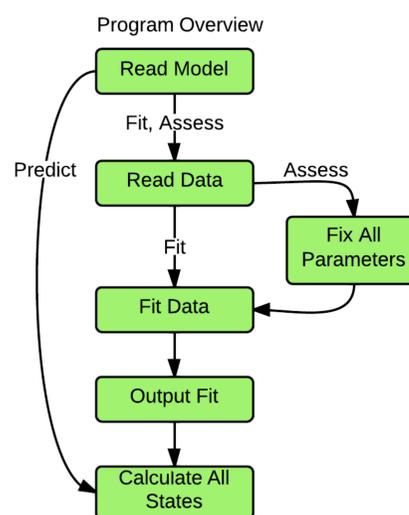
User-editable Model File

The model file that contains spectroscopic constant definitions is editable by the user and read at runtime. This allows the user to run the software on any molecule as well as to change which resonances are included in the model. The sample model file for water contains harmonic frequencies, anharmonic terms, and the 11,33 resonance between the symmetric stretch and anti-symmetric stretch.
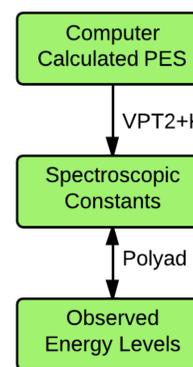
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Sample H2O Model for Polyad Program
w1o      1  0  0   1  0  0      3697.03194042   1
w2o      0  1  0   0  1  0      1615.17900009   1
w3o      0  0  1   0  0  1      3798.83343125   1
x11      2  0  0   2  0  0       -43.00848705   1
x12      1  1  0   1  1  0       -15.70510403   1
x13      1  0  1   1  0  1      -166.26347260   1
x22      0  2  0   0  2  0       -17.03745131   1
x23      0  1  1   0  1  1       -20.05464720   1
x33      0  0  2   0  0  2       -48.63864305   1
K11,33   2  0  0   0  0  2      -160.94308828   1
$Emin             0.00000000
$Emax          4000.00000000
$Vmin      0  0  0
$Vmax      3  3  3
$VThresh          0.45000000
$CoThresh         0.05000000
```

Results

The ability to fit observed vibrational levels of water depends on the model. Polyad outputs optimal values for each of the spectroscopic constants defined in the model file as well as a root mean square error, which is the standard deviation between the optimized model's estimated energy levels and the experimentally observed energy levels. Only including harmonic constants for water yields an error of 140 cm^{-1}. Adding anharmonic constants reduces the error to 56.9 cm^{-1}, and adding merely the single 11,33 resonance reduces the error to 3.5 cm^{-1}.

Parameter	Harmonic (cm^{-1})	Anharmonic (cm^{-1})	Polyad (cm^{-1})
	3511.3	3679.5	3698.3
	1572.8	1612.3	1613.5
	3643.4	3822.9	3804.2
		-40.4	-41.7
		-12.5	-17.5
		-179.9	-162.6
		-20.1	-19.3
		-13.6	-18.5
		-47.4	-47.6
			-152.8
Error	140.0	56.9	3.5

Computer Calculated PES → VPT2+K → Spectroscopic Constants → Polyad → Observed Energy Levels

This research intends to act as a segment of a bridge between theory and experiment. Computational methods can be used to calculate a potential energy surface (PES) for a molecule. Work by Rosnik and Polik (Molecular Physics, 2013) calculates spectroscopic constants from a PES. The Polyad program connects these spectroscopic constants to observed energy levels, meaning that observable energy levels can now be accurately calculated for a molecule even when resonances cause significant mixing and shifting. Polyad has been used on a number of different molecules including water and formaldehyde, their deuterated derivatives, formal flouride, acetylene, and even molecules as large as benzene.

Conclusions

Resonances are key to accurately matching theoretical and experimental energy levels for highly excited vibrational states. Polyad provides a bidirectional algorithm that connects spectroscopic constants to energy levels while accounting for the mixing and shifting effects of resonance. The program is easily used by experimentalists to fit and predict spectra and by theorists to assess potential energy surface calculations.

Acknowledgements