The Classical-Quantum Correspondence of Polyatomic Molecules

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

<table>
<thead>
<tr>
<th>Citation</th>
<th>Pittman, Suzanne Michelle. 2016. The Classical-Quantum Correspondence of Polyatomic Molecules. Doctoral dissertation, Harvard University, Graduate School of Arts &amp; Sciences.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citable link</td>
<td><a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:33493526">http://nrs.harvard.edu/urn-3:HUL.InstRepos:33493526</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at <a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA">http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA</a></td>
</tr>
</tbody>
</table>
The Classical-Quantum Correspondence of Polyatomic Molecules

A DISSERTATION PRESENTED
BY
SUZANNE MICHELLE PITTMAN
TO
THE DEPARTMENT OF PHYSICS

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE SUBJECT OF
PHYSICS

HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
DECEMBER 2015
The Classical-Quantum Correspondence of Polyatomic Molecules

Abstract

In this thesis, we study the classical-quantum correspondence of polyatomic molecules to further understand their rotational and vibrational behavior. More specifically, we focus on two different scenarios: (1) completely rigid asymmetric top molecules and (2) molecules with purely vibrational behavior. In the first part, we study the dynamics of the two asymmetric top molecules ortho-aminobenzonitrile (OABN) and para-aminobenzonitrile (PABN) in a static electric field. These structural isomers feature differing asymmetries and dipole moments. We show that the dynamics of each molecule depends on the region of phase space of the initial rotational state, the asymmetry of the molecule, and the direction of the dipole. We also show that the ergodicity of the system varies gradually with energy, except where the rotational energy of the initial state is much less than the Stark interaction. We find that both molecules are far from full chaos for total angular momentum quanta $J \in [0, 45]$, which counters the results presented in reference 1. However, the initial rotational states in OABN access much more of the available phase space than in PABN, which is a strong cause for the experimental discrepancies observed in the molecular beam deflection experiment of reference 1. In the second part, we address the 0.01-0.1 cm$^{-1}$ peak splittings found in high-resolution IR spectra of polyatomic molecules. Narrow splittings lead to energy flow on extremely long time scales. For polyatomics
molecules, there are two main competing mechanisms that occur over such time scales: (1) dynamical tunneling, which connects classically disconnected regions of phase space by tunneling through dynamical barriers, and (2) Arnol’d Diffusion, which describes diffusion in phase space along a resonance network called the Arnol’d web. As a result of the ubiquitous numerical errors that accumulate during numerical studies of Arnol’d Diffusion, we use a physically motivated non-convex Hamiltonian that features fast diffusion along the Arnol’d web. Fast diffusion is a worst case scenario as a competitor to dynamical tunneling. We show how dynamical tunneling dominates fast diffusion, suggesting that dynamical tunneling is the prime culprit of the narrow peak splittings in high-resolution IR spectra of polyatomic molecules.
# Contents

1 Introduction .......................... 1

2 Background .......................... 6
   2.1 Quantum Ergodicity .................... 6
   2.2 Phase Space Flow for General Initial State .............................. 14
   2.3 Quantum Matrix Elements in Classical Limit .............................. 17

3 Free Rigid Rotor .......................... 20
   3.1 Introduction .......................... 20
   3.2 Classical Approach .................... 22
   3.3 Semiclassical Treatment .................. 26
   3.4 Quantum Approach ..................... 32

4 The Degree of Ergodicity of ortho- and para-Aminobenzonitrile in an Electric Field 43
   4.1 Introduction .......................... 43
   4.2 Theoretical Methods ..................... 46
   4.3 Results ................................ 54
   4.4 Conclusion ............................. 76

5 Intramolecular Vibrational Energy Redistribution 79
   5.1 Introduction .......................... 79
   5.2 Zeroth Order Picture ..................... 80
   5.3 Statistical IVR .......................... 83
   5.4 Sparse IVR .............................. 84
   5.5 Harmonic Approximation .................. 85
   5.6 Classical Approach ..................... 86
   5.7 Classical Quantum Correspondence .................. 94
6 Dynamical Tunneling Versus Fast Diffusion For a Non-convex Hamiltonian

6.1 Introduction ......................................................... 98
6.2 The Model ........................................................... 103
6.3 Method ............................................................... 118
6.4 Results ............................................................... 120
6.5 Classical Limit ....................................................... 130
6.6 Conclusion ........................................................... 133

7 Conclusion ............................................................. 135

References ............................................................... 137
2.1 Figures (a)-(d) show the spectral envelope as a function of energy (Equation 2.29) as $T$ varies .......................... 16

3.1 Phase space and Harter$^2$ RE surface of free rigid rotor .................. 25
3.2 Separatrix angle of Free Rigid Rotor .................................. 27
3.3 Dynamical tunneling path along RE Surface .............................. 31
3.4 Quantum energies of asymmetric top as $\kappa$ varies .................... 42

4.1 Harter$^2$ RE surface for OABN ($\kappa = -0.498$) and PABN ($\kappa = -0.938$) 48
4.2 Energy levels for OABN and PABN with increasing field strength .... 55
4.3 Energy levels for OABN in energy window $E = 7.8 - 8.3 \text{ cm}^{-1}$ and electric field range $E_z = 10 - 50 \text{ kV/cm}$ .............................. 56
4.4 $\mu_{n,z,L,M}$ for OABN and PABN with microcanonical average ........ 60
4.5 $P(a|a)$ for each $|J K 1\rangle$ state in OABN ................................. 64
4.6 $P(a|a)$ for each $|J K 1\rangle$ states in PABN ................................. 65
4.7 Percent of initial $|J K 1\rangle$ states below a given $P(a|a)$ value for OABN and PABN ......................................................... 66
4.8 $S_T(E)$ for an extremal state and small-K state .......................... 68
4.9 Number of Avoided Crossings in OABN for $\mu_0$ and $\mu_R$ ............ 71
4.10 Percent of initial states below a given $P(a|a)$ value for $\mu_R$ .......... 72
4.11 $P(a|a)$ for OABN and PABN for $J = 10$, $|K| < 8$ for $\mu_0$ ........... 74
4.12 $P(a|a)$ for OABN and PABN for $J = 10$, $|K| < 8$ for $\mu_R$ ........... 75

5.1 (a) Spectral coefficients $|C_{s,m}(E)|^2$ from IVR process and (b) Survival probability of initial bright state $|s\rangle$ ................................. 82
5.2 Morse and Harmonic potential with the corresponding bound state quantized energy levels. .................................................. 88
5.3 Phase space portraits in the $(J_1, \Psi_1)$ plane for Triatomic Molecule ... 93
6.1 Plot of the vector field $\omega(I_1, I_2)$ for (a) convex Hamiltonian (Equation 6.13) and (b) nonconvex Hamiltonian (Equation 6.14)  
6.2 Plot of the resonance surfaces $\mathcal{M}_\pm$ in red for (a) a convex Hamiltonian (Equation 6.13) and (b) a non-convex Hamiltonian (Equation 6.14)  
6.3 Contour plot of the Hamiltonian described by equation 6.24  
6.4 Plot of the classical evolution of the initial state $(I_1, I_2, I_3) = (5.5, 0.5, 0.5)$  
6.5 Arnol’d Web for $D = 3$ and $D = 4$ using the reduced coordinates  
6.6 Plot of classical and quantum $\langle I_3(t) \rangle$ for $D = 3$ Coupling Schemes I and II  
6.7 (a)-(c) Plots of quantum and classical $\langle I_{3,4}(t) \rangle$ for $D = 4$  
6.8 (a)-(c) Plots of quantum and classical $\langle I_{3,4,5}(t) \rangle$ for $D = 5$  
6.9 (a)-(d) Plots for the time evolution of $J$  
6.10 Plot of the overlap probability with all states lying on the resonance surface for $D = 3$ and Coupling Scheme I  
6.11 Overlap Probability for Coupling Scheme III and $D = 3$ in the quantum system  
6.12 Plot of the location of quantum states in action space for $D = 3$ for $\hbar = 1, \frac{1}{3},$ and $\frac{1}{5}$ for $D = 3$ using the reduced actions $J_1$ and $J_2$  
6.13 Plot of semiclassical limit for $D=3$ with $\frac{1}{7} \leq \hbar \leq 1$ for (a) Coupling Scheme I and (b) Coupling Scheme III
Citations to Previous Work

All or a portion of the content in the following chapters have appeared in first-author publications of the author:

Chapter 2, Chapter 3: Section 2, Chapter 4


Chapter 6

Acknowledgments

Graduate school has been both a challenging and rewarding experience. First and foremost, I would like to thank my research adviser, Eric J. Heller, for the stimulating discussions, research opportunities, and academic guidance throughout the years. Before meeting Eric, I was unaware of the beautiful world of chaos and its relevance to molecular systems. I would also like to thank the members of the Heller Group for their support, guidance, and research advice. A critical part of graduate school is learning from your colleagues, and I can’t imagine my graduate experience without the fruitful discussions I had with my research group and colleagues. Finally, I would like to thank my husband, Caleb Baker, for all the love, encouragement, and support that he has given me throughout the years. Even at my most frustrated moments, his tireless encouragement reminded me that perseverance always pays off.
“The starting point of our theoretical approach was the conviction that the difficulties that have been encountered at every step in quantum theory in the last few years could be surmounted only by establishing a mathematical system for the mechanics of atomic and electronic motions, which would have a unity and simplicity comparable with the system of classical mechanics...further development of the theory, an important task will lie in the closer investigation of the nature of this correspondence and in the description of the manner in which symbolic quantum geometry goes over into visualizable classical geometry.”\(^3,^4\)

–Born, Heisenberg, and Jordan

Polyatomic molecules are composed of three or more atoms. An \(N\)-atom molecule has \(3N\) total degrees of freedom (DOF). After accounting for translational and rotational motion about the center of mass, there are \(3N - 6\) \((3N - 5)\) remaining DOF for vibrational motion in nonlinear (linear) molecules.  

Spectroscopy is a robust experimental method used to determine the structural and dynamical characteristics of a molecule. Spectroscopy experiments generally involve a radiation source, an analyser, and a detection device.\(^5\) The molecular structure of interest determines the type of spectroscopy used. Generally microwave spectroscopy is used to probe rotation structure \((\sim 0.1 - 50 \text{ cm}^{-1})\), and IR spectroscopy is used to

\*For linear molecules, there are only two independent rotational modes
probe vibrational structure ($\sim 50 - 5000 \text{ cm}^{-1}$). Although spectroscopy was invented over a century ago,  it has evolved over the years to include several high resolution techniques. Such techniques are extremely useful in determining the spectra of large molecules, which often feature small energy level spacings and rotational constants, in addition to nearly degenerate conformers in a given energy range. \textit{Ab initio} calculations, which provide potential energy and dipole moment surfaces, are a crucial supplement to the assignments of ro-vibrational spectroscopic data.\textsuperscript{8,6}

The dielectric properties of polar molecules can be found experimentally using Molecular Beam Deflection (MBD). MBD entails sending a collimated molecular beam through an inhomogeneous electric field. The electric dipole moment couples to electric field through the Stark Interaction and will experience a force due to the field inhomogeneity. Consequently, the beam will deflect and the dipole moment can be extracted by relating the beam profile with simulations based on parameters found through quantum chemistry calculations.\textsuperscript{9,10}

Another important property of polyatomic molecules is how an initially localized bond-excitation will redistribute throughout other bonds in time. This relaxation process is called Intramolecular Vibrational Energy Redistribution (IVR). The relaxation rate has a large impact on kinetics and chemical reactions. In typical IVR studies, the initial excited state is prepared using a laser pulse and its survival probability can be calculated from the experimental spectrum. A large range of different theoretical methods, ranging from statistical to \textit{Ab initio} methods, have been developed to understand the mechanisms of energy flow throughout the molecule.\textsuperscript{11}

In recent years, even the chirality of enantiomers\textsuperscript{†} can be experimentally determined using a sophisticated microwave spectroscopy technique.\textsuperscript{12,13} With all these

\textsuperscript{†}Enantiomers are chiral molecules that are mirror images of each other.
powerful experimental and quantum chemistry methods available, one might wonder why classical studies on polyatomic molecules are necessary or useful? The importance of classical studies is two-fold. Not only do they provide physical intuition, but most importantly they serve as a backbone to study quantum behavior. There are even certain regimes in which predictions from the classical model can be related to quantum system using a semiclassical approach.

Dynamical tunneling is a well-known quantum mechanism that was discovered through classical-quantum correspondence studies of molecules. For systems with \( N = 2 \) degrees of freedom (DOF), KAM tori act as barriers in phase space and prevent diffusion over the entire energy hypersurface. However, quantum mechanically a system can access classically disconnected regions of phase space by dynamical tunneling through these barriers. Dynamical tunneling describes the hyperfine splitting in rigid rotor molecules for a large total angular momentum \( J \).\(^{14,2} \) It also plays integral role in the IVR rate of small molecules.\(^{15,16,17,18,19,20,21} \) Recent work speculates that dynamical tunneling also impacts the IVR rate of large molecules with \( N > 2 \) DOF.\(^{15,18,22,23} \) However, several complications arise in classical systems with \( N > 2 \) DOF, especially in the presence of chaos.\(^{24} \) Phase space transport becomes increasingly complex, and new transport mechanisms such as Arnold Diffusion arise. Arnol’d diffusion describes diffusion in phase space along a resonance network called the Arnol’d web and can lead to global instability in nearly integrable systems with \( N > 2 \) DOF. The other challenge is the lack of visual tools, such as the Poincare Surface of Section, available for \( N > 2 \) DOF.\(^{18} \) We will explore systems of this type later in this thesis when we study vibrational models with \( N > 2 \) in the nearly integrable regime.

In this thesis, we use classical-quantum correspondence to further understand the
behavior of polyatomic molecules. In particular, we specifically focus on two different scenarios: (1) completely rigid asymmetric top molecules and (2) molecules with purely vibrational behavior. These scenarios will be discussed in the first and second parts of this thesis, respectively. The structure of the thesis is as follows. Chapter 2 provides background theoretical methods that are used throughout this thesis. Chapter 3 provides background on the classical, semiclassical, and quantum behavior of a rigid asymmetric top molecule in the absence of torque. In Chapter 4, we specifically study the dynamics of the two asymmetric top molecules, ortho-aminobenzonitrile (OABN) and para-aminobenzonitrile (PABN), in a static electric field. These structural isomers feature differing asymmetries and dipole moments. We show that the dynamics of each molecule depends on the region of phase space of the initial rotational state, the asymmetry of the molecule, and the direction of the dipole. We also show that the ergodicity of the system varies gradually with energy, except where the rotational energy of the initial state is much less than the Stark interaction. We find that both molecules are far from full chaos for total angular momentum quanta $J \in [0, 45]$ and field strength $E_z = 120$ kV/cm, which counters the results presented in reference 1. However, the initial rotational states in OABN access much more of available phase space than in PABN, which is a strong cause for the experimental discrepancies observed in the MBD experiment of reference 1.

Chapter 5 provides background on Intramolecular Vibrational Energy Redistribution. In Chapter 6, we address the mystery of the 0.01-0.1 cm$^{-1}$ peak splittings found in high-resolution IR spectra of polyatomic molecules. Such narrow splittings lead to energy flow on extremely long time scales. For polyatomics molecules, there are two plausible competing physical mechanisms that occur over such time scales: dynamical tunneling and Arnol’d diffusion. As a result of the ubiquitous numerical errors
that accumulate during numerical studies of Arnol’d Diffusion, we use a physically motivated non-convex Hamiltonian that features fast diffusion along the Arnol’d web. Fast diffusion is a worst case scenario as a competitor to dynamical tunneling. We show how dynamical tunneling dominates fast diffusion in this system. This suggests that dynamical tunneling is the prime culprit for the narrow peak splittings in high-resolution IR spectra of polyatomic molecules.

We conclude in Chapter 7 by suggesting further work to follow the results presented in this thesis.
2.1 Quantum Ergodicity

Ergodic Theory concerns the longterm behavior of dynamical system. The initial physical intuition was provided by Boltzmann. He used the word “monode” for what is referred to today as a statistical ensemble and “ergode” as a monode in which uniformly covers the constant energy hypersurface $M$. The word “ergodic” came from Boltzmann’s term ergode, with the Greek interpretation of energy ($\epsilon\rho\gamma\nu$) and path ($o\delta\sigma$).\textsuperscript{25,26}

According to Boltzmann’s ergodic conjecture,\textsuperscript{27} the infinite time average of an ob-
servable $\psi$ will equivalent to the ensemble average of $\psi$ over $M$,

$$\lim_{T \to \infty} \frac{1}{T} \int_0^T \psi(O_t(x)) dt = \frac{1}{\mu(M)} \int_M \psi(x) d\mu(x)$$

(2.1)

where $O_t$ is a measure preserving transformation that describes the flow of the phase point $x \in M$ in time and $\mu(x)$ is the measure of $x$. * This was merely a conjecture until much later, when ergodic theory was developed under the context of measure theory.\textsuperscript{26,27}

A Quantum Measure Theory\textsuperscript{30,31} was developed, in analogy to measure theory, in attempt to rigorously understand the stochastic properties of quantum systems and their relation to classical ergodicity. One starts with a review of basic measure theory. A sigma algebra $X$ is a collection of subsets $B$ of the set $M$ (space) with the following properties:

1. It contains the null-set: $\emptyset \in X$

2. If $B \in X$, then its complement $B^c \in X$

3. Closed under countable unions

The set operations of addition $\oplus$ and multiplication $\otimes$ are both commutative and associative, where $\otimes$ is defined by the intersection and $\oplus$ by the symmetric difference $A \triangle B = A \cup B - A \cap B$. Thus, one has $A \oplus A = A \triangle A = 0$ and $A \otimes A = A \cap A = A$. A $\sigma$-algebra is a $\sigma$ ring that contains the space $M$. Since a $\sigma$-ring is closed under intersection and symmetric difference, the $\sigma$-algebra will be closed under these as well.

* The equivalence between the time-space average is justified when $M$ is metrically transitive,\textsuperscript{28,26,29} which means that the space cannot be reduced into two invariant disjoint subsets with measure greater than zero. The time-space average will be true for all $x \in M$ except for those from a set of zero measure.
Here is a simple instructive example of a $\sigma$-algebra for $M = \{1, 2, 3\}$. The smallest $\sigma$-algebra is $X_s = \{\emptyset, M\}$ and largest is given by the power set $X_p = P(M) = 2^M$,

$$X_p = \{\emptyset, \{1\}, \{2\}, \{3\}, \{1, 2\}, \{2, 3\}, \{1, 3\}, \{1, 2, 3\}\} \quad (2.2)$$

In general, $X_s \leq X \leq X_p$.

Classical dynamical systems are described by $(M, \mu, O_t)$, where $M$ is a smooth manifold with an associated measure $\mu$. Flows along $M$ are governed by a measure preserving map $O_t$, where $\mu(O_tB) = \mu(B)$. For Hamiltonian systems, $O_t$ is described by the Hamilton equations, $\dot{q} = \frac{\partial H}{\partial p}$, $\dot{p} = -\frac{\partial H}{\partial q}$ and $M = \{(q, p) \in \mathbb{R}^{2n} | H(q, p) = E\}$ is the constant energy hypersurface. The measure $\mu$ is the Lebesgue measure constrained to $M$, $\lambda_M(dpdq) = \delta(H(q, p) - E)$.

Abstract dynamical systems $(X, M, \mu, O_t)$ are described by $O_t$ and the triple $(X, M, \mu)$, the measure space for space $M$ with sigma algebra $X$ and corresponding measure $\mu$ defined on $X$. Quantum measure algebra $^{30}$ (QMA) is built off the measure algebra for abstract dynamical systems, except that addition and multiplication is no longer commutative or associative. This is necessary as quantum operators do not commute in general.

A system is ergodic if $\mu(A) = 0$ or $\mu(A) = \mu(M)$ for every invariant set $A \in M$ under the map $O_t$. A well-known example of this is the Stadium Billiard, which is a rigorously chaotic system. In the Stadium Billiard, there is a family of unstable “Bouncing Ball” orbits, which occupy a very small region of phase space. However, this family is a set of measure zero in the space of all possible orbits in the Stadium Billiard. In contrast, the complement to this special set will densely cover all of phase space.
One can understand the consequences of ergodicity by looking at how much of the time-evolving set $O_t A$ intersects set $B$ in time, where $A, B \in M$ are subregions of $M$. One defines the ergodicity function of sets $A, B$,

$$f(A, B, \Gamma) = \frac{1}{\Gamma} \int_0^\infty dt \exp\left(-\frac{t}{\Gamma}\right)\mu(O_t A \cap B)$$  \hspace{1cm} (2.3)$$

where $\Gamma$ represents the averaging time of the system. This function describes the flow between $A$ and $B$. For an ergodic system,

$$\lim_{\Gamma \to \infty} f(A, B, \Gamma) = \frac{\mu(A)\mu(B)}{\mu(M)}$$  \hspace{1cm} (2.4)$$

A strongly mixing system is defined,

$$\lim_{t \to \infty} \mu(O_t A \cap B) = \frac{\mu(A)\mu(B)}{\mu(M)}$$  \hspace{1cm} (2.5)$$

which describes the approach towards the independence of sets $A$ and $B$ in an ergodic system. A weakly mixing system is characterized by the function,

$$\lim_{\Gamma \to \infty} \frac{1}{\Gamma} \int_0^\infty dt \exp\left(-\frac{t}{\Gamma}\right)\left|\mu(O_t A \cap B) - \frac{\mu(A)\mu(B)}{\mu(M)}\right| = 0$$  \hspace{1cm} (2.6)$$

which permits fluctuations about the ergodic limit. These definitions for a quantum dynamical system will soon be defined using QMA.

When picking a space $M$ for the QMA, one wants a space that includes all of the available phase space given the symmetries and constraints of the system. If these are not considered, the entire space will be reducible and will not feature metric transitivity for different states in $M$. A natural constraint on the system is the spectral enve-
lope. The spectral envelope of an initial state is given by the low resolution spectral distribution, \( S(\omega) \). The spectral envelope is determined in very short time, before any nontrivial dynamics have taken place, but it constrains the energy span of eigenstates that can be accessed by the initial state. It provides a baseline in which to measure the amount of stochastic flow that occurs. For an ergodic system, an initial state will have significant overlap with the eigenstates underneath its envelope. In contrast, an initial state will not have significant overlap with many of the eigenstates underneath its envelope in a non-ergodic system.

The space \( M \) is given by the time-invariant state \( \hat{\rho}_M, \ i\hbar \frac{\partial \hat{\rho}_M}{\partial t} = [\hat{\rho}_M, H] = 0 \). This means the density is diagonal in the energy representation, \( \hat{\rho}_M = x_n \delta_{nl} \). Here \( x_n \) are the spectral intensities and characterize the spectral envelope. The quantum measure for the state, \( \mu(M) = \frac{1}{\text{Tr}[\hat{\rho}(M)^2]} = \frac{1}{x \cdot x} \), gives the number of energy eigenstates underneath the spectral envelope of \( M \).

The collection \( X \) of states \( A \) are constrained by the spectral envelope, but allowed to feature fluctuations \( \Delta_A \) about the envelope. The diagonal components of \( A \),

\[
\hat{\rho}_{A,nn} = x_n + \Delta_{A,n} \tag{2.7}
\]

where fluctuations are orthogonal to the envelope \( x \cdot \Delta_A = 0 \) and \( \langle \Delta_A \rangle = \sum_n \Delta_{A,n} = 0 \). The measure of state \( A \),

\[
\mu(A) = \frac{1}{\text{Tr}[\hat{\rho}(A)^2]} \tag{2.8}
\]
As a result of the envelope constraint, the projection of any state $A \in X$ onto $M$,

$$\text{Tr}[\hat{\rho}_A \hat{\rho}_M] = x \cdot x + x \cdot \Delta_A = x \cdot x$$

(2.9)

This means that for any state $A$ in $X$, $A \subset M$. The quantum measures for states $A, B \subset M$ under set operations,

$$\mu(A \cap B) = \mu(A)\mu(B)\text{Tr}[\hat{\rho}_A \hat{\rho}_B]$$

(2.10)

$$\mu(A \triangle B) = \mu(A)\mu(B)\text{Tr}[(\hat{\rho}_A - \hat{\rho}_B)^2]$$

(2.11)

where $\mu(A \triangle B)$ can be further simplified,

$$\mu(A \triangle B) = \mu(A)\mu(B)\text{Tr}[\hat{\rho}_A^2 + \hat{\rho}_B^2 - \hat{\rho}_A \hat{\rho}_B - \hat{\rho}_B \hat{\rho}_A]$$

$$= \mu(A)\mu(B)\left(\text{Tr}[\hat{\rho}_A^2] + \text{Tr}[\hat{\rho}_B^2] - \text{Tr}[\hat{\rho}_A \hat{\rho}_B] - \text{Tr}[\hat{\rho}_B \hat{\rho}_A]\right)$$

$$= \mu(A) + \mu(B) - \mu(A \cap B) - \mu(B \cap A)$$

(2.12)

Using equation 2.10 and 2.11, one can show

$$\mu(A \triangle A) = \mu(A)^2\text{Tr}[(\hat{\rho}_A - \hat{\rho}_A)^2] = 0$$

(2.13)

$$\mu(A \cap A) = \mu(A)^2\text{Tr}[\hat{\rho}_A^2] = \mu(A)$$

(2.14)

which shows the connection between the QMA and our $\sigma$-algebra. When one considers the full density of state $A$,

$$\hat{\rho}_{A,ln} = (x_n + \Delta_{A,n})\delta_{ln} + A_{nl}(1 - \delta_{ln})$$

(2.15)
where \( \text{Tr} \left[ \hat{\rho}_A^2 \right] = x \cdot x + \Delta_A \cdot \Delta_A + A \cdot A \) such that \( \mu(A) \leq \mu(M) \). This further verifies that \( A \subset M \). The time evolution of the state \( A \) is given,

\[
O_t A = \hat{\rho}_A(t) = \exp(-i\hat{H}t/\hbar)\hat{\rho}_A \exp(i\hat{H}t/\hbar)
\]

(2.16)

\[
\hat{\rho}_{A,\text{nl}}(t) = (x_n + \Delta_{A,n})\delta_{n,l} + A_{\text{nl}}(t)(1 - \delta_{nl})
\]

(2.17)

where \( A_{\text{nl}}(t) = \exp\left[i(E_n - E_l)t/\hbar\right] A_{\text{nl}} \). The quantum measure of the time-evolving state \( \mu(O_t A) \) is also measure-preserving, as \( \text{Tr} \left[ \hat{\rho}_A^2 \right] = \text{Tr} \left[ \hat{\rho}_A^2 \right] \) so that \( \mu(O_t A) = \mu(A) \). The quantum analog of the ergodicity function for \( A, B \in M \),

\[
f(A, B, \Gamma) = \frac{1}{\Gamma} \int_0^\infty dt \exp(-t/\Gamma) \mu(O_t A \cap B)
\]

\[
= \frac{\mu(A)\mu(B)}{\Gamma} \int_0^\infty dt \exp(-t/\Gamma) \text{Tr} \left[ \hat{\rho}_A(t) \hat{\rho}_B \right]
\]

\[
= \frac{\mu(A)\mu(B)}{\Gamma} \int_0^\infty dt \exp(-t/\Gamma) \sum_{n,l} \left[ (x_n^2 + \Delta_{A,n}\Delta_{B,n})\delta_{n,l} + (1 - \delta_{nl})A_{\text{nl}}^*(t)B_{\text{nl}} \right]
\]

\[
= \frac{\mu(A)\mu(B)}{\mu(M)} \left[ 1 + \sum_{n,l} \frac{A_{\text{nl}}^*B_{\text{nl}}}{x \cdot x(1 + \omega_{nl}^2/\Gamma^2)} \right]
\]

(2.18)

where \( \omega_{nl} = \frac{E_n - E_l}{\hbar} \) and the spectrum is assumed to be nondegenerate. Averaging over all time,

\[
\hat{f}(A, B) = \lim_{\Gamma \to \infty} f(A, B, \Gamma) = \frac{\mu(A)\mu(B)}{\mu(M)} \left[ 1 + \frac{\Delta_A \cdot \Delta_B}{x \cdot x} \right]
\]

(2.19)

Ergodicity in the classical sense requires \( \Delta_A \cdot \Delta_B = 0 \) and \( \Delta_A \cdot \Delta_A = 0 \) for any \( A, B \in M \). Unfortunately, the later condition cannot be satisfied quantum mechanically for a pure state. According to Berry’s Random Wave Hypothesis,\(^\text{32}\) an ergodic
wavefunction $|A\rangle$ is given by the random superposition of energy eigenstates $|n\rangle$,

$$|A\rangle = \sum_{n,A} c_{n,A}|n\rangle$$  \hspace{1cm} (2.20)

where the overlap coefficients $c_{n,A} = \langle A|n \rangle$ distributed according to a Normal Distribution. Relating this to the spectral intensities, $x_n(1 + \Delta_{A,n}/x_n) = x_n\delta_{A,n} = |c_{n,A}|^2$, it is easy to see that $\delta_{A,n}$ will be distributed according to a $\chi^2$-distribution of $2z_a$ degrees of freedom with mean and variance,

$$P(x, z_A) = \frac{(z_A)^{2z_A}x^{2z_A-1}\exp(-xz_A)}{\Gamma(z_A)}$$  \hspace{1cm} (2.21)

$$\langle x \rangle = \int_0^\infty xP(x, z_A)dx = 1$$  \hspace{1cm} (2.22)

$$\sigma^2 = \int_0^\infty (x-1)^2P(x, z_A)dx = \frac{1}{z_A}$$  \hspace{1cm} (2.23)

where the degrees of freedom ranges $\mu(A) \leq z_A \leq 2\mu(A)$ for real to complex initial states. The quantum analogy of the time-averaged ergodicity function (Equation 2.26),

$$\langle \tilde{f}(A, B) \rangle = \frac{\mu(A)\mu(B)}{\mu(M)} \left[1 + \frac{\delta_{A,B}}{z_A}\right]$$  \hspace{1cm} (2.24)

This means that the flow between states $A$ and $B$ agrees with the classical ergodic estimate for $A \neq B$. One can define a normalized auto-correlation $F(A, A) = \frac{(f(A,A))\mu(M)}{\mu(A)^2}$, which describes the probability for an initial state $A$ to return as time evolves. It is clear that the quantum result is larger than the classical result, $F(A, A) = 1$, by a factor of $(1 + 1/z_A)$. For real and complex overlap coefficients, $2z_A = 1$ and $2z_A = 2$ respectively. This means $F(A, A) = 3$ or 2 for real or complex initial states, respec-
tively. This describes the system spending more time around the initial state $A$ than other states $B \in M$.

One can determine the amount of available phase space $M$ in which $A$ accesses,

$$F_e = \frac{1}{F(A, A)} = \frac{1}{(1 + 1/z_A)}$$ (2.25)

Thus, the fractional amount $M$ in which $A$ can access is $F_e = \frac{1}{3} \left( \frac{1}{2} \right)$ for initial states with real (complex) coefficients. The enhancement of the autocorrelation function from unity due to quantum fluctuations results in a reduction of phase-space exploration for quantum systems. This means nonergodic quantum system will explore less than $F_e$ of phase space. In the classical limit, the initial states are coarse grained ($z_A \to \infty$) and agree with the classical result.

2.2 Phase Space Flow for General Initial State

In the former section, the collection of states $X$ was constrained by the envelope constraint. The amount of phase space an ergodic quantum state can access was then found. Here it is discussed how one finds the envelope and spectral intensities subject to the envelope constraint for a general initial state, as well as the amount of phase spaced accessed. The time-averaged autocorrelation function reads,

$$P(a|a) = \lim_{T \to \infty} \frac{1}{T} \int_0^T \langle a | e^{-iHt/\hbar} | a \rangle |^2 dt$$

$$= \sum_{n,n'} p_{n,a} p_{n',a} \lim_{T \to \infty} \frac{1}{T} \int_0^T e^{-i(E_n - E_{n'})t/\hbar} dt = \sum_n p_{n,a}^2$$ (2.26)

which describes the probability for the initial state $|a\rangle$ to return as time evolves. Here $p_{n,a} = |\langle E_n | a \rangle|^2 = |c_{n,a}|^2$ are the spectral intensities between the initial state and
the corresponding eigenstates of the system and \( c_{n,a} = \langle E_n | a \rangle \) are the overlap coefficients. The states \(| a \rangle\) can be from any physically relevant basis set. It is also assumed in equation 2.26 that the energy spectrum is non-degenerate.

Equation 2.26 is well known as the Inverse Population Ratio (IPR). The total number of states in phase space \( N^a_\infty \) in which \(| a \rangle\) accesses is given by,

\[
N^a_\infty = \frac{1}{P(a|a)}
\] (2.27)

The larger the value of \( P(a|a) \), the longer \(| a \rangle\) lingers in its original state and the smaller \( N^a_\infty \) will be. In the limiting case where \(| a \rangle\) is an eigenstate of the full Hamiltonian, \( P(a|a) = 1 \) and consequently \( N^a_\infty = 1 \).

The spectral envelope \( S^a_T(E) \) is a smoothed version of the fully-resolved spectrum of the initial state, \(| a \rangle\),

\[
S(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-iEt/\hbar} \langle a|e^{-iHt/\hbar}|a \rangle dt = \sum_n \delta(E - E_n)p_{n,a}
\] (2.28)

The spectral envelope is defined by the finite Fourier Transform of the fully-resolved spectrum (equation 2.28),

\[
S^a_T(E) = \frac{1}{2\pi\hbar} \int_{-T}^{T} e^{-iEt/\hbar} \langle a|e^{-iHt/\hbar}|a \rangle dt = \sum_n p_{n,a} \Omega(E - E_n)
\] (2.29)

where \( \Omega(E - E_n) = \frac{\sin[(E - E_n)T/\hbar]}{(E - E_n)^2} \) is the cutoff function. By choosing \( T \) to be the time before the first recurrence, as the survival probability \( P(t) = |\langle a|a(t) \rangle|^2 \) first drops to zero, the spectral envelope for \(| a \rangle\) will spread over the entire range of states the system can access. Choosing an earlier or later value of \( T \) will either provide too little or too much dynamical information about the system. The faster \( P(t) \) decays
to zero, the larger the dispersion of the initial state $\Delta E$—the spread of the spectral envelope, will be. This is to be expected from the time-energy uncertainty principle $\Delta E \Delta T \sim \hbar$. Figure 2.1 shows the spectral envelope varies with $T$.

Figure 2.1: Figures (a)-(d) show the spectral envelope as a function of energy (Equation 2.29) using different values of $T$. The red data corresponds to the fully resolved spectrum. The survival probability first drops to zero at $T = T^*$. Figure (b) shows that the spread of the spectral envelope matches the spread of the spectra and does not reveal specific information on the spectral intensities. These figures show how the spread and nature of the envelope depends on $T$. Figure (a) shows that choosing $T < T^*$ provides too little information about the system’s dynamics. Figure (c)-(d) show how choosing $T > T^*$ provides too much information on the system’s dynamics.
The spectral intensities subject to the envelope constraint are given by\textsuperscript{33,34}

\[ p_{n,a}^T = \frac{S^a_p(E_n)}{D_T(E_n)} \]  

(2.30)

where the density of states is \( D_T(E) = \sum_n' \Omega(E - E'_n) \). Using these as the spectral intensities, the time-average autocorrelation function subject to the envelope constraint can be expressed,

\[ P_T(a|a) = \sum_n (p_{n,a}^T)^2 = \frac{1}{N_{a,T}} \]  

(2.31)

where \( N_{a,T} \) is the number of states in which \(|a\rangle\) can access. The fraction of available phase space explored is given by

\[ \mathcal{F} = \frac{N_{a,\infty}}{N_{a,T}} \]  

(2.32)

If \( \mathcal{F} < \mathcal{F}_e \), then the system is not fully ergodic in the quantum sense.

2.3 QUANTUM MATRIX ELEMENTS IN CLASSICAL LIMIT

The semiclassical wavefunctions in action-angle variables,

\[ \langle \theta | \mathbf{m} \rangle = \frac{e^{|\mathbf{m}| \theta}}{(2\pi)^{D/2}} \]  

(2.33)

where \(|\mathbf{m}\rangle = (m_1, m_2, \cdots, m_D)\) are integers in which the actions are EBK quantized \( I_{\mathbf{m}} = \hbar(m_1 + \frac{1}{2}, m_2 + \frac{1}{2}, \cdots, m_D + \frac{1}{2}) \), of a classical Hamiltonian \( H_0 \), which has energies \( H_0(I_{\mathbf{m}}) = E_m \). In order to calculate the appropriate matrix elements of \( H_0(I_{\mathbf{m}}) \) in the classical limit, a correspondence between the classical density \( \rho^{C}_{t,k}(I, \theta) \) and quantum
\[ \rho_{m,n}^Q \text{ density must be established,} \]

\[ \langle m | H | n \rangle = \text{Tr}[\rho_{m,n}^Q H] \rightarrow \int dI \ d\phi \ \rho_{I',k}^C(I, \theta) H(I, \theta) \tag{2.34} \]

where the relation between \( I' \) and \( k \) on \( m, n \) are to be determined. The classical and quantum densities are solutions to the time-independent Liouville operator, \( \mathcal{L}_\rho = \lambda \rho \).

For an \( N \) degree of freedom integrable system with actions \( I \) and frequencies \( \omega(I) \), the classical density is given by,

\[ \rho_{I,\lambda}^C = \frac{1}{(2\pi)^N} \delta[I' - I] \exp[i(k \cdot \theta)] \tag{2.35} \]

where the eigenvalue of the classical Liouville operator is \( \lambda = k \cdot \omega(I) \). The quantum density is given by,

\[ \rho_{m,n}^Q = |m\rangle \langle n|, \tag{2.36} \]

and the corresponding eigenvalue of the quantum Liouville operator is \( \lambda = \frac{1}{\hbar}(E_m - E_n) \). As shown in references 35 and 36, the correspondence between these two densities can then be found by taking the classical limit of the Wigner function,

\[ \rho_{I,j}^Q = \frac{1}{(2\pi \hbar)^N} \int_{-\pi/2}^{\pi/2} d\theta e^{-2iI_j \theta / \hbar} \langle \theta + z | m \rangle \langle m | \theta - z \rangle = \frac{1}{(2\pi \hbar)^N} \delta \left[ j - \frac{1}{2}(m + n) \right] e^{i(n-m) \cdot \theta} \tag{2.37} \]
The correspondence between the classical and quantum densities can be found by comparing equation 2.35 and 2.37,

$$\langle m | H | n \rangle = \text{Tr}[\rho^Q_{m,n} H] \rightarrow \int dI \, d\phi \, \rho^C_{I',k}(I, \theta) H(I, \theta)$$

(2.38)

which is true for $I' = \frac{I_m + I_n}{2}$ and $k = m - n$. The classical analog of the quantum matrix elements is the $k$-th Fourier component of the classical Hamiltonian evaluated at the average of both quantized actions,

$$H_{m,n} = H_{k=m-n}(\frac{I_m + I_n}{2})$$

(2.39)
3.1 Introduction

The free asymmetric rigid rotor has been studied in a variety of contexts. The classical free asymmetric rotor belongs to general set of Euler-Poinsot problems, which concern the rotational motion of a rigid body in the absence of external torque. The asymmetric rotor has three degrees of freedom (DOF), though reduces to an effective 1.5 DOF system using the Andoyer-Deprit variables—variables that are well known in the field of celestial mechanics and engineering.\textsuperscript{37,38} It is therefore a degenerate (super-integrable) system,\textsuperscript{37} as it has more constants of motion than degrees of freedom. The system can also be equivalently reduced in Euler angles and momenta by
rotating the total angular momentum to the $z$-axis in the inertial frame. This is the typical approach taken when studying the semiclassical behavior of asymmetric top molecules.$^2$\textsuperscript{39}

In Section 3.2, we follow this later approach when we discuss the background on the classical asymmetric rigid rotor. Here we are interested in the behavior of asymmetric top molecules, whose dynamics are well described by quantum mechanics. However, understanding the classical dynamics provides crucial physical intuition to understand its quantum behavior, both with and without an external torque. In Section 3.2, we also discuss the Harter Rotational Energy (RE) Surface,$^2$ which greatly clarifies the dynamics of the asymmetric rigid rotor and how it varies with the degree of asymmetry of the rotor.

Quantum Mechanically, the energy levels of the asymmetric top tend to cluster in pairs for large total angular momentum $J$ and feature as hyperfine energy splitting between pairs, referred to as rotational clusters. The semiclassical approach well describes the mechanism for this hyperfine energy splitting, which results from dynamical tunneling between classically degenerate states.$^2$\textsuperscript{16}$^3$\textsuperscript{39} In Section 3.3, we quantize the classical actions using the Einstein-Brillouin-Keller quantization method and derive the hyperfine splitting.

In Section 3.4, we derive the quantum mechanical matrix elements, which are used in Chapter 4 when calculating the energy levels of ortho-aminobenzylenitrile (OABN) and para-aminobenzylenitrile (PABN). The quantum calculations greatly simplify by accounting for the good quantum numbers-- $J$ and $M$, as well as the symmetry of the system. In Section 3.4.1, we analyze the symmetry of the asymmetric rotor, which intimately connects the three different approaches and explains the nature of the hyperfine splitting between rotational clusters.
3.2 **Classical Approach**

The free asymmetric rigid rotor describes a rotating body in the absence of external torque,

\[ H(J) = CJ_x^2 + BJ_y^2 + AJ_z^2 \]  

(3.1)

where \( J_i \) is the angular momentum about the \( i \)-th body axis, the total angular momentum \( J^2 = J_x^2 + J_y^2 + J_z^2 \), and \( A = \frac{1}{2I_z}, \ B = \frac{1}{2I_y}, \ C = \frac{1}{2I_z} \) are the rotational constants. The degree of asymmetry of the rigid rotor is given,

\[ \kappa = \frac{2B - A - C}{A - C} \]  

(3.2)

where \( \kappa = -1 \) for prolate tops and \( \kappa = 1 \) for oblate tops. The prolate and oblate representation correspond to \( C \leq B < A \), and in the oblate the \( A \leq B < C \).

The configuration space is described by \( SO(3) \). Parameterizing the space of rotations using Euler angles, \( (\alpha, \beta, \gamma) \), the phase space is described by the cotangent bundle of Euler angles and the canonically conjugate angular momentum, \( (J_\alpha, J_\beta, J_\gamma) \in \mathbb{R}^3 \). The Euler angles describe the orientation of the body axes \( (x, y, z) \) relative to the lab-frame axes \( (\bar{x}, \bar{y}, \bar{z}) \). The rotational matrix that relates the body frame to the lab frame reads

\[
\begin{pmatrix}
  x \\
y \\
z
\end{pmatrix} =
\begin{pmatrix}
  \cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma & -\cos \alpha \cos \beta \sin \gamma - \sin \alpha \cos \gamma & \cos \alpha \sin \beta \\
  \sin \alpha \cos \beta \cos \gamma + \cos \alpha \sin \gamma & -\sin \alpha \cos \beta \sin \gamma + \cos \alpha \cos \gamma & \sin \alpha \sin \beta \\
  -\sin \beta \cos \gamma & \sin \beta \sin \gamma & \cos \beta
\end{pmatrix}
\begin{pmatrix}
  \bar{x} \\
  \bar{y} \\
  \bar{z}
\end{pmatrix}
\]  

(3.3)
The projection of the conjugate momentum \((J_\alpha, J_\beta, J_\gamma)\) onto the body and lab axes,\(^2,3^9\)

\[
\begin{pmatrix}
J_x \\
J_y \\
J_z
\end{pmatrix} =
\begin{pmatrix}
-\cos \alpha \cot \beta & -\sin \alpha & \frac{\cos \alpha}{\sin \beta} \\
-\sin \alpha \cot \beta & \cos \alpha & \frac{\sin \alpha}{\sin \beta} \\
1 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
J_\alpha \\
J_\beta \\
J_\gamma
\end{pmatrix}
\] (3.4)

\[
\begin{pmatrix}
J_x \\
J_y \\
J_z
\end{pmatrix} =
\begin{pmatrix}
\frac{\cos \gamma}{\sin \beta} & \sin \alpha & \cos \gamma \cot \beta \\
\frac{\sin \gamma}{\sin \beta} & \cos \alpha & -\sin \gamma \cot \beta \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
J_\alpha \\
J_\beta \\
J_\gamma
\end{pmatrix}
\] (3.5)

where \(J_m\) correspond to the angular momentum in the lab-frame. The independence of the angular momentum in the lab and body frame can be shown using equations 3.4 and 3.5, \(\{J_m, J_\beta\} = 0\), as well as the invariance of \(J\) in both frames, \(J^2 = J_x^2 + J_y^2 + J_z^2 = J_\beta^2 + J_\alpha^2 + J_\gamma^2\).

The Hamiltonian as given in Euler angles and momenta greatly simplifies by rotating the total angular momentum vector \(J\) to the lab z-axis, and \((\beta, \pi - \gamma)\) are the polar and azimuthal angles of \(J\) relative to the body frame. This rotation corresponds to \(J_x = 0\), \(J_y = 0\), \(J_\beta = 0\), \(J_\gamma = J_\alpha = J\), and \(J_\beta = J\cos \beta\). This greatly simplifies the projection of the angular momentum onto the body-axes, \((J_x, J_y, J_z) = (-J \sin \beta \cos \gamma, J \sin \beta \sin \gamma, J_\gamma)\), where \(J_\gamma = J \cos \beta\). Equation 3.1 becomes,

\[
H(\alpha, \beta, \gamma, J_\alpha = J, J_\beta = 0, J_\gamma) = \left(C \cos^2 \gamma + B \sin^2 \gamma\right) (J^2 - J_\gamma^2) + AJ_\gamma^2
\] (3.6)
where $J \sin^2 \beta = (J^2 - J_{x}^2)$. In this representation, $J_{\alpha} = J$ and $J_{\beta}$ are constants of motion because the Hamiltonian is cyclic $\alpha, \beta$. The total energy $E$ and total angular momentum $J$ are also constants of motion, which means the number of integrals of motion are larger than the dimensionality of the system. This coordinate rotation therefore reduces the Hamiltonian to an effective 1.5 DOF Hamiltonian depending on $(\gamma, J_{\gamma})$. The variable $\alpha$ will be varying in time because $H$ depends on $J_{\alpha} = J$, such that $\dot{\alpha} = \frac{\partial H}{\partial J_{\alpha}} \neq 0$. However, $(\gamma, J_{\gamma})$ do not depend on its evolution, and we therefore can analyze the phase space of exclusively $(\gamma, J_{\gamma})$. We can now easily understand the dynamics $(\gamma, J_{\gamma})$ with Hamilton’s equations of motion,

$$\dot{\gamma} = \frac{\partial H}{\partial J_{\gamma}} = 2\left[A - (C \cos^2 \gamma + B \sin^2 \gamma)\right]J_{\gamma} \quad (3.7)$$

$$\dot{J}_{\gamma} = -\frac{\partial H}{\partial \gamma} = (C - B)(J^2 - J_{x}^2) \sin 2\gamma \quad (3.8)$$

In the general case of $A \neq B \neq C$, the Hamiltonian (Equation 3.6) has four fixed points at $J_{\gamma} = 0, \gamma = 0, \pi/2, \pi, 3\pi/2$. In the symmetric case where $A = B = C$, there are additional fixed points at $J_{\gamma} = \pm J$. The fixed points at $\gamma = 0, \pi$ are elliptic and $\gamma = \pi/2, 3\pi/2$ are hyperbolic. The stable and unstable manifolds of the hyperbolic fixed points connect to form a separatrix, which follows the energy contour $H(\gamma, J_{\gamma}) = BJ^2$ and $J_{\gamma,s}$ varies,

$$J_{\gamma,s}(J, \gamma) = J \sqrt{\frac{(B - C) \cos^2 \gamma}{A - (C \cos^2 \gamma + B \sin^2 \gamma)}} \quad (3.9)$$

---

*Using Andoyer-Deprit variables will lead to an equivalent expression. These variables relate the inertial and body reference frames to an invariable plane that is perpendicular to the total angular momentum $J$.}
Figure 3.1: Phase space of $H(\gamma, J_\gamma)$ with constant energy contours are shown in black and the separatrix in red for a nearly prolate top, $A = 1$, $B = 0.5$, $C = 0.3$ and $J = 9$. The librational motion is characterized by classical turning points $\gamma_{\pm}$ and occurs for $E < BJ^2$. The rotation motion does not have classical turning points and occurs for $E > BJ^2$. (b) The Harter-RE surface for the asymmetric top described in figure (a). The classical trajectories for a given $J$ and energy marked in red to yellow, where the color of the trajectory depends on the ratio of $|J_\gamma/J|$ as shown in the color bar. The blue-dashed line is the separatrix.

The separatrix separates librational ($E < BJ^2$) from rotational motion ($E > BJ^2$) about $J$. Figure 3.1(a) shows the phase space of $(\gamma, J_\gamma)$ for $A = 1$, $B = 0.5$, $C = 0.3$ and $J = 9$. The constant energy contours in black and the separatrix in red. Classical trajectories that lie symmetrically across the separatrix are degenerate. In the prolate limit ($C = B < A$), the librational region in figure 3.9 vanishes and $J_\gamma$ becomes a constant of motion, $\dot{J}_\gamma = 0$. This describes precession of $J$ about the body $z$-axis. According to equation 3.8, the evolution of the system is counterclockwise ($\dot{\gamma} > 0$) for $J_\gamma > 0$ and clockwise ($\dot{\gamma} < 0$) for $J_\gamma < 0$. Since the azimuth of $J$ is $\gamma' = \pi - \gamma$, the precession of $J$ about the body $z$-axis is clockwise for $J_\gamma > 0$ ($\dot{\gamma}' < 0$) and is
counterclockwise for \( J_\gamma < 0 \) (\( \dot{\gamma}' > 0 \)).

In the oblate limit (\( A = B < C \)), the rotational region in figure 3.9 vanishes. The purely librational motion about the body z-axis corresponds to \( J \) rotational motion about the body x-axis. Thus, the oblate limit is best described by treating the body x-axis as the effective body z-axis by switching \( A \) and \( C \) in eqns. 3.6-3.9.

The Harter rotational energy (RE) surface provides another way to understand the dynamics of the free asymmetric top molecule, in addition to the symmetry properties of the rigid rotor (See Section 3.4.1). The RE surface is defined by constant \( J \), and a radius \( R \) from the origin given by the energy using polar-coordinates for the angular momenta \((J_a, J_b, J_c) = (J \sin \theta \cos \phi, J \sin \theta \sin \phi, J \cos \theta)\).

The trajectories along the surface lie at the intersection of the constant energy surface with the rotational energy surface, as shown in red to yellow depending on the ratio of \(|K/J|\) in figure 3.1(b). The width of the two different regions are characterized by the angle between the two planes of the separatrix,

\[
\theta_{sep} = 2 \tan^{-1} \left( \frac{1 + \kappa}{1 - \kappa} \right)
\]

as shown in figure 3.2. For a symmetric prolate top (\( \kappa = -1 \)), \( \theta_{sep} = 0 \), and the system is defined completely by rotational motion about the \( J_a \)-axis. For a symmetric oblate top (\( \kappa = 1 \)), \( \theta_{sep} = \pi \), and the system is defined by rotational motion about the \( J_c \)-axis.

3.3 **Semiclassical Treatment**

We are interested in establishing a semiclassical representation for the free rigid rotor to understand how classical phase space structures influence the quantum behavior.
Figure 3.2: The angle between the two planes of the separatrix characterize the relative width of the rotational and librational regions on the Harter RE surface. Reproduced from reference 14 with permission.

The wavefunction depends on the action according to $\psi \sim \exp(iS_{\gamma})$, where the classical action $S(J,E,\gamma) = \int J_\gamma d\gamma + S_0$. We start by solving for $J_\gamma$ in equation 3.6,

$$J_\gamma(E, J, \gamma) = \sqrt{\frac{E - (C \cos^2 \gamma + B \sin^2 \gamma)J^2}{A - (C \cos^2 \gamma + B \sin^2 \gamma)}} \quad (3.11)$$

As mentioned previously, in the oblate representation the body $x$-axis is treated as the effective $z$-axis, and $J_\gamma$ in the oblate representation is given by switching $A$ and $C$ in equation 3.12,

$$J_\gamma(E, J, \gamma) = \sqrt{\frac{E - (A \cos^2 \gamma + B \sin^2 \gamma)J^2}{C - (A \cos^2 \gamma + B \sin^2 \gamma)}} \quad (3.12)$$
For rotational motion about the body $z$-axis with an unbounded azimuth, the Einstein-Brillouin-Keller (EBK) quantization of the action requires,

$$S(J, E, \gamma) = \int_{\gamma}^{2\pi+\gamma} J_\gamma(E,J,\gamma) d\gamma = 2\pi k_{A,R}$$

where $k_{C,R} = J, J - 1 \ldots$ and the $R$ subscript represents rotational motion about the $z$-axis. The integral evaluates to,

$$k_{A,R} = \frac{J}{2\pi} \int_{\gamma}^{2\pi+\gamma} \sqrt{\frac{\lambda + \cos 2\gamma}{\lambda_0 + \cos 2\gamma}} d\gamma = \frac{J}{\pi} \int_{-1}^{1} \sqrt{\frac{x + \epsilon}{(x + \epsilon_0)(1 - x^2)}} dx = \frac{2J}{\pi \sqrt{(\lambda + 1)(\lambda_0 - 1)}} \left[ (\lambda_0 + 1)\Pi - (\lambda_0 - \lambda)F \right]$$

where $\lambda = \frac{2E - J^2(C+B)}{J^2(B-C)}$, $\lambda_0 = \frac{2A - (C+B)}{2(B-C)}$, $\Pi = \Pi\left(\frac{\pi}{2}, \frac{-2}{\lambda_0 - 1}, \sqrt{\frac{2(\lambda_0 - \lambda)}{(\lambda + 1)(\lambda_0 - 1)}}\right)$ is an elliptic integral of the third kind, and $F = F\left(\frac{\pi}{2}, \sqrt{\frac{2(\lambda_0 - \lambda)}{(\lambda + 1)(\lambda_0 - 1)}}\right)$ is an elliptical integral of the first kind.

For librational motion about the body $z$-axis, the classical turning points are $\gamma_\pm = \pm \cos^{-1}(-\gamma/2)$. The EBK quantization of action requires,

$$S(J, E, \gamma) = \int_{\gamma_-}^{\gamma_+} J_\gamma(E,J,\gamma) d\gamma = 2\pi (k_{A,L} + 1/2)$$

where $k_{A,L} = 0, 1, 2, \ldots$ and the $L$ subscript denotes to librational motion about the $z$-axis. The integral can be expressed,

$$k_{A,L} + \frac{1}{2} = \frac{J}{2\pi} \int_{-\cos^{-1}(\lambda)}^{\cos^{-1}(\lambda)} \sqrt{\frac{\lambda + \cos \gamma}{\lambda_0 + \cos \gamma}} \, d\gamma = \frac{J}{\pi} \int \sqrt{\frac{x + \epsilon}{(x + \epsilon_0)(1 - x^2)}} \, dx$$
Using the following identity, \[39\]
\[
\int_b^a \sqrt{x-b} \sqrt{(a-x)(x-c)(x-d)} \, dx = \frac{2}{\sqrt{(a-c)(b-d)}} \times \left[ (a-d) \Pi \left( \frac{\pi}{2}, \frac{b-a}{b-d} ; \sqrt{\frac{(a-b)(c-d)}{(a-c)(b-d)}} \right) \right. \\
\left. - (b-d) F \left( \frac{\pi}{2}, \sqrt{\frac{(a-b)(c-d)}{(a-c)(b-d)}} \right) \right] 
\] (3.17)

where \(a > b > c > d\), equation 3.16 can be found explicitly,

\[k_{A,L} + \frac{1}{2} = \frac{J \sqrt{2}}{\pi \sqrt{\lambda_0 - \lambda}} \left[ (\lambda_0 + 1) \Pi \left( \frac{\pi}{2}, n, m \right) - (\lambda_0 - \lambda) F \left( \frac{\pi}{2}, m \right) \right] \] (3.18)

where \(n = \frac{-1 + \lambda}{\lambda_0 - \lambda} \), \(m = \sqrt{\frac{(\lambda+1)(\lambda_0-1)}{2(\lambda_0-\lambda)}} \), and \(\lambda < \lambda_0\) are the same as in equation 3.14.

One can do similarly for motions about the body \(x\)-axis to find \((k_{C,R}, k_{C,L})\). If a trajectory is rotational about the \(z\)-axis, then it will be librational about \(x\)-axis. With these expressions, one can verify that \(k_{A,R} + k_{C,L} = J + \frac{1}{2}\) Similarly, if the classical trajectory is rotational about the \(x\)-axis and librational about the \(z\)-axis, then \(k_{A,L} + k_{C,R} = J + \frac{1}{2}\). This means that either axis can be used to determine the energy and quantization number for a particular classical trajectory. Another relation between the quantize actions is \(k_{A,R} + k_{C,R} = J \) or \(J + 1\), which provides a correlation between the projection of momentum along the \(x\)-axis in the oblate limit and the projection of momenta along the \(z\)-axis in the prolate limit. The important thing to note is that the semiclassical approximation works best for large \(J\) and far away from the separatrix. As you approach the separatrix \(\frac{dJ}{dE} \rightarrow \infty\) and the expressions above are not well defined.

Classically, the corresponding trajectory for each \((k_{A,R}, k_{C,L})\) or \((k_{A,L}, k_{C,R})\) is doubly degenerate and will not mix as a result of the separatrix– a dynamical barrier to classical transport in phase space. However, quantum mechanically these degener-
ate states can tunnel across the separatrix and interact. As to be discussed in Section 3.4.1, states far away from the separatrix form symmetric and antisymmetric pairs of the classically degenerate states. These pairs feature a hyperfine splitting $\Delta E$. We now calculate the energy splitting that occurs due to dynamical tunneling.

The semiclassical rate of tunneling through a potential barrier,

$$\Gamma = \frac{dP}{dt} = \frac{1}{T} \exp(-2\theta)$$

(3.19)

where $\theta$ is given by the integral of the classical action along a path $C$ through the potential barrier,

$$\theta = \text{Im} \int_C J_\gamma d\gamma$$

(3.20)

and $T = \frac{\partial S}{\partial E}$ is the classical period of motion. We can relate equation 3.19 to the transition rate as given by Fermi’s Golden Rule between two states $|\psi_1\rangle$ to $|\psi_2\rangle$ that located on opposite sides of the potential barrier,

$$\Gamma = \frac{dP}{dt} = \frac{2\pi}{\hbar} |W_{1,2}|^2 \frac{dn}{dE}$$

(3.21)

where $\frac{dn}{dE} \sim (h\omega)^{-1} = \frac{T}{2\pi\hbar}$ and the matrix element $W_{12} = \langle 1 | H | 2 \rangle$. Matching these two expressions for the tunneling rate between two states, the matrix element are thus given,

$$W_{12} = \frac{\hbar}{T} \exp \left[ -|\theta| \pm i\text{Re} \int J_\gamma d\gamma \right]$$

(3.22)

The tunneling integral $\theta$ is over a path through each of the hyperbolic fixed points at
Figure 3.3: Figure shows the tunneling path along the RE Surface for $J = 9$, $A = 1 \text{ cm}^{-1}$, $B = 0.5 \text{ cm}^{-1}$, $C = 0.3 \text{ cm}^{-1}$ and $k_A = 8$.

$\gamma_s = \frac{\pi}{2}, \frac{3\pi}{2}$, as shown in figure 3.3.

The semiclassical wavefunction $\psi \sim \exp(iS_{\gamma})$ is exponential suppressed over this region. When going through the separatrix, the phase of the wavefunction changes from $\psi \sim \exp(iS_{\gamma})$ to $\psi \sim \exp(-iS_{\gamma})$. We can calculate the tunneling integral by doubling the integral from $J_{\gamma}(E, J, \gamma)$ to the separatrix,

$$\theta = \text{Im} \int_C J_{\gamma}(E, J, \gamma')d\gamma' = 2J \int_{\gamma_s}^{\gamma_s+i\delta} \sqrt{\frac{\lambda + \cos 2\gamma'}{\lambda_0 + \cos 2\gamma'}}d\gamma'$$

(3.23)

where $J_{\gamma}(E, J, \gamma_s + i\delta) = 0$ and $\delta = \cosh^{-1}(\lambda/2)$. This integral can explicitly be
evaluated by replacing $\gamma' = \gamma_s + i\gamma_i$ and integrating over $\gamma_i$,

$$\theta = 2J \int_{0}^{\cosh^{-1}(\lambda/2)} \frac{\cosh 2\gamma_i - \lambda}{\cosh 2\gamma_i - \lambda_0} d\gamma_i = J \int_{1}^{\lambda} \sqrt{\frac{x - \lambda}{(x - \lambda_0)(x^2 - 1)}} dx$$

$$= \frac{2J(\lambda_0 - \lambda)}{\sqrt{(\lambda_0 - 1)(\lambda + 1)}} \left[ \Pi \left( \frac{\pi}{2}, \frac{\lambda - 1}{\lambda_0 - 1}, p \right) - F \left( \frac{\pi}{2}, p \right) \right] \tag{3.24}$$

where $p = \sqrt{\frac{(\epsilon - 1)(\epsilon_0 + 1)}{(\epsilon_0 - 1)(\epsilon + 1)}}$. The total matrix element is double eqn 3.22 as a result of the two possible tunneling paths at $\gamma_s = \frac{\pi}{2}, \frac{3\pi}{2}$. Using this as our matrix element, the level splitting $\Delta E_n$ between two classically degenerate states with energy $E_n$ can be found,

$$\langle i | H | j \rangle = \begin{pmatrix} E_n & 2W_{12} \\ 2W_{12} & E_n \end{pmatrix} \tag{3.25}$$

$$\Delta E_n = 4W_{12} = \frac{4\hbar}{T} \exp \left( -|\theta| \right) \tag{3.26}$$

### 3.4 Quantum Approach

The Hamiltonian of the quantum asymmetric rigid rotor,

$$H = \frac{4\pi^2}{\hbar} (A\hat{j}_a^2 + B\hat{j}_b^2 + C\hat{j}_c^2) \tag{3.27}$$

where $a, b, c$ correspond to the principle axes of the rotor, the rotational constants in frequency units $A = \frac{\hbar}{8\pi^2 I_a}, B = \frac{\hbar}{8\pi^2 I_b}, C = \frac{\hbar}{8\pi^2 I_c}$, $A > B > C$ and $\hat{j}_i$ corresponds to the angular momentum operator about the $i$-th axis. For molecules, there are six different conventions used to identify $(a, b, c)$ with the body coordinates $(x, y, z)$, as shown in Table 3.1. $I$ is the natural convention for nearly prolate tops, and $III$ is the natural convention for nearly oblate tops. $II$ is best for the in between case, $\kappa = 0$. 32
The $l$– and $r$– superscripts designate a left- and right-handed coordinate system for $(x, y, z)$. While the off-diagonal matrix elements of the Hamiltonian (Equation 3.27) will change sign when going from the $r$ to $l$ convention, the energy eigenvalues will be unchanged because the Hamiltonian is Hermitian. However, the energy eigenvalues will change when going from the $I$ – $III$ convention. Therefore, it is extremely important to reference the convention being used for a particular $A, B, C$. Here we use the $I^l$ convention as used in references 14,2,39.

| Conventions for Principle Axes of Asymmetric Top |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $I^r$ | $I^l$ | $II^r$ | $II^l$ | $III^r$ | $III^l$ |
| $x$ | b | c | c | a | a | b |
| $y$ | c | b | a | c | b | a |
| $z$ | a | a | b | b | c | c |

Table 3.1: Conventions for Identifying Principle Axes $(a, b, c)$ to Body Coordinates $(x, y, z)$. The superscripts $l$ and $r$ designate a left and right-handed coordinate system, respectively. $I$ is ideal for nearly prolate tops. $III$ is ideal for nearly oblate tops.

The eigenstates of the asymmetric top rotor are linear combinations of the $|J K M\rangle$ states, where $\langle\alpha, \beta, \gamma|J K M\rangle = (-1)^{M-K}\frac{2J+1}{8\pi^2}^{1/2} D_{M,K}^{J} (\alpha, \beta, \gamma)$ and $D_{M,K}^{J} (\alpha, \beta, \gamma) = e^{-iM\alpha} d_{MK}^{J} (\beta) e^{-iK\gamma}$ is the Wigner D-matrix. The $d_{MK}^{J} (\beta)$ is often referred to as the small Wigner D-matrix and given by a sum of polynomials of $\sin^2 \frac{\beta}{2}$ and $\cos^2 \frac{\beta}{2}$. The $|J K M\rangle$ states are eigenstates of the angular momentum operators $\hat{J}^2$, $\hat{J}_z$, and $\hat{J}_\bar{z}$,

$$\hat{J}_z|J K M\rangle = \hbar K|J K M\rangle$$  \hspace{1cm} (3.28)
$$\hat{J}_\bar{z}|J K M\rangle = \hbar M|J K M\rangle$$  \hspace{1cm} (3.29)
$$\hat{J}^2|J K M\rangle = \hbar^2 J(J+1)|J K M\rangle$$  \hspace{1cm} (3.30)

In order to find the matrix elements for the quantum Hamiltonian, we must know
how the operators $\hat{J}_x$ and $\hat{J}_y$ act on the $|JKM \rangle$ state. We can do so by expressing $J_x, J_y$ as linear combination of the angular momentum ladder operators,

$$\hat{J}_x = \frac{\hat{J}_+ + \hat{J}_-}{2}$$

$$\hat{J}_y = \frac{\hat{J}_+ - \hat{J}_-}{2i}$$

(3.31)

(3.32)

where $\hat{J}_\pm |J \ K \ M \rangle = \hbar [J(J + 1) - K(K \pm 1)]^{1/2} |J \ K \ -1 \ M \rangle$. The $J_z^2, J_y^2$ terms in the Hamiltonian can therefore be written in ladder-operators,

$$\hat{J}_z^2 = \frac{1}{4} \left[ \hat{J}_+^2 - \hat{J}_-^2 + \hat{J}_- \hat{J}_+ + \hat{J}_+ \hat{J}_- \right] = \frac{1}{4} \left[ \hat{J}_z^2 - 2(\hat{J}_+^2 - \hat{J}_-^2) \right]$$

(3.33)

$$\hat{J}_y^2 = \frac{1}{4} \left[ -\hat{J}_+^2 - \hat{J}_-^2 + \hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+ \right] = \frac{1}{4} \left[ -\hat{J}_z^2 + 2(\hat{J}_+^2 - \hat{J}_-^2) \right]$$

(3.34)

Using these relations, the quantum rigid rotor Hamiltonian can be expressed,

$$H_{\text{rot}} = \frac{4\pi^2}{\hbar} \left[ \frac{\hat{J}_z^2 - \hat{J}_y^2}{2} (A + B) + C \hat{J}_z^2 + \frac{\hat{J}_+^2 + \hat{J}_-^2}{4} (A - B) \right]$$

In this form, the matrix elements of the Hamiltonian can easily be evaluated,

$$\langle J \ K \ M | H_{\text{rot}} | J \ K \ M \rangle = \hbar \frac{(A + B)}{2} (J(J + 1) - K^2) + CK^2$$

(3.35)

$$\langle J \ K \pm 2 \ M | H_{\text{rot}} | J \ K \ M \rangle = \hbar \frac{(A - B)}{4} \sqrt{J(J + 1) - K(K \pm 1)} \times \sqrt{J(J + 1) - (K \pm 1)(K \pm 2)}$$

(3.36)

The matrix elements only mix states with different $K$’s, which means that $J$ and $M$ are good quantum numbers. Another thing to note from eqns. 3.35 and 3.36 is that
$K$’s with different parities do not mix. The diagonalization procedure can be greatly simplified by separating basis states by $J$ and $M$ and using basis states that incorporate the symmetry of the asymmetric top, as to be discussed in the next section.

### 3.4.1 Symmetry Analysis of Asymmetric Top

The importance of understanding the symmetry of the rigid rotor is twofold. For one, the quantum Hamiltonian block diagonalizes using a basis with the appropriate symmetry, which reduces the size of the matrices to diagonalize in order to find the energy eigenvalues. Understanding the symmetry properties of the Hamiltonian also provides insight on the clustering of energy levels at high $J$ and the hyperfine splittings, as described in Section 3.3, between rotational clusters.

The symmetry of the asymmetric rigid rotor can be related to the symmetry of the corresponding Harter RE surface. The RE surface has an overall $D_2$ point group symmetry, which leaves the Hamiltonian invariant under transformations of momenta via symmetry operations. The group symmetry operations are,

$$D_2 = \{E, R_2(x), R_2(y), R_2(z)\}$$

where $E$ is identity and $R_2(x_i) \in SO(3)$ corresponds to a rotation by $\pi$ about the $x_i$-axis, with eigenvalues $\pm 1$. Table 3.2 gives the characters for the four irreducible representations (symmetry species) of $D_2$, $\{A_1, A_2, B_1, B_2\}$. Table 3.3 shows how the body coordinates and Euler angles are transformed under the symmetry operations of the group. We can then find how the $|JKM\rangle$ state transforms under the symmetry operations.
Character Table for $D_2$

<table>
<thead>
<tr>
<th>Rep</th>
<th>$E$</th>
<th>$R_2(x)$</th>
<th>$R_2(y)$</th>
<th>$R_2(z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.2: Characters for the four irreducible representations (symmetry species) of $D_2$: \{$A_1, A_2, B_1, B_2$\}.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Coordinate</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$x \rightarrow x$</td>
<td>$\alpha \rightarrow \alpha$</td>
</tr>
<tr>
<td></td>
<td>$y \rightarrow y$</td>
<td>$\beta \rightarrow \beta$</td>
</tr>
<tr>
<td></td>
<td>$z \rightarrow z$</td>
<td>$\gamma \rightarrow \gamma$</td>
</tr>
<tr>
<td>$R_2(z)$</td>
<td>$x \rightarrow -x$</td>
<td>$\alpha \rightarrow \alpha$</td>
</tr>
<tr>
<td></td>
<td>$y \rightarrow y$</td>
<td>$\beta \rightarrow \beta$</td>
</tr>
<tr>
<td></td>
<td>$z \rightarrow z$</td>
<td>$\gamma \rightarrow \pi + \gamma$</td>
</tr>
<tr>
<td>$R_2(y)$</td>
<td>$x \rightarrow -x$</td>
<td>$\alpha \rightarrow \alpha + \pi$</td>
</tr>
<tr>
<td></td>
<td>$y \rightarrow y$</td>
<td>$\beta \rightarrow \pi - \beta$</td>
</tr>
<tr>
<td></td>
<td>$z \rightarrow -z$</td>
<td>$\gamma \rightarrow \pi - \gamma$</td>
</tr>
<tr>
<td>$R_2(x)$</td>
<td>$x \rightarrow x$</td>
<td>$\alpha \rightarrow \alpha$</td>
</tr>
<tr>
<td></td>
<td>$y \rightarrow -y$</td>
<td>$\beta \rightarrow \pi - \beta$</td>
</tr>
<tr>
<td></td>
<td>$z \rightarrow -z$</td>
<td>$\gamma \rightarrow -\gamma$</td>
</tr>
</tbody>
</table>

Table 3.3: Transformation of body coordinates and Euler angles under $D_2$ Group Operations

\[
E|J K M\rangle = \left[\frac{2J+1}{8\pi^2}\right]^{1/2} e^{i\alpha M} d^J_{MK}(\beta) e^{iK(\chi)} = |J K M\rangle \quad (3.38)
\]

\[
R_2(z)|J K M\rangle = \left[\frac{2J+1}{8\pi^2}\right]^{1/2} e^{iM(\alpha+\pi)} d^J_{MK}(\beta) e^{iK(\pi+\chi)} = (-1)^K |J K M\rangle \quad (3.39)
\]

\[
R_2(y)|J K M\rangle = \left[\frac{2J+1}{8\pi^2}\right]^{1/2} e^{iM(\alpha+\pi)} d^J_{MK}(\pi - \beta) e^{iK(\pi-\chi)} = (-1)^{J-K} |J -K M\rangle \quad (3.40)
\]

\[
R_2(x)|J K M\rangle = \left[\frac{2J+1}{8\pi^2}\right]^{1/2} e^{iM(\alpha+\pi)} d^J_{MK}(\pi - \beta) e^{iK(-\chi)} = (-1)^{-J} |J -K M\rangle \quad (3.41)
\]
where various identities of $d_{MK}^J(\beta)$ were used from reference 45 to obtain the compact expressions on the right. To be clear, we are using $K$ to denote $K_a$ ($k_A$), the projection of $J$ onto the principle axis $a$, which is the body $z$-axis in the $I$ convention. At the end of this section, we will briefly discuss the oblate representation.

The trajectories on the RE surface have a local symmetry about the $z$- and $x$-axis, with the symmetry subgroup $C_2(z) = \{E, R_2(z)\}$ and $C_2(x) = \{E, R_2(x)\}$ respectively. The rotational clusters are based on the correlation between the irreducible representations of the RE surface, $D_2$, and the local symmetry of the subgroup, $C_2(x_i)$. Let’s consider the clusters that form about the $z$-axis. Following the notation as in references 2 and 39, we use $|0_2z\rangle$ and $|1_2z\rangle$ to designate states that have nodal symmetry and antisymmetry about the $z$-axis, respectively. These states correspond to $|JKM\rangle$ states with even or odd $K$, or semiclassically trajectories with even or odd $k_A$ \(^\dagger\) The rotational clusters are linear combinations of these states,

\[
\begin{align*}
|A_1\rangle & = \frac{1}{\sqrt{2}} \left( |0_2z\rangle + R_2(y)|0_2z\rangle \right) \\
|B_2\rangle & = \frac{1}{\sqrt{2}} \left( |0_2z\rangle - R_2(y)|0_2z\rangle \right) \\
|A_2\rangle & = \frac{1}{\sqrt{2}} \left( |1_2z\rangle + R_2(y)|1_2z\rangle \right) \\
|B_1\rangle & = \frac{1}{\sqrt{2}} \left( |1_2z\rangle - R_2(y)|1_2z\rangle \right) \quad \text{(3.42)}
\end{align*}
\]

where $R_2(y)$ changes $K \rightarrow -K$ and adds a prefactor $(-1)^{J-K}$ in $|JKM\rangle$. We now show that these rotational clusters are indeed the symmetry species of $D_2$ and reproduce the character table as given in Table 3.2. Specifically, we show that $T_i|j\rangle = \chi_{ij}|j\rangle$ for $T \in \{E, R_2(x), R_2(y), R_2(z)\}$ and $j \in \{A_1, A_2, B_1, B_2\}$, where $\chi_{ij}$ is the

\(^\dagger\)We drop the subscripts $R$ and $L$ on $k_A$ because we are working in the prolate limit here.
character from the $i$-th column and $j$-th row. Starting with $|A_1\rangle$,

$$E|A_1\rangle = |A_1\rangle \quad (3.43)$$

$$R_2(z)|A_1\rangle = \frac{1}{\sqrt{2}} \left( R_2(z)|0_{2z}\rangle + R_2(z)R_2(y)|0_{2z}\rangle \right)$$

$$= \frac{1}{\sqrt{2}} \left( |0_{2z}\rangle + R_2(z)R_2(y)R_2^2(z)|0_{2z}\rangle \right)$$

$$= \frac{1}{\sqrt{2}} \left( |0_{2z}\rangle + R_2(y)|0_{2z}\rangle \right) = |A_1\rangle \quad (3.44)$$

$$R_2(y)|A_1\rangle = \frac{1}{\sqrt{2}} \left( R_2(y)|0_{2z}\rangle + R_2^2(y)|0_{2z}\rangle \right) = \frac{1}{\sqrt{2}} \left( R_2(y)|0_{2z}\rangle + |0_{2z}\rangle \right) = |A_1\rangle \quad (3.45)$$

$$R_2(x)|A_1\rangle = R_2(z)R_2(y)|A_1\rangle = R_2(z)|A_1\rangle = |A_1\rangle \quad (3.46)$$

where we simplified these expressions using $R_2^2(x_i) = E$ and the multiplicative relations, $R_2(z)R_2(x) = R_2(y)$, $R_2(y)R_2(z) = R_2(x)$. For $|B_2\rangle$, which is also composed of states with even $K (K_A)$,

$$E|B_2\rangle = |B_2\rangle \quad (3.47)$$

$$R_2(z)|B_2\rangle = \frac{1}{\sqrt{2}} \left( R_2(z)|0_{2z}\rangle - R_2(z)R_2(y)|0_{2z}\rangle \right)$$

$$= \frac{1}{\sqrt{2}} \left( |0_{2z}\rangle - R_2(z)R_2(y)R_2^2(z)|0_{2z}\rangle \right)$$

$$= \frac{1}{\sqrt{2}} \left( |0_{2z}\rangle - R_2(y)|0_{2z}\rangle \right) = |B_2\rangle \quad (3.48)$$

$$R_2(y)|B_2\rangle = \frac{1}{\sqrt{2}} \left( R_2(y)|0_{2z}\rangle - R_2^2(y)|0_{2z}\rangle \right) = \frac{1}{\sqrt{2}} \left( R_2(y)|0_{2z}\rangle - |0_{2z}\rangle \right) = -|B_2\rangle \quad (3.49)$$

$$R_2(x)|B_2\rangle = R_2(z)R_2(y)|B_2\rangle = -R_2(z)|B_2\rangle = -|B_2\rangle \quad (3.50)$$
For $|A_2\rangle$, which is composed of states with odd $K$ ($k_A$),

\[
E|A_2\rangle = |A_2\rangle \quad (3.51)
\]

\[
R_2(z)|A_2\rangle = \frac{1}{\sqrt{2}} \left( R_2(z)|1_{2z}\rangle + R_2(z)R_2(y)|1_{2z}\rangle \right)
\]

\[
= \frac{1}{\sqrt{2}} \left( -|1_{2z}\rangle + R_2(z)R_2(y)R_2^2(z)|1_{2z}\rangle \right)
\]

\[
= \frac{1}{\sqrt{2}} \left( -|1_{2z}\rangle - R_2(y)|1_{2z}\rangle \right) = -|A_2\rangle \quad (3.52)
\]

\[
R_2(y)|A_2\rangle = \frac{1}{\sqrt{2}} \left( R_2(y)|1_{2z}\rangle + R_2^2(y)|1_{2z}\rangle \right) = \frac{1}{\sqrt{2}} \left( R_2(y)|1_{2z}\rangle + |1_{2z}\rangle \right) = |A_2\rangle \quad (3.53)
\]

\[
R_2(x)|A_2\rangle = R_2(z)R_2(y)|A_2\rangle = R_2(z)|A_2\rangle = -|A_2\rangle \quad (3.54)
\]

and for $|B_1\rangle$,

\[
E|B_1\rangle = |B_1\rangle \quad (3.55)
\]

\[
R_2(z)|B_1\rangle = \frac{1}{\sqrt{2}} \left( R_2(z)|1_{2z}\rangle - R_2(z)R_2(y)|1_{2z}\rangle \right)
\]

\[
= \frac{1}{\sqrt{2}} \left( -|1_{2z}\rangle - R_2(z)R_2(y)R_2^2(z)|1_{2z}\rangle \right)
\]

\[
= \frac{1}{\sqrt{2}} \left( -|1_{2z}\rangle + R_2(y)|1_{2z}\rangle \right) = -|B_1\rangle \quad (3.56)
\]

\[
R_2(y)|B_1\rangle = \frac{1}{\sqrt{2}} \left( R_2(y)|1_{2z}\rangle - R_2^2(y)|1_{2z}\rangle \right) = \frac{1}{\sqrt{2}} \left( R_2(y)|1_{2z}\rangle - |1_{2z}\rangle \right) = -|B_1\rangle \quad (3.57)
\]

\[
R_2(x)|B_1\rangle = R_2(z)R_2(y)|B_1\rangle = -R_2(z)|B_1\rangle = |B_1\rangle \quad (3.58)
\]

Thus each of the states $|A_1\rangle, |A_2\rangle, |B_1\rangle, |B_2\rangle$ transform under the symmetry operations as predicted by the character table. These states can also be found using a Wang-
Transformation $\hat{\Gamma}$ on the $|J K M\rangle$ basis,\textsuperscript{46,47}

\[
\hat{\Gamma} = \frac{1}{\sqrt{2}} \begin{pmatrix}
\ddots & \ddots & \\
-1 & 0 & 0 & 0 & 1 \\
\vdots & -1 & 0 & 1 & 0 & \ddots \\
\vdots & 0 & \sqrt{2} & 0 & 0 & \ddots \\
\vdots & 0 & 0 & 1 & 0 & \ddots \\
1 & 0 & 0 & 0 & 1 & \\
\ddots & \ddots & \ddots & 
\end{pmatrix}
\]

(3.59)

(3.60)

where $\hat{\Gamma} = \hat{\Gamma}^{-1}$ and acts on the $2J + 1$ dimensional vector $\Psi = \{|J,-K,M⟩, |J,-K+1,M⟩, \cdots, |J,K-1,M⟩, |J,K,M⟩\}$. This yields states with the equivalent form as Equation 3.42,

\[
|JKM\beta⟩ = \frac{1}{\sqrt{2}} \left(|JKM⟩ + (-1)^\beta|J-KM⟩\right), \ K \neq 0
\]

(3.61)

\[
|J0M⟩, \ K = 0
\]

(3.62)

The Wang-Transformation separates the Hamiltonian into four submatrices, $\hat{\Gamma}H\hat{\Gamma} = E_+ + E_- + O_+ + O_-$, where the letter $E$ ($O$) represents the parity of $K$ and $\pm$ represents the sign of $\beta$. The correlation between the submatrices and the $D_2$ symmetry species is given in Table 3.4. One can do similarly in the oblate representation, using $K = K_c (k_C)$. One then finds the symmetry species that are linear combinations of the states that have nodal symmetry or antisymmetry about the $x$-axis, $|0_{2x}\rangle$ with even $K_c$ and $|1_{2x}\rangle$ with odd $K_c$. Table 3.4 describes the correlation between the parity of $K_c$ and the symmetry species.
Correlation of Submatrices to $D_2$ symmetry species

<table>
<thead>
<tr>
<th>class</th>
<th>$K_a$</th>
<th>$\beta$</th>
<th>$J_e(K_a, K_c)$</th>
<th>$J_o(K_a, K_c)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^+$</td>
<td>e</td>
<td>0</td>
<td>$A_1$ (ee)</td>
<td>$B_2$ (eo)</td>
</tr>
<tr>
<td>$E^-$</td>
<td>e</td>
<td>1</td>
<td>$B_2$ (eo)</td>
<td>$A_1$ (ee)</td>
</tr>
<tr>
<td>$O^+$</td>
<td>o</td>
<td>0</td>
<td>$A_2$ (oo)</td>
<td>$B_1$ (oe)</td>
</tr>
<tr>
<td>$O^-$</td>
<td>o</td>
<td>1</td>
<td>$B_1$ (oe)</td>
<td>$A_2$ (oo)</td>
</tr>
</tbody>
</table>

Table 3.4: Here $e$ designates even parity and $o$ represents odd parity of $K_a = K$. This table also includes how the types and symmetry species relate to the parity of $K_c$ in the oblate representation ($K = K_c$)

In summary, the Hamiltonian block diagonalizes in a symmetrized basis, which correlates to the symmetry of the RE surface and the local symmetry subgroup, $C_2(x_i)$. In the prolate representation, for sufficiently high $J$ and far away from the separatrix, the rotational clusters, $(A_1, B_2)$ for even $K_a$ and $(A_2, B_1)$ for odd $K_a$, have nearly the same energy with hyperfine splitting between them. In the oblate representation, for sufficiently high $J$ and far away from the separatrix, the rotational clusters, $(A_1, B_1)$ for even $K_c$ and $(A_2, B_2)$ for odd $K_c$, have nearly the same energy with hyperfine splitting between them. Given that the rotational clusters have the form, $\psi_\pm = \frac{1}{\sqrt{2}}(|J KM \rangle \pm |J-KM \rangle)$, we see that the rotational clusters are linear combinations of the classically degenerate states. The observed energy splitting between $\psi_\pm$ can therefore be related to semiclassical energy splitting that result from dynamical tunneling.

Figure 3.4 shows the quantum energies for $J = 9$, $A = 1$ cm$^{-1}$, $B = 0.3 - 1$ cm$^{-1}$ and $C = 0.3$ cm$^{-1}$ in the prolate limit ($\kappa = -1$) and the oblate limit ($\kappa = 1$). While there are a total of $2J + 1 = 19$ states, we see that only nine energy levels at this resolution. In the prolate and oblate limits, the quantum energy levels for $\pm K$ are degenerate. Going between both limits, there will be hyperfine energy splittings between the clusters ranging from $\Delta E_n \sim [1 \times 10^{-14}, 1 \times 10^{-4}]$ depending on the value
Figure 3.4: The quantum energies for $J = 9$, $A = 1 \text{ cm}^{-1}$, $B = 1 \text{ cm}^{-1}$ in the prolate limit ($\kappa = -1$) and the oblate limit ($\kappa = 1$). At this resolution, only the energies of the rotational clusters can be seen. The hyperfine splittings range from $\Delta E_n \sim [1 \times 10^{-14}, 1 \times 10^{-4}]$ depending on $\kappa$ and $K$. Along the diagonal line lies the separatrix, which is where the energy levels split from $(A_1, B_2)$ for even $K_a$ and $(A_2, B_1)$ for odd $K_a$ to $(A_1, B_1)$ for even $K_c$ and $(A_2, B_2)$ for odd $K_c$.
The Degree of Ergodicity of ortho- and para-Aminobenzonitrile in an Electric Field

4.1 Introduction

Molecular beam electric field deflection\(^9\) (MBD) is a robust experimental method used to measure the dielectric properties of atoms, molecules and clusters.\(^{48,49,50,51,52,53,54,55}\) The basic protocol of these experiments involves running a collimated molecular beam through an inhomogeneous static electric field and measuring the resultant beam i-
tensity to calculate the deflection of the beam. This can be related to the force exerted on the dipole by the field gradient and extrapolated to find the molecule’s permanent dipole moment and polarizability. In recent years, measuring the electric dipole using MBD has helped provide structural information of various biomolecules.

Experimental deflection does not always agree with theoretical predictions. One issue that occurs is when the inversion splittings of a molecule are much larger than its rotational constants. In this case, the rate of tunneling between inversion coordinates is quite rapid compared to the rotational motion, and the dipole components perpendicular to the molecular $J_z$-axis experimentally average to zero.

There have been other issues reported on MBD experiments using highly asymmetric and flexible molecules. In References 1 and 58, the discrepancies are attributed to the chaotic behavior of an asymmetric molecule in an electric field, making it extremely sensitive to perturbations caused by collisions with other particles. They claim that these molecules have a tendency to lose their rotational orientation, and consequently feature a universal deflection as given by linear response theory. Reference 57 was able to successfully measure the dipole moment of the same asymmetric top molecules as in reference 1 by using a much lower electric field strength, which reduced the number of avoided crossings in the rotational energy levels. It is known that avoided crossings can reduce the amount of deflection as a result of the extensive mixing of rotational states at the avoided crossings, especially when the density of states is large.

Studies have highlighted the nonintegrability of the asymmetric top molecule in an electric field by Wigner-like Nearest Neighbor Level Distributions (NND)*, the pres-

---

*Nearset Neighbor Level Distributions can be unreliable due to ambiguities in histogram fitting and the number of levels used. It has even been shown that certain regular systems, such as $n$-dimensional harmonic oscillators, have a Wigner-like NND.
ence of avoided crossings, and symmetry arguments. However, the NND does not describe the actual amount of phase space transport given a particular initial rotational state, energy, dipole moment and degree of asymmetry. When a system is partially chaotic, the phase space transport depends on the initial conditions and the strength of the perturbation. We hope to gain insight as to which molecular properties lead to chaos and how this impacts deflection.

In this paper, the dynamics of the two molecules ortho-aminobenzonitrile (OABN) and para-aminobenzonitrile (PABN) are studied. These two molecules have been previously found to behave differently in molecular beam deflection experiments at high field strengths. PABN– a nearly prolate top, deflected as predicted by theoretical simulations given its predicted dipole moment, the deflector geometry and the beam density. OABN– a highly asymmetric top, deflected by nearly a constant amount, independent of the molecule’s initial rotational state. In reference 1 the NND for OABN was approximately a Wigner distribution and for PABN was approximately Poissonian for the first 700 lowest lying energy levels. For the next 700 energy levels, the NND was nearly Poissonian for both molecules. A similar dependency of the NND on energy was found for H$_2$O.

Here we are interested in a detailed study of ergodicity and its origins in an external field for asymmetric molecules, going beyond a specific study on OABN and PABN. We additionally rotate the dipole of each molecule to the body-fixed $z$-axis, in the prolate representation, in order to determine the effect on subsequent dynamics. Experimentally, one of course does not have the discretion to rotate the direction of the permanent dipole of a molecule or cluster. It is reasonable to do it artificially because the direction of the dipole is nearly independent of the asymmetry of the molecule. We hope to gain insight on the relative importance of the dipole versus
the degree of asymmetry on phase space transport. In the literature, no such direct comparison has been made.

We show that the dynamics of the system largely depend not only on the direction of the dipole and the asymmetry of the molecule, but also on the region of phase space occupied by the initial rotational state. We show that the ergodicity of the system varies gradually with energy, except in the regime where the rotational energy of the molecule is much less than the Stark interaction. In this regime, the Stark interaction dictates the dynamics of the molecule and a majority of initial rotational states are chaotic for both molecules.

In 4.2 we discuss the dynamics of the rigid rotor and the measures used to determine the phase space flow starting from different initial states. Results are given in 4.3. We use theoretical parameters as given in reference 1 for the molecular constants, dipole moments and value of electric field to compare our results with their previous measures of ergodicity for OABN and PABN. In addition, we rotate the dipole of each molecule to the body-fixed $z-$axis, relating these results to the original molecule. We draw conclusions in 4.4.

4.2 THEORETICAL METHODS

4.2.1 RIGID-ROTOR

The dynamics of a free, rigid asymmetric top molecule are governed by,

$$H_0 = A J_a^2 + B J_b^2 + C J_c^2$$

where $J_a$, $J_b$, and $J_c$ are projections of the total angular momentum along the body-fixed axes and $A > B > C$ are the corresponding rotational constants along these axes
in the prolate representation. The asymmetry parameter for a particular molecule is given by

\[ \kappa = \frac{2B - A - C}{A - C} \]  

(4.2)

where \( \kappa = -1 \) is the limit of a symmetric prolate top and \( \kappa = 1 \) is the limit of a symmetric oblate top. PABN is nearly a prolate top at \( \kappa = -0.938 \), while OABN is much more asymmetric at \( \kappa = -0.498 \) (See 4.1). The asymmetric top in the absence of an electric field is integrable; the energy, total angular momentum \( J \), and the projection of the angular momentum along the lab-frame \( z \)-axis \( M \) are conserved quantities.

Using a Harter\(^2\) rotational energy (RE) surface clarifies the dynamics of the free asymmetric top molecule. In figure 4.1 the RE surfaces for OABN and PABN are shown. As clearly observed in figure 4.1, the librational region of phase space is much larger in OABN than PABN, where \( \theta_{\text{separatrix}}^{\text{OABN}} = 0.206 \pi \) and \( \theta_{\text{separatrix}}^{\text{PABN}} = 0.020 \pi \).

### 4.2.2 Stark Interaction

<table>
<thead>
<tr>
<th>Isomer</th>
<th>A (cm(^{-1}))</th>
<th>B (cm(^{-1}))</th>
<th>C (cm(^{-1}))</th>
<th>( \mu_a ) (D)</th>
<th>( \mu_b ) (D)</th>
<th>( \mu_c ) (D)</th>
<th>( \mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>OABN</td>
<td>0.09951</td>
<td>0.04989</td>
<td>0.03326</td>
<td>-3.61</td>
<td>1.62</td>
<td>0.94</td>
<td>4.07</td>
</tr>
<tr>
<td>PABN</td>
<td>0.18549</td>
<td>0.03270</td>
<td>0.02782</td>
<td>5.94</td>
<td>0</td>
<td>1.03</td>
<td>6.03</td>
</tr>
</tbody>
</table>

**Table 4.1:** Rotational Constants and Dipole Moments for OABN and PABN. The theoretical values for the rotational constants and dipole moments for OABN and PABN are given in reference 1 from Hartree-Fock with MP2 calculations. Here the II convention is being used.

When a polar molecule is placed into an electric field, its electric dipole moment \( \mu \)
Figure 4.1: (a) The Harter $^2$ RE surface for OABN ($\kappa = -0.498$) is shown for $J = 9$. The classical trajectories for a given $J$ and energy marked in red to yellow, where the color of the trajectory depends on the ratio of $|K/J|$ as shown in the color bar. The blue-dashed line is the separatrix. (b) The Harter $^2$ RE surface for PABN is shown for $J = 9$. The width of the region enclosed by the separatrix is much smaller for PABN ($\kappa = -0.938$), which is consistent with it being nearly a prolate symmetric top ($\kappa = -1$). As $\kappa \to -1$, the separatrix disappears and $K$ becomes a constant of motion.
couples to the field $\mathbf{E}$ as given by the Stark interaction,

$$
H_a = -\mathbf{\mu} \cdot \mathbf{E} = -\sum_i E_z \mu_i \gamma_{i,z}
$$

(4.3)

where the electric field is oriented along the $z$-direction in the lab frame and $\gamma_{i,z}$ is the projection of the lab $z$-axis onto the body-fixed axes given by the direction cosines matrix (Equation 3.3). The full dipole moment is given by the molecule’s permanent and induced components,

$$
\mathbf{\mu} = \mathbf{\mu}_0 + \hat{\alpha} \mathbf{E}
$$

(4.4)

where the polarizability $\hat{\alpha}$ is a second-rank symmetric tensor. In MBD experiments, only the average of the trace of the polarizability, $\alpha = \frac{1}{3}(\alpha_x + \alpha_y + \alpha_z)$, can be measured.\textsuperscript{10} The theoretically predicted value for $\alpha_{OABN} = 13.4$ Å$^3$,\textsuperscript{1} and the ratio of the induced over the permanent dipole is 0.0013 at the highest field strength used in the results, $E_z = 120$ kV/cm. Therefore, the induced dipole is ignored in our calculations.

The matrix elements of the Stark interaction are shown below for completeness.

We calculate the matrix elements for the Stark interaction using the general expression for the integral over the triple product of rotational matrices,

$$
\int d\Omega \ D_{M_3K_3}^{J_3}(\mathbf{R})D_{M_2K_2}^{J_2}(\mathbf{R})D_{M_1K_1}^{J_1}(\mathbf{R})
= \frac{8\pi^2}{2J_3 + 1} \langle J_1 M_1, J_2 M_2 | J_3 M_3 \rangle \langle J_1 K_1, J_2 K_2 | J_3 K_3 \rangle
$$

(4.5)

where $\langle J_1 M_1, J_2 M_2 | J_3 M_3 \rangle$ are Clebsch Gordon Coefficients. The matrix elements of
the Stark interaction for the projection of $E_z$ onto the $J_a$-axis, $H_{s,a} = -\mu_a E_z \cos \beta$,

$$-(J'K'M'|\mu_a E_z \cos \beta|JKM)$$

$$= -\mu_a E_z \left[ \frac{2J' + 1}{8\pi^2} \right]^\frac{1}{2} \left[ \frac{2J + 1}{8\pi^2} \right]^\frac{1}{2} \int d\Omega D_{J'K'M'}^*(\mathbf{R}) D_{0,0}^1(\mathbf{R}) D_{J-K}^J(\mathbf{R})$$

$$= -\mu_a E_z \frac{\sqrt{2J + 1}}{\sqrt{2J' + 1}} \langle J - M, 1 0 | J' - M' \rangle \langle J - K, 1 0 | J' - K' \rangle$$

(4.6)

where $\cos \beta = D_{00}^1(\mathbf{R})$. For $J' \geq J$, there are two possible coefficients for $|J'K'M'\rangle$,

$$\langle J K M|H_{s,a}|J K M \rangle =$$

$$= -\mu_a E_z \langle J - M, 1 0 | J - M \rangle \langle J - K, 1 0 | J - K \rangle$$

$$= -\mu_a E_z \left[ \frac{-M}{J(J+1)} \right] \left[ \frac{-K}{J(J+1)} \right]$$

$$= -\frac{\mu_a E_z MK}{J(J+1)}$$

(4.7)

$$\langle J + 1 K M|H_{s,a}|J K M \rangle$$

$$= -\mu_a E_z \frac{\sqrt{2J + 1}}{\sqrt{2J + 3}} \langle J - M, 1 0 | J + 1 - M \rangle \langle J - K, 1 0 | J + 1 - K \rangle$$

$$= -\mu_a E_z \frac{\sqrt{2J + 1}}{\sqrt{2J + 3}} \left[ \frac{(J - 1)^2 - K^2}{2J + 1}(J + 1) \right]^\frac{1}{2} \left[ \frac{(J - 1)^2 - M^2}{2J + 1}(J + 1) \right]^\frac{1}{2}$$

$$= -\frac{\mu_a E_z}{(J + 1)} \left[ \frac{(J - 1)^2 - K^2}{(2J + 1)(2J + 3)} \right]^\frac{1}{2} \left[ \frac{(J - 1)^2 - M^2}{(2J + 1)(2J + 3)} \right]^\frac{1}{2}$$

(4.8)

The matrix elements of the Stark interaction for the projection of $E_z$ onto the $J_c$-
axis, $H_{s,c} = -\mu c E_z \sin \beta \cos \gamma$,

\[- \langle J'K'M'\vert \mu c E_z \sin \beta \cos \gamma \vert JKM \rangle \]

\[= - \mu c E_z \left[ \frac{2J' + 1}{8\pi^2} \right]^{\frac{1}{2}} \left[ \frac{2J + 1}{8\pi^2} \right]^{\frac{1}{2}} \int d\Omega D_{J'M'-K'}(R) \left( \frac{D_{0,1}^1(R)}{\sqrt{2}} - \frac{D_{0,-1}^1(R)}{\sqrt{2}} \right) D_{J-M-K}(R) \]

\[= - \mu c E_z \frac{\sqrt{2J + 1}}{\sqrt{2J' + 1}} \langle J - M, 1 0 \vert J' - M' \rangle \left( \langle J' - K, 1 1 \vert J' - K' \rangle - \langle J' - K, 1 - 1 \vert J' - K' \rangle \right) \quad (4.9)\]

where $D_{0,\pm 1}^1 = \pm \frac{e^{i\gamma}}{\sqrt{2}} \sin \beta$. For $J' \geq J$ there are four possible Clebsch-Gordon coefficients,

\[\langle J' K \pm 1 M \vert H_{s,c} \vert J K M \rangle =\]

\[= \frac{\mu c E_z}{\sqrt{2}} \left[ \frac{M}{(J + 1)} \right] \left[ \frac{(J \pm K + 1)(J \mp K)}{2J(J + 1)} \right]^{\frac{1}{2}} = \frac{\mu c E_z M}{2J(J + 1)} \left[ \frac{(J + K + 1)(J \mp K)}{2J(J + 1)} \right]^{\frac{1}{2}} \quad (4.10)\]

\[\langle J + 1 K \pm 1 M \vert H_{s,c} \vert J K M \rangle =\]

\[= \pm \frac{\mu c E_z \sqrt{2J + 1}}{\sqrt{2} \sqrt{2J + 3}} \left[ \frac{(J + 1)^2 - M^2}{(2J + 1)(J + 1)} \right]^{\frac{1}{2}} \left[ \frac{(J \pm K + 1)(J \pm K + 2)}{2(2J + 1)(J + 1)} \right]^{\frac{1}{2}}\]

\[= \pm \frac{\mu c E_z}{2(J + 1)} \left[ \frac{(J + 1)^2 - M^2}{(2J + 1)(2J + 3)} \right]^{\frac{1}{2}} \quad (4.11)\]

The matrix elements of the Stark interaction for the projection of $E_z$ onto the $J_b$-
axis, $H_{s,b} = -\mu_b E_z \sin \beta \sin \gamma$, 

$$
- \langle J'K'M'|\mu_b E_z \sin \beta \sin \gamma|JKM \rangle 
= - \mu_b E_z \left[ \frac{2J' + 1}{8\pi^2} \right] \left[ \frac{2J + 1}{8\pi^2} \right] \frac{1}{2} \int d\Omega D_{-J'-K'}(R) \left( \frac{D_{0,1}^\dagger(C)}{i\sqrt{2}} + \frac{D_{0,-1}^\dagger(C)}{i\sqrt{2}} \right) D_{J'-K}(R)
= - \frac{\mu_b E_z}{i\sqrt{2}} \frac{\sqrt{2J' + 1}}{\sqrt{2J' + 1}} \left( \langle J' - M, 1 0 \rangle \left| J' - K' \rangle \right. \right) \left[ \langle J' - K', 1 1 \rangle \langle J' - K' \rangle \rangle \right] + \langle J' - K, 1 -1 \rangle \langle J - K' \rangle \rangle
$$

Noting the similarity to equation 4.9, the allowed matrix elements can easily be found,

$$
\langle J'K'\pm 1 M|H_{s,b}|JKM \rangle = \pm i\mu_b E_z M \left[ \langle J \pm K + 1 \rangle \langle J \mp K \rangle \right] \frac{1}{2} \quad (4.12)
$$

$$
\langle J + 1 K \pm 1 M|H_{s,b}|JKM \rangle = \frac{i\mu b E_z}{2(J + 1)} \left[ \langle (J + 1)^2 - M^2 \rangle \langle J \pm K + 1 \rangle \langle J \pm K + 2 \rangle \right] \frac{1}{2} \quad (4.13)
$$

The former $D_2$ symmetry of the RE surface is lost in the presence of the field and the total angular momentum $J$ is no longer conserved. The only constants of motion that remain are the energy and $M$, and the system is no longer completely integrable.

For a dipole that points along the $J_a$-axis and $M \neq 0$, the states with even $K$ ($A$ and $B_a$ species), do not interact with the states with odd $K$ ($B_b$ and $B_c$ species). However, the $A$ and $B_a$ ($B_b$ and $B_c$) species do interact with each other for varying $J$. When the dipole points along two or more directions of the body fixed axes, all the symmetry species interact with each other for $M \neq 0$.47 This is true of course for both PABN and OABN (See Table 4.1). Therefore, we expect OABN and PABN to feature more regular dynamics when the dipole lies along $J_a$-axis than when the
A polar molecule will deflect when it is placed in a field with a potential gradient. Assuming an adiabatic passage, the force exerted on the dipole in an inhomogeneous field for the $i$-th quantum state and $M$ is,

$$f_{i,M} = -\frac{\partial E_{i,M}}{\partial E_z} \frac{\partial E_z}{\partial z}$$

(4.14)

The overall deflection of the $i$-th quantum state relies not only on the field gradient, but also on the geometry of the deflector and the mass and velocity of the molecule,$^{10,1}$

$$d_{i,M} = -\frac{\sigma}{mv^2} \left( \frac{\partial E_{i,M}}{\partial E_z} \right) = \frac{\sigma}{mv^2} \mu_{i,ZM}$$

(4.15)

where the field gradient is grouped into the apparatus constant, $\sigma$. With this expression, the average projection of the dipole moment along the lab $z$-axis of the $i$-th quantum state can be related to the gradient of its energy level versus field strength.

### 4.2.3 Quantum Ergodicity Predictions for OABN and PABN

As described in Chapter 2, Sect. 2.1, if a system is fully ergodic, the most ergodic spectral intensities $p_{n,a}$ come from a $\chi^2$-distribution for one (two) degree of freedom for real (complex) coefficients $c_{n,a}$. $^{31,63}$ The corresponding ergodic limit of $F$ is given by

$$F_e = \frac{1}{s}$$

(4.16)
where $s = 2$ or $3$ for complex or real coefficients $c_{n,a}$, respectively. When the total Hamiltonian,

$$H = H_0 + H_s$$

(4.17)

is diagonalized for each molecule using $|J K M\rangle$ basis states and the original dipole $\mu_0$, $\mathcal{F}_{e,OABN} = 1/2$ for OABN and $\mathcal{F}_{e,PABN} = 1/3$ for PABN. For the artificially rotated dipole $\mu_R$, both molecules have $\mathcal{F}_{e,\mu_R} = 1/3$. An initial state with a fraction $\mathcal{F}$ smaller than the corresponding ergodic limit $\mathcal{F}_e$ is not fully chaotic.

4.3 Results

For the results presented below, the full Hamiltonian (Equation 4.17) is diagonalized using the $|J K M\rangle$ states for $M = 1$, $J \in [1, 45]$ and $E_z = 120$ kV/cm. We use the $|J K M\rangle$ basis, as opposed to the eigenstates of the rigid rotor Hamiltonian, because they more closely resemble the classical trajectories of the asymmetric top. This allows us to better understand the differences between its quantum behavior and its classical behavior. As mentioned in the introduction, we use the parameters for the rotational constants and dipole moment (See Table 4.1), as well as the value of the electric field and $M = 1$ in which reference 1 found OABN to be chaotic and PABN to be mostly regular.

4.3.1 Original Dipole Moment

Figure 4.2 displays the energy levels of OABN (Figure 4.2(a)) and PABN (Figure 4.2(b)) as the electric field varies from $E_z \in [0, 120]$ kV/cm for the energy window $E = 7.25 – 8.25$ cm$^{-1}$. The color of each point is given by $P_a(n|n)^{1/3}$ for each of the
Figure 4.2: Shown are the energy levels for OABN in figure (a) and PABN in figure (b) as the electric field is increased in a lower energy range energy. The color at each point corresponds to the value of $P_a(n|n)^{1/3}$ for the $n$th energy eigenstate as shown in the color bar. Eigenstates of $H_{tot}$ that are very mixed in the $|J K M\rangle$ basis at a particular $E_z$ will be orange to yellow with $P_a(n|n)^{1/3} \sim 0$. In the opposite limit, eigenstates of $H_{tot}$ that are not very mixed relative to the $|J K M\rangle$ basis will be black to blue $P_a(n|n)^{1/3} \sim 1$. 

55
Figure 4.3: (a) Detail of the energy levels for OABN in the energy window $E = 7.8 - 8.3 \text{ cm}^{-1}$ and electric field range $E_z \in [10, 50] \text{ kV/cm}$. Note that at an isolated avoided crossing, the purity (value of $P_a(n|n)$ and color of each point) of two different levels exchanges between the upper and lower when going through the avoided crossing. (b) The number of avoided crossings with $\Delta E_{i,i+1} < 0.01 \text{ cm}^{-1}$ for the first 700 eigenstates in OABN (blue) is larger than in PABN (red) for $E_z < 30 \text{ kV/cm}$. On average, 3.2% of the avoided crossings will unlikely pass the condition for adiabatic passage (Equation 4.19). For PABN, the average is higher at 7%. 

56
$n$ energy levels at a given $E_z$. An eigenstate of $H_{tot}$ that is nearly pure with respect to the initial $|J K M\rangle$ basis at a specific value of $E_z$ will be a black data point with a $P_a(n|n)^{1/3} \sim 1$. A eigenstate of $H_{tot}$ that is extremely mixed with respect to the $|J K M\rangle$ basis at a specific value of $E_z$ will be an orange to yellow data point with a $P_a(n|n)^{1/3} \sim 0$. From these two figures, it is clear that the rotational energy levels of OABN become much more mixed relative to the $|J K M\rangle$ states than PABN in this energy window and electric field range.

In figure 4.3(a), a close up of the energy levels of OABN in the energy window $E = 7.8 - 8.3$ cm$^{-1}$ and electric field range $E_z \in [10, 50]$ kV/cm is shown. This figure highlights that the purity (value of $P_a(n|n)$) of two different levels exchange between the upper and lower state when traveling adiabatically through an avoided crossing. This occurs due to tunneling between the two interacting levels at the avoided crossing. Classically, the energy levels would cross and the purity of the energy level would remain constant. In general, any character of a state continues diabatically after an avoided crossing. If the dynamics is nonetheless adiabatic, a high-field seeking state$^\dagger$ will adiabatically continue into a low-field seeking state through an avoided crossing, and conversely for a low-field seeking state. In the presence of several avoided crossings, the force on the state (Equation 4.14) could keep shifting from high to low field seeking, causing no deflection on average.$^{59}$

Figure 4.3(b) shows that the number of avoided crossings with energy splitting $\Delta E_{i,i+1} < 0.01$ cm$^{-1}$ is slightly larger in OABN (blue line) than PABN (red line) for the lowest 700 energy eigenstates between $E_z \in [0, 30]$ kV/cm. Starting around $E_z \sim 30$ kV/cm, the number of avoided crossings in OABN drops below PABN as the

$^\dagger$A high-field seeking state is a state whose energy decreases as the field increases. A low-field seeking state is a state whose energy increases as the field increases.
field is increased. However, an avoided crossing will not always be crossed adiabatically if the energy gap is small enough. The condition for adiabatic passage through an avoided crossing between the $i$-th and $j$-th state is given,\textsuperscript{64,65}

$$\beta = \frac{\hbar}{(E_i - E_j)^2} \left( \frac{\partial H_s}{\partial t} \right)_{ij} << 1$$

(4.18)

where $(E_i - E_j)$ is the energy splitting of the avoided crossing, $H_s$ is the Stark interaction (Equation 4.3), $\left( \frac{\partial H_s}{\partial t} \right)_{ij}$ is the matrix element for the $i$-th and $j$-th state with $\frac{\partial H_s}{\partial t}$. We can roughly approximate equation 4.18 as,

$$\beta \approx \frac{\hbar}{\Delta E_{i,i+1}^2} \left( \mu_i \frac{\partial E_z}{\partial z} v_z \right) << 1$$

(4.19)

where $\mu_i$ is the magnitude of the dipole for each molecule, $\frac{\partial E_z}{\partial z} = 2.09 \times 10^9 \text{ V/m}^2$ is the field gradient in reference 1 and $v_z \sim 1 \text{ m/s}$ is an order of magnitude estimate on the velocity along the gradient.\textsuperscript{10,64} For the avoided crossings in the first 700 eigenstates of OABN (Figure 4.3(b) in blue), the average splitting is $\langle \Delta E_{i,i+1} \rangle = 0.0056 \text{ cm}^{-1}$ with $\beta = 0.0015$ and the average minimum splitting is $\langle \Delta E_{i,i+1} \rangle_{\text{min}} = 0.00044 \text{ cm}^{-1}$ with $\beta = 0.24$. For the avoided crossings in the first 700 eigenstates of PABN (Figure 4.3(b) in red), the average splitting is $\langle \Delta E_{i,i+1} \rangle = 0.0052 \text{ cm}^{-1}$ with $\beta = 0.0026$ and the average minimum splitting is $\langle \Delta E_{i,i+1} \rangle_{\text{min}} = 0.00019 \text{ cm}^{-1}$ with $\beta = 1.95$. We calculate the percent of avoided crossings as the field varies with $\beta \geq 0.1$, a marginal condition for diabatic passage. On average, 3.2\% of the avoided crossings will likely be diabatically crossed for OABN. For PABN, the average is slightly higher at 7\%.  

58
To determine how $P_a(n|n)$ varies with the strength of the dipole, we calculate the projection of the dipole moment in the lab-frame z-axis for OABN and PABN, where $\mu_{n,zL,M}$ for each eigenstate at $E_z = 120 \text{ kV/cm}$ is shown in figure 4.4. Here we approximated the gradient of the energy with field strength by $\frac{\partial E_i;M}{\partial E_z} \approx \frac{\Delta E_i;M}{\Delta E_z}$ with $\frac{\Delta E}{E_z} = 0.0033$. The color for each data point is given by the value of $P_a(n|n)^{1/3}$ as also shown in figure 4.2. In these figures, the dipole moment is divided by the absolute magnitude of each molecules’ dipole moment (Table 4.1).

The dipole moment decreases approximately linearly with energy up until around 7.43 cm$^{-1}$ for OABN and 9.90 cm$^{-1}$ for PABN, where the dipole first becomes negative. We can understand the linear behavior by the following. The expectation of the average projection of the dipole along the lab-frame z-axis for the $n$-th energy eigenstate,

$$\mu_{n,zL,M} = \langle \Psi_n | \mu_{zL} | \Psi_n \rangle = \langle \Psi_n | \sum_i \mu_i \gamma_{i,z} | \Psi_n \rangle$$  \hspace{1cm} (4.20)$$

We can relate this to the energy of the $n$th eigenstate using equations 4.3 and 4.17,

$$E_n = \langle \Psi_n | H_{tot} | \Psi \rangle = \langle \Psi_n | H_0 | \Psi_n \rangle + \langle \Psi_n | H_s | \Psi_n \rangle$$

$$= \langle \Psi_n | H_0 | \Psi_n \rangle - E_z \langle \Psi_n | \sum_i \mu_i \gamma_{i,z} | \Psi_n \rangle$$

$$= \langle H_0 \rangle_n - E_z \mu_{n,zL,M}$$ \hspace{1cm} (4.21)$$

With this we find that the average projection of the dipole along the lab-frame z axis decreases approximately linearly with $E_n$ when the rotational energy $\langle H_0 \rangle_n << \langle \mu \cdot$
Figure 4.4: The average projection of the dipole moment along the lab z-axis divided by the magnitude of the relative dipole moment, \( \frac{\mu_z}{\mu} \), for each of the eigenstates for (a) OABN and (b) PABN at \( E_z = 120 \text{ kV/cm} \). The color for each point is given by the \( P_n(n|n)^{1/3} \). The relative dipole moment for PABN is much more aligned with the field than OABN. The inset in each plot shows the classical microcanonical average in the ergodic limit of \( \mu_{z_{1,1}}/\mu \) (in red) as a function of energy versus the quantum result (in black). Both show a near linear decrease of the dipole with energy, as seen in the quantum calculation in this energy range. Thus a nonzero average of \( \mu_{z_{1,1}} \) is to be expected for an ergodic state at low \( J \) in the presence of the field. The discrepancy from the microcanonical average in PABN is due to non-ergodicity.
While this linear trend is quite prominent in OABN, there are quite a few states in PABN that do not follow this and are not as mixed with $P_a(n|n)^{1/3} = 0.497$. When analyzing the spectral intensities $p_{n,a}$ for these states, we find that these eigenstates only have significant overlap with $K \sim J$ states for low $J$ and states with the same $K$. This behavior is due to non-ergodicity.

Between 7.43 to 43.37 cm$^{-1}$ in OABN and 9.90 to 33.90 cm$^{-1}$ in PABN, the dipole’s alignment with the field greatly fluctuates between positive to negative values. The relative dipole averages to nearly zero for both molecules. For states with energy greater than 43.37 cm$^{-1}$ (33.90 cm$^{-1}$) in OABN (PABN), the relative dipole averages to -0.05 (-0.09). In this range, the dipole anti-aligns with the field in general and tends not to be very mixed with respect to the $|J K 1\rangle$ basis.

Figures 4.4(a) and 4.4(b) reveal how highly mixed the eigenstates are up to 7.43 cm$^{-1}$ for OABN and 9.90 cm$^{-1}$ for PABN, even though dipole aligns with the field. Although perhaps counterintuitive, an ergodic sampling of phase space does not necessarily mean the average orientation of the molecule is random. In the presence of an electric field, the states will in general orient in the direction of the field and thus, a nonzero average is to be expected for an ergodic state. We show this by calculating
the classical microcanonical average at energy $E$ for $\mu_{zL,1}(E)$ in the ergodic-limit,$^{66}$

$$
\mu_{zL,1}(E) = \frac{1}{N} \int dp \, d\Omega \left[ \mu(p, \Omega) \cdot \hat{z} \right] \rho(E, p, \Omega)
= \frac{1}{N} \sum_i \mu_i \int dp \, d\Omega \, \gamma_{i,z}(p, \Omega) \rho(E, p, \Omega)
$$

(4.23)

where the integral is over Euler angles $\Omega$ and the conjugate angular momentum $p$.

The density in the ergodic limit, constrained to constant $E$ and $M = 1$, is given by,

$$
\rho(E, p, \Omega) = \delta(E - H(p, \Omega)) \, \delta(M - 1)
$$

(4.24)

and $N = \int dp \, d\Omega \, \rho(E, p, \Omega)$ is a normalization factor. To evaluate this integral numerically, we replaced the $\delta$-function with a normal distribution of standard deviation $\sigma = 1$. The insets in figures 4.4(a) and 4.4(b) show the classical microcanonical average of $\mu_{zL,1}(E)/\mu$ in the ergodic-limit in red, in comparison to the quantum expectation value in black. Both show an approximately linear decrease with energy. The dipole for OABN crosses zero around $E = 7.5 \text{ cm}^{-1}$ and for PABN crosses zero at $E = 9 \text{ cm}^{-1}$. Such characteristics are seen in the quantum calculation of the dipole. However, the quantum calculation of the relative dipole for PABN has a quite a few states that deviate from its classical microcanonical average. These deviations show that the dipole aligns more with the field than predicted by the ergodic estimate.

Nevertheless, this estimate shows that dipole of energy states within this energy range should have a nonzero average at low energies. It has been shown the states in this energy range, with $E_z \sim 20 \text{ kV/cm}$, behave in a pendular-like matter with respect to their orientation with the field.$^{67,64,68}$ In light of this, the nonzero average of the dipole in an external field is not too surprising.
In figures 4.5 and 4.6, the time-averaged auto-correlation function is shown for OABN and PABN for each of the states up to \( J = 38 \) at \( E_z = 120 \text{ kV/cm} \). The ordering of the \(|J K 1⟩\) basis states is by their expectation value of the full Hamiltonian, \( \langle H_{\text{tot}} \rangle \) (Equation 4.17). The first dashed line in figures 4.5(a) and 4.6(a) marks the 700th lowest energy value of the full Hamiltonian in each of these systems. In this energy range, reference 1 found nearly Wigner-Dyson statistics for the eigenstates of OABN and nearly Poissonian statistics for the eigenstates of PABN. The second marks the 1400th lowest energy of \( H_{\text{tot}} \), which is the energy range that reference 1 found Poissonian Statistics for both molecules.

What immediately stands out from these figures is the large variation in the magnitudes of the \( P(a|a) \) values. Upon inspection of the color of each \( P(a|a) \), as shown in 4.5(b) and 4.6(b), we find that the majority of states with large \( P(a|a) \) values are polar states, where \( K ∼ J \). The states with the smallest \( P(a|a) \) values are “small-K states”, which are located classically near the separatrix to \( K = 0 \). Classically, the separatrix is the region of instability; trajectories nearby the separatrix feature irregular motion.\(^{69,2}\) It is where chaos develops first in the presence of a perturbation.

It is quite interesting that low \( P(a|a) \)’s occur for \( K = 0 \) states even though they are technically polar with respect to the \( J_{\text{c}} \)-axis. However, the states orbiting the \( J_{\text{c}} \)-axis are closer to the separatrix than the states orbiting the \( J_{\text{a}} \)-axis (\( K ∼ J \)) states. This is especially so in PABN, where the separatrix lies very close to the \( J_{\text{c}}-J_{\text{b}} \) plane (\( \theta_{\text{sep}}^{\text{PABN}} = 0.020 \pi \)). As the electric field is turned on, a band of chaos develops around the separatrix. The separatrix is the classically unstable region of the RE surface.\(^{70}\) Thus, we can expect the states closer in distance to the separatrix to become more mixed by the perturbation. As to be shown and discussed in Section 4.3.2, the direction of the dipole also has an large impact on \( P(a|a) \) for the states nearby the
Figure 4.5: Shown in (a) is $P(a|a)$ for each of the $|J\ K\ 1\rangle$ states for OABN arranged by their expectation value of the full Hamiltonian $\langle H \rangle$ at $E_z = 120$ kV/cm. The dashed lines marks the 700th and 1400th lowest energy level of the full Hamiltonian. In (b) the figure is zoomed into to show the behavior of the initial states in the lower energy range. The color of each point corresponds to the ratio of $|K/J|$. This plot clearly shows how the small-K states, shown as orange to yellow, tend to have lower values of $P(a|a)$ and thus access more of phase space.
Figure 4.6: Shown in (a) is $P(a|a)$ for each of the $|J K 1\rangle$ states for PABN arranged by their expectation value of the full Hamiltonian $\langle H \rangle$ at $E_z = 120$ kV/cm. In (b) the energy range is zoomed into to show the behavior at the initial states with $\langle H_{tot} \rangle$ within the 700th lowest energy level of $H_{tot}$. This plot clearly shows how the small-K states tend to have lower values of $P(a|a)$ for PABN as well and consequently will explore more of phase space.
When we compare the $P(a|a)$ values for both molecules in figures 4.5(b) and 4.6(b), we find that the states near the separatrix form a line around $P(a|a) \approx 0.01$ for OABN and $P(a|a) \approx 0.017$ for PABN. In figure 4.7 we find the percent of initial $|J K 1\rangle$ states within this lower energy range that are below a specific $P(a|a)$. Here the blue line is for OABN and the red line for PABN. While approximately 50% of these initial states have a $P(a|a) < 0.01$ for OABN, only 1.3% of these states have a $P(a|a) < 0.01$ in PABN. The percentage of states for PABN does not hit 50% until $P(a|a) \leq 0.023$, which is where approximately 79.3% of the states lie for OABN. From this figure it is quite clear that a larger fraction of the initial $|J K 1\rangle$ states have a lower value of $P(a|a)$ for OABN than for PABN, and hence access significantly more of phase space (Equation 2.27).

We calculate the spectral envelope and the fraction of phase space explored for a sample small-K and polar state to better understand how ergodicity varies between
these two types of states (See Figure 4.8). In blue is the polar state $|J \ K \ M \rangle = |18 \ 18 \ 1\rangle$ (Figure 4.8(a)) and the small-K state $|J \ K \ M \rangle = |22 \ 6 \ 1\rangle$ in OABN (Figure 4.8(b)) with corresponding values of $P(a|a) = 0.126$, $N_{a,\infty} = 7.94$ and $\mathcal{F} = 0.05$ and $P(a|a) = 0.007$, $N_{a,\infty} = 138.90$ and $\mathcal{F} = 0.35$ respectively. Below each of these envelopes is the fully-resolved spectrum in red as given by equation 2.28. In black are the energy eigenstates of the full Hamiltonian are marked below the horizontal axis.

The spread of $S^a_\alpha(E)$ for the polar state is much smaller than that of the small-K state, and the fully-resolved spectrum highlights that very few eigenstates underneath the envelope are actually populated by $|18 \ 18 \ 1\rangle$. The fraction of states visited over those accessible is $\mathcal{F} = 0.05$ for the polar state, which is much less than the ergodic estimate of $\mathcal{F}_e, OABN = 0.5$. In comparison, the small-K state $|22 \ 6 \ 1\rangle$ accesses a majority of the available states underneath the spectral envelope and leads to a much larger fraction, $\mathcal{F} = 0.35$, of phase space being explored.

To generalize this result between polar and small-K states, we find the spectral envelopes and $\mathcal{F}$ for a range of initial states as shown in Table 4.2. Doing so also allows us to find how ergodicity varies with energy. In these plots, the chosen small-K states are semi-classically located right below the each molecules’ separatrix and have a $P(a|a) < 0.008$ ($P(a|a) < 0.013$) for OABN (PABN). Here the electric field is constant at $E_z = 120$ kV/cm.

Table 4.2 shows there is a gradual decrease of ergodicity with energy amongst a majority of the states. However, there is a significant drop of $\mathcal{F}$ between $|5 \ 5 \ 1\rangle$ and $|8 \ 8 \ 1\rangle$ for both OABN and PABN. The expectation value of $H_{tot}$ for $|5 \ 5 \ 1\rangle$ is $\langle H_{tot} \rangle = 3.9 \text{ cm}^{-1}$ ($2.80 \text{ cm}^{-1}$) for OABN (PABN), which lies in the energy region where $\mu_{n,z,L,M}$ decreases linearly with energy and follows the ergodic estimate. The state $|8 \ 8 \ 1\rangle$ lies just outside this region at $\langle H_{tot} \rangle = 7.51 \text{ cm}^{-1}$ ($10.78 \text{ cm}^{-1}$) for OABN (PABN).
Figure 4.8: The spectral envelope in blue for (a) an extremal state $|J K M\rangle = |18 18 1\rangle$ for OABN with $P(a|a) = 0.126$ and $\mathcal{F} = 0.05$ and (b) a small-K state $|J K M\rangle = |22 6 1\rangle$ with $P(a|a) = 0.007$ and $\mathcal{F} = 0.35$ at $E_z = 120$ kV/cm. In the inset plots are a magnified view of the density of states in black below the axis and the spectral intensities $p_{n,a}$ in red.
<table>
<thead>
<tr>
<th>molecule</th>
<th>state</th>
<th>$\langle H_{\text{tot}} \rangle$</th>
<th>$N_{a,\infty}$</th>
<th>$\mathcal{F}$</th>
<th>$\mathcal{F}/\mathcal{F}_{e,i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OABN</td>
<td>5 5 1</td>
<td>3.91</td>
<td>66.4</td>
<td>0.45</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>6 6 1</td>
<td>4.87</td>
<td>72.9</td>
<td>0.46</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>8 8 1</td>
<td>7.51</td>
<td>40.7</td>
<td>0.22</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>12 12 1</td>
<td>15.40</td>
<td>16.5</td>
<td>0.1</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>14 14 1</td>
<td>20.57</td>
<td>16.5</td>
<td>0.09</td>
<td>0.18</td>
</tr>
<tr>
<td>polar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>small-K</td>
<td>10 -3 1</td>
<td>4.90</td>
<td>110.3</td>
<td>0.47</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>15 4 1</td>
<td>11.03</td>
<td>146.2</td>
<td>0.42</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>18 4 1</td>
<td>15.23</td>
<td>151.6</td>
<td>0.40</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>22 6 1</td>
<td>23.21</td>
<td>139.4</td>
<td>0.35</td>
<td>0.70</td>
</tr>
<tr>
<td>PABN</td>
<td>5 5 1</td>
<td>2.80</td>
<td>41.3</td>
<td>0.33</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>6 -6 1</td>
<td>8.57</td>
<td>33.2</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>8 8 1</td>
<td>10.78</td>
<td>8.80</td>
<td>0.05</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>12 12 1</td>
<td>26.2</td>
<td>6.53</td>
<td>0.042</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>14 14 1</td>
<td>35.98</td>
<td>5.6</td>
<td>0.04</td>
<td>0.12</td>
</tr>
<tr>
<td>small-K</td>
<td>10 0 1</td>
<td>3.33</td>
<td>87.2</td>
<td>0.33</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>15 1 1</td>
<td>7.37</td>
<td>85.3</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>18 1 1</td>
<td>10.50</td>
<td>84.9</td>
<td>0.21</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>23 2 1</td>
<td>17.28</td>
<td>91.8</td>
<td>0.18</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table 4.2: $\langle H_{\text{tot}} \rangle$, $N_{a,\infty}$, $\mathcal{F}$ and $\mathcal{F}/\mathcal{F}_{e,i}$ for OABN and PABN. Here we show $\langle H_{\text{tot}} \rangle$ in units of (cm$^{-1}$), $N_{a,\infty}$ and $\mathcal{F}$ for a range of initial states from OABN and PABN. The ergodic limit for each molecule is $\mathcal{F}_{e,OABN} = 1/2$ and $\mathcal{F}_{e,PABN} = 1/3$. While half of the states are polar, the other half are small-K states that are located semi-classically right below the separatrix.
Here the ergodic estimate predicts the dipole to anti-align with the field; the quantum result largely differs from this estimate, especially for PABN. Indeed this state lies outside the more ergodic energy range, which corresponds to \( \langle H_0 \rangle_n \ll \langle \mu \cdot E \rangle_n \).

In this region, even a polar state can be unstable and mix sufficiently with other states. However, as shown in 4.4, ergodicity does not cause a random orientation of the dipole as expected from reference 1. At \( E_z = 120 \text{ kV/cm} \), ergodicity predicts a nearly linear decrease of \( \mu_{n,z_L,M} \) with increasing energy.

Outside of the \( \langle H_0 \rangle_n \ll \langle \mu \cdot E \rangle_n \) regime, Table 4.2 shows that the \( F \) values are continually closer to the ergodic limit \( F_e \) in OABN than PABN for both types of states. For example, \(|15 4 1\rangle\) in OABN is nearly chaotic with \( F/F_{e,OABN} = 0.84 \), while the small-K state with the same \( J \) in PABN, \(|15 1 1\rangle\), is slightly further from chaos with \( F/F_{e,PABN} = 0.75 \). This means that a given initial rotational state in OABN is more mixed and likely to be unstable than in PABN. This result was anticipated from figure 4.7. Nevertheless, Table 4.2 shows how few of the states are nearly chaotic for both molecules, as the majority of \( F \) values are far away from the corresponding ergodic limit for each molecule.

4.3.2 Rotated Dipole Moment

To understand the impact the direction of the dipole relative to the body axes makes on the ergodicity of the system, we rotate the dipole to along the \( J_a \)-axis, the \( J_z \)-axis in the prolate representation, without a loss of generality.‡

When the dipole is artificially rotated to lie along the \( J_a \)-axis, the initial states sep-

‡The dipole can alternatively be rotated to along the \( J_c \)-axis, which is the \( J_z \)-axis in the oblate representation. Doing so will separate states in two groups according to the parity of \( K_c \). This will have a nearly equivalent effect in the oblate representation as rotating the dipole to the \( J_a \)-axis in the prolate representation.
arate into the two remaining symmetry classes, \( E = \{E_+, E_-\} \) and \( O = \{O_+, O_-\} \), which correspond to states with even and odd \( K \). This means that the basis states will not have as many other states to mix with as when the dipole is rotated off-axis.

In order to find the degree of chaos given prior constraints, we separate the initial states by the parity of \( K \) and then calculate the measures of ergodicity on only \( E \) parity states without a loss of generality. The question then arises of whether the degree of ergodicity of OABN and PABN will change when we only look at the mixing between \( E \) parity states.

**Figure 4.9:** Shows that the number of avoided crossings with \( \Delta E_{i,i+1} < 0.01 \text{ cm}^{-1} \) for the first 700 eigenstates in OABN for \( \mu_0 \), the original dipole (solid), is much larger than for \( \mu_R \), the artificially rotated dipole (dashed).

When we compare the number of avoided crossings in the energy levels of OABN with the artificially rotated dipole (\( \mu_R \)) versus the original dipole (\( \mu_0 \)), we find a significant reduction of avoided crossings for \( \mu_R \) as shown in Table 4.9. This is to be expected since only states with with the same parity of \( K \) can interact when the dipole lies upon a single symmetry axis, which reduces the amount of mixing between levels.

Figure 4.10 displays the percent of initial states, from the same energy range as in figures 4.5(b) and 4.6(b), with \( P(a|a)'s \) below a specific value for \( \mu_R \). This figure
shows how a larger percentage of initial rotational states from the $E$ symmetry class have a lower value of $P(a|a)$ for OABN than PABN up until $P(a|a) \sim 0.1$. After these curves intersect, a larger percentage of initial states with $P(a|a) > 0.1$ have lower values of $P(a|a)$ in PABN than in OABN. This shows that the direction of the dipole has a large impact on the amount of phase space accessed by an initial rotational state.

![Figure 4.10](image)

**Figure 4.10**: A plot of the percent of initial states below a given $P(a|a)$ value, where the blue line represents OABN and the red represents PABN. A larger fraction of OABN’s states are below a specific value of $P(a|a)$ than for PABN up until $P(a|a) \sim 0.1$. After these curves intersect, a larger percentage of initial states with $P(a|a) > 0.1$ have lower values of $P(a|a)$ in PABN than in OABN.

Table 4.3 shows $N_{a,\infty}$ and $\cal F$ for a range of small-K and polar initial states in both molecules with $\mu_R$, which features many of the same trends as in Table ???. The exceptions include the following. All of the states in PABN with the rotated dipole feature much lower $\cal F/\cal F_e$ values, where $\cal F$ is not even close to the ergodic limit $\cal F_e,\mu_R = 1/3$. However, the $\cal F/\cal F_e$ values for OABN with the rotated dipole remain nearly the same as those for the original dipole, even though $N_{a,\infty}$ is much smaller for $\mu_R$. This illustrates how important it is to measure ergodicity relative to prior constraints.

The polar states for PABN also no longer feature a distinct drop of ergodicity be-
tween the first two polar states $|6\ 6\ 1\rangle$ to $|8\ 8\ 1\rangle$. Instead, the ergodicity decreases gradually with increasing $J$. The highest energy polar state $|18\ 18\ 1\rangle$ is also slightly less ergodic in OABN than in PABN for the artificially rotated dipole, as anticipated from figure 4.10.

<table>
<thead>
<tr>
<th>molecule</th>
<th>state</th>
<th>$\langle H_{\text{tot}} \rangle$</th>
<th>$N_{a,\infty}$</th>
<th>$\mathcal{F}$</th>
<th>$\mathcal{F}/F_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OABN</td>
<td>polar $</td>
<td>6\ 6\ 1\rangle$</td>
<td>5.00</td>
<td>16.13</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>polar $</td>
<td>8\ 8\ 1\rangle$</td>
<td>7.61</td>
<td>6.42</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>polar $</td>
<td>14\ 14\ 1\rangle$</td>
<td>20.63</td>
<td>3.14</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>polar $</td>
<td>18\ 18\ 1\rangle$</td>
<td>33.4</td>
<td>2.5</td>
<td>0.06</td>
</tr>
<tr>
<td>small-K</td>
<td>$</td>
<td>10\ 2\ 1\rangle$</td>
<td>4.95</td>
<td>35.9</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>11\ 2\ 1\rangle$</td>
<td>5.84</td>
<td>40.6</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>15\ 4\ 1\rangle$</td>
<td>11.04</td>
<td>52.7</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>22\ 6\ 1\rangle$</td>
<td>23.22</td>
<td>59.8</td>
<td>0.29</td>
</tr>
<tr>
<td>PABN</td>
<td>polar $</td>
<td>6\ 6\ 1\rangle$</td>
<td>5.13</td>
<td>7.4</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>polar $</td>
<td>8\ 8\ 1\rangle$</td>
<td>10.77</td>
<td>6.5</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>polar $</td>
<td>14\ 14\ 1\rangle$</td>
<td>35.97</td>
<td>4.9</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>polar $</td>
<td>18\ 18\ 1\rangle$</td>
<td>60.00</td>
<td>4.1</td>
<td>0.08</td>
</tr>
<tr>
<td>small-K</td>
<td>$</td>
<td>10\ 0\ 1\rangle$</td>
<td>3.33</td>
<td>15.5</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>11\ 0\ 1\rangle$</td>
<td>4.00</td>
<td>17.7</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>15\ 2\ 1\rangle$</td>
<td>7.78</td>
<td>33.0</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>23\ 2\ 1\rangle$</td>
<td>17.28</td>
<td>42.4</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 4.3: $\langle H_{\text{tot}} \rangle$, $N_{a,\infty}$, $\mathcal{F}$, and $\mathcal{F}/F_e$ for OABN and PABN with $\mu_R$. Here we show the $\langle H_{\text{tot}} \rangle$ in units of (cm$^{-1}$), $\Delta E$, $N_{a,\infty}$ and $\mathcal{F}$ for a range of initial states from OABN and PABN. The ergodic limit for each molecule with $\mu_R$ is $F_{e,\mu_R} = 1/3$ for both molecules. While half of the states are polar, the other half are small-K states that are located semi-classically right below the separatrix.

Another difference between the two dipoles is that the first small-K state for OABN and PABN in Table 4.3 now has a lower $\mathcal{F}$ value than the second highest energy small-K state for OABN, $|11\ 2\ 1\rangle$, and all of the other small-K states for PABN. To
Figure 4.11: $P(a|a)$ of the basis states ordered by increasing $J$ and from $K = [J, -J]$ for OABN with (a) the original dipole and (b) the rotated dipole. At low $J$, the ergodicity varies nontrivially depending on proximity to the separatrix. For $J = 10$, the basis states nearest the separatrix start to have the lowest $P(a|a)$. The rotated dipole features an enhancement of $P(a|a)$ at the “polar” state, with respect to the $J_c$-axis at $K = 0$, which means chaos does not spread far for the separatrix region.

examine this further, we examine $P(a|a)$ ordered by increasing $J$ and range of $K = [J, -J]$ for OABN in figure 4.11 and for PABN in figure 4.12. The inset features a close up view of the plot for $J = 10$, and $|K| \leq 8$. The state semi-classically right below the separatrix for $J = 10$ is $|10 \pm 3 \rangle$ for OABN and $|10 0 1 \rangle$ for PABN.

For low $J$, the $P(a|a)$ values of each state vary nontrivially with respect to their
Figure 4.12: Shown is $P(a|a)$ for a group of states with $J = 10$ in order of decreasing $K$ for PABN with (a) the original dipole and (b) the rotated dipole. The rotated dipole features an enhancement of $P(a|a)$ at the “polar” state, with respect to the $J_c$-axis at $K = 0$, while the same state has the smallest $P(a|a)$ for the original dipole.

proximity to the separatrix. As $J$ increases, the states closest to the separatrix have lower values of $P(a|a)$ than the polar states and thus, become more ergodic than the polar states.

When the dipole is oriented along the $J_a$-axis (Figures 4.11(b) and 4.12(b)) , the $P(a|a)$’s values at $J \geq 10$ are nearly symmetric with respect to $K = 0$ and there is an enhancement of the values of $P(a|a)$ at $K = 0$. In terms of dynamics, the chaotic
regions do not spread as far from the separatrix when the dipole is rotated, and thus the states near $K = 0$ are less likely to mix and become unstable.

For the original dipole in OABN (Figure 4.11(a)), the $P(a|a)$'s values are not symmetric with respect to $K = 0$, as more clearly shown in the inset for $J = 10$, $|K| \leq 8$. The $K = -3$ state has the smallest value of $P(a|a) = 0.009$ with $F = 0.47$, which is to be expected as this state is semi-classically located right below the separatrix. However, the classically degenerate $K = 3$ state has a larger $P(a|a) = 0.010$ with $F = 0.40$. Upon changing only the $z$-component of the original dipole to be positive, $\mu'_{0,z} = |\mu_{0,z}|$, the $P(a|a)$ values for the $K = 3$ and $K = -3$ states switch. Thus, the direction of the dipole greatly impacts the dynamics of a given initial state.

For the original dipole in PABN (Figure 4.12(a)), $P(a|a)$ is also approximately symmetric about $K = 0$ for $J \geq 10$, but the $K = 0$ state has the smallest value of $P(a|a)$ and has $F = 0.329$. In this case, the slightly off-axis dipole of PABN allows for chaos to spread further than when the dipole points along the $J_a$-axis, as indicated by the lower values of $P(a|a)$.

The most important thing to draw by comparing Figures 4.11 and 4.12 and Table 4.2 and 4.3 is that the asymmetry of the molecule largely determines the degree of ergodicity of the system. However, the orientation of the dipole does impact the amount of mixing of initial states and the number of avoided crossings in the energy spectrum.

4.4 Conclusion

In this work, we examined the phase space transport of OABN and PABN. When the Stark interaction is much greater than the rotational energy, we find the projection of the dipole onto the lab-frame $z$-axis closely follows the microcanonical average for
both molecules. PABN showed deviations from the classical microcanonical average of the dipole, where the projection of the dipole onto the lab-frame z-axis is larger than the ergodic estimate. This is due to non-ergodicity and shows that the dipole aligns more with the field for PABN than OABN at low rotational energies.

Outside of this region, the ergodicity of the states decreases gradually with energy, and the phase space is partially chaotic, mixed with regions of chaos near the separatrix and near-integrability near the $J_e$-axis. Therefore, we find the division of eigenstates into the first and second 700th energy levels as in reference 1 a convenient, but arbitrary division of states to determine the average behavior of each system. Our results show that the eigenstates with lower energy tend to be more mixed by the Stark interaction. Hence a nearest-neighbor distribution for these set of states would tend to produce a more Wigner-like distribution than outside this energy range, especially for OABN, whose basis states are nearly all chaotic at lower energy.

When comparing the two different types of states, the significantly larger values of $F$ for the small-K states at a certain energy show that they are significantly more ergodic than the polar states around that same energy. As previously stated, the polar states are located much further from the separatrix, which makes them more stable upon perturbation than the small-K states and less likely to mix with other states. Another reason why the polar states are more localized in phase space could be because they have a much faster classical period than the small-K states for a given $J$. This means they would have a greater tendency to rotationally average out the perturbation of the electric field. This helps explain why the energy eigenstates that do not follow the linear trend for $\mu_{n,zL,M}$ in PABN are largely composed of polar states.

As energy increases, the phase space becomes mixed with slightly chaotic small-$K$ states and more localized polar states. Between the two molecules, the chaos was able
to spread much further from the separatrix for OABN and the basis states evolved consistently more ergodically than in PABN. Although both molecules are far from global chaos, a given initial rotational state in OABN mixes stronger and explores much more of phase space than in PABN. Consequently, the energy levels in OABN will be tend to repel more and feature wider avoided crossings than in PABN. This is consistent with the corresponding nearest-neighbor level distributions for the 700 lowest energy eigenstates calculated in reference 1. A larger percent of avoided crossings in PABN are likely to be nonadiabatic than in OABN. This is a strong cause for the experimental and theoretical discrepancies observed in OABN at high field strengths. For future work, more rigorous calculations should be done on the avoided crossings to determine precisely how many of the crossings will be nonadiabatic and how this impacts deflection.

When we rotated the direction of their dipoles to along the $J_a$-axis, we found that the ergodicity given prior constraints for PABN drastically reduced. The ergodicity given prior constraints remained nearly the same for OABN. However, the number of avoided crossings for OABN significantly reduced by rotating the dipole. This provides insight on why experimental and theoretical discrepancies in the MBD of rigid asymmetric top molecules have only been reported when the dipole moment is off-axis.56,1,57,58
5.1 Introduction

Intramolecular Vibrational Energy Redistribution (IVR) describes the energy flow from an initially excited bond to other bonds throughout molecule. The initially excited vibrational state of the molecule is referred to as the bright state, and the background of states, inaccessible by the initial excitation, are referred to as the dark states. The bright state is typically created through direct vibrational excitation using a narrow laser pulse. The width of the laser pulse determines whether a single or
superposition of bright states will be created.\textsuperscript{11}

In this chapter, we provide a general picture of IVR in Section 5.2 and its different regimes in Sections 5.3 and 5.4. We then review the Harmonic approximation for IVR in Section 5.5. Polyatomic molecules are quantum in nature. However, studying the classical dynamics of IVR not only provides physical intuition, but it also provides insight on the possible quantum mechanisms for energy flow. We discuss this in Section 5.6. We also discuss the classical-quantum correspondence in the harmonic basis in Section 5.7.

5.2 Zeroth Order Picture

A zeroth order picture\textsuperscript{71,11} provides a very general description of the IVR process. The bright state \{\ket{s}\} is strongly coupled by the potential to a set of dark states \{\ket{l}\}. The dark states \{\ket{l}\} are then weakly coupled to a near continuum of dark states \{\ket{q}\}. The \textit{m}th eigenstate of the full vibrational Hamiltonian using a harmonic basis,\textsuperscript{71}

\begin{equation}
\ket{m} = C_{m,s}\ket{s} + \sum_l C_{m,l}\ket{l} + \sum_q C_{m,q}\ket{q}
\end{equation}

where $C_{m,i} = \langle m|i \rangle$ is an overlap coefficient. If the Hamiltonian is diagonalized with only the coupling $V_{sl}$ between $\ket{s}$ and \{\ket{l}\}, the zeroth order state can be expressed as a linear combinations of the initial eigenstates $\ket{n}$,

\begin{equation}
\ket{s} = \sum_n C_{n,s}\ket{n}
\end{equation}
The resulting spectral distribution of $|C_{n,s}|^2$ features sharp peaks at each $|n\rangle$ contained by an envelope with spread $\Gamma$. However, as a result of the indirect coupling between $|s\rangle$ to the near continuum of dark states $|q\rangle$, each of the spectral peaks will feature a broadening by $2\gamma$. The typical distance between resonance peaks is $\epsilon$. Consequently, the states $|n\rangle$ are often referred to resonance states.

The time-evolution of the bright state,

$$|s(t)\rangle = \sum_m \exp(-iE_m t) C_{m,s}(E_m)|m\rangle$$

(5.3)

where the spectral coefficients are $|C_{s,m}(E)|^2$ when both the coupling to the dark states $\{|l\rangle\}$ and to the near continuum of states $\{|q\rangle\}$ are included. (See Figure 5.1(a)).

The survival probability can be found by converting the sum over $m$ into an integral,

$$P_s(t) = |\langle s|\Psi(t)\rangle|^2 = \int dE \rho(E)|C_{s,m}(E)|^2 \exp(-iEt/\hbar)$$

(5.4)

where $\rho(E)$ is the density of eigenstates. Figure 5.1(b) shows the survival probability for a constant density of states. This figure shows how there are three relevant timescales in this zeroth order picture. The initial decay of the bright state is dictated by the spread of the spectral envelope and goes as $\sim e^{-\Gamma t}$. The decay of recurrences goes as $\sim e^{-\gamma t}$. The time period between recurrences $\tau \propto \frac{1}{\epsilon}$.

The characteristic time scales characterize three different regimes of IVR: Sparse (nonstatistical), Intermediate, and Statistical.
Figure 5.1: (a) Spectral coefficients $|C_{s,m}(E)|^2$ from IVR process for initial state $|s\rangle$ with spectral envelope of width $\Gamma$, resonance width $2\gamma$, and distance between peaks $\epsilon$. (b) Survival probability of initial bright state $|s\rangle$ with constant density of states.
5.3 **Statistical IVR**

Molecules relax statistically when the zeroth order state $\ket{s}$ couples to a dense manifold of dark states $\{\ket{l}\}$ and the resonances are strongly overlapping, where $\Gamma \gg \epsilon$.\(^{72}\) In this case, the IVR features an irreversible decay, meaning no longterm recurrences persist. Molecules with at least 6-10 atoms\(^ {73}\) tend to feature this behavior and are well described by the RRKM and Bixon-Jortner\(^ {74}\) models\(^ \ast \) for unimolecular reaction rates. The decay of the initial state approximately goes as $P_s(t) = |\langle \psi | \psi(t) \rangle|^2 \sim \exp(-\Gamma t)$, where the decay rate $\Gamma$ is given by Fermi’s Golden rule,

$$\Gamma = 2\pi \langle V^2 \rangle \rho$$  \hspace{1cm} (5.5)

Here $\rho$ is the mean density of states and $\langle V^2 \rangle^{1/2}$ is the rms off-diagonal coupling.\(^ {74,75}\) Molecules such as those within the series $(\text{CX}_3)_3 \text{Y} - \text{C} \equiv \text{C} - \text{H}$ have been found to relax statistically for an initial excitation in the first overtone of the acetylenic CH stretch. Here X can be H, D or F and Y can be C or Si.\(^ {76}\)

The spectra of very large molecules is often described using a statistical approach.\(^ {77}\) The Brody Distribution\(^ {78}\) gives the distribution of spacings between adjacent energy levels and interpolates between uncorrelated ($\beta = 0$) and strongly correlated ($\beta = 1$) levels,

$$P(s) = a(1 + \beta)s^\beta \exp(-bs^{\beta+1})$$  \hspace{1cm} (5.6)

where $b = \Gamma \left( \frac{2+\beta}{1+\beta} \right)$. In the limit of completely uncorrelated levels, $\beta = 0$, the energy

\(^ \ast \)The Bixon-Jortner model\(^ {74}\) takes the limit where the bright state couples to an infinite number of dark states.\(^ {72}\)
level statistics are described by a Poissonian Distribution. In the limit of strongly
correlated levels, $\beta = 1$, the energy level statistics are described by a Wigner Distri-
bution, which derives from the Gaussian Orthogonal Ensemble from Random Matrix
Theory (RMT). $^{78,77}$

5.4 Sparse IVR

In the Sparse regime, the initial bright state couples to a small number of dark states. $^{72}$
The resonances are well separated ($\Gamma << \epsilon$), and the recurrences of the initial state
will decay very little in time. When the bright state is coupled to one or a few dark
states, quantum beating is observed. $^{75}$ A well-known example of this is the local
mode doublets in $\text{H}_2\text{O}$, where the $\text{X} - \text{H}$ stretching modes behave as weakly coupled
Morse oscillators. Each oscillator represents a local mode $|n, \pm q\rangle$. In order to preserve
the symmetry of the molecule ($C_{2v}$), $^{79,80}$ the quantum states form symmetric and an-
tisymmetric combinations of the local modes,

$$|\Psi_{n,q}\rangle = \frac{1}{\sqrt{2}}\left(|n, q\rangle \pm |n, -q\rangle\right)$$  \hspace{1cm} (5.7)

which are referred to as doublets. Lawton and Child $^{19,20}$ found a semiclassical expres-
sion for the doublet splitting,

$$\Delta E_{nq} = \frac{2\hbar\omega_{nq}}{\pi} \exp\left[-\frac{1}{\hbar} \int_{\mathcal{C}} |p| \cdot dq\right]$$  \hspace{1cm} (5.8)

where $\omega_{nq}$ corresponds to the corresponding classical frequency of $|n, \pm q\rangle$ and $\mathcal{C}$ is
the path across the connecting the two classical invariant tori representing the local
modes. This exponential small splitting leads to energy transfer between the two lo-
cal modes on very long time scales. Heller and Davis later coined this phenomenon as “Dynamical Tunneling” and suggested it as a mechanism for IVR in polyatomic molecules.\(^{17}\)

In the case where quantum beating is not observed, the experimental spectrum can be modeled as a finite sum of Lorentzian line shapes with equal half-width at half-maximum \(\Gamma\),

\[
I(\omega) = \sum_{j=1}^{N} \frac{A_j \Gamma^2}{(\omega - \omega_j)^2 + \Gamma^2}
\]  

(5.9)

where \(\omega_j\) is the location of the \(j\)th resonance. Such has been done\(^{81}\) for the experimental spectrum of rotationally cold benzene (\(\sim 5\)K) excited to the third and fourth overtone.\(^{82,83,84,85}\)

5.5 HARMONIC APPROXIMATION

The vibrations of a molecule can be described using Canonical Van-Vleck Perturbation Theory (CVPT).\(^{86}\) The effective vibrational Hamiltonian of the molecule under this perturbative approach,

\[
\hat{H} = \hat{H}_0 + \hat{V}
\]  

(5.10)

where the zeroth order Hamiltonian \(\hat{H}_0\) is given by the Dunham Expansion\(^{87}\)

\[
\hat{H}_0(\hat{n}_1, \cdots \hat{n}_D) = E_0 + \sum_{i=1}^{D} c_i (\hat{n}_i + \frac{d_i}{2}) + \sum_{i,j \geq i} c_{ij} (\hat{n}_i + \frac{d_i}{2})(\hat{n}_j + \frac{d_j}{2}) + \cdots
\]  

(5.11)
\[ n_i = a_i^\dagger a_i \] give the number of quanta in the \( i \)-th mode, \( a_i^\dagger, a_i \) are creation and annihilation operators, and \( d_i \) is the degeneracy of the \( i \)-th mode. The zeroth order Hamiltonian is diagonal in a harmonic basis. The perturbation \( \hat{V} \) describes anharmonic couplings between different vibrational modes and contains off-diagonal terms in the harmonic basis. It can be expanded in creation and annihilation operators,

\[
\hat{V} = \sum_m \phi_m \prod_j (a_j^\dagger)^{m_j^+} (a_j)^{m_j^-} + \text{h.c.} 
\]  

(5.12)

where \( m = \{m_1^\pm, m_2^\pm, \cdots, m_n^\pm\} \) describe the number of quanta transferred between a set of modes. As an example, consider the coupling for a 2 : 1 bend-stretch mode,

\[ \hat{V}_{2:1} = k_{12} \hat{Q}_1 \hat{Q}_2^2, \]  

where \( \hat{Q}_i = \frac{1}{\sqrt{2}} (a_i^\dagger + a_i) \) are position operators and the physical units have been absorbed into \( k_{12} \). Expanding this in creation and annihilation operators,

\[
\hat{V}_{2:1} = \frac{k_{12}}{2\sqrt{2}} \left[ (a_1^\dagger + a_1)(a_2^\dagger + a_2)^2 \right] = \frac{1}{2\sqrt{2}} \left[ (a_1^\dagger + a_1)(2a_2^\dagger a_2 + a_2 a_2^\dagger + a_2^\dagger a_2 + 1) \right] 
\]  

(5.13)

The parameters for the effective Hamiltonian can found by fitting it with spectroscopic data.

5.6 Classical Approach

A ball and spring model is often used to describe bond excitations, which assumes a nearly harmonic interaction and harmonic basis. Anharmonicities in the bond-vibrations are then expanded to a specific order, which results in the Dunham Expansion (Equation 5.11). However, a Morse Potential incorporates all orders of bond
anharmonicity,

\[ V(x) = D_e \left( 1 - e^{-a(x-x_e)} \right)^2 \] (5.14)

where \( x_e \) is the bond distance at equilibrium, \( D_e \) is the dissociation energy and \( a \) characterizes the width of the well. The Morse Potential has the following features,

1. Strong repulsion at short internuclear distance

2. Asymptotic to vanishing force at large internuclear distance

3. Frequencies reduce as energy increases

Figure 5.2 shows the Morse and Harmonic potentials with the bound state quantized energy levels. While the quantum energy levels are equally spaced for the Harmonic oscillator, \( E_n = \hbar \omega (n + \frac{1}{2}) \), the distances between energy levels get smaller with \( n \) for the Morse oscillator, \( E_n = \hbar \omega (n + \frac{1}{2}) - \left( \hbar \omega (n + \frac{1}{2}) \right)^2 / 4D_e \). This figure illustrates how a Morse oscillator behaves harmonically for low energies. This justifies the Harmonic approximation at low energies. However, the Harmonic Potential predicts an increasingly large attraction as \( x \to \infty \), whereas the Morse Potential correctly describes dissociation. A local mode corresponds to a vibrational mode within a specific bond.

We thus model each of the molecule’s local modes as a Morse Oscillators,

\[ H_0(q_i, p_i) = \frac{p_i^2}{2m_i} + D_{e,i} \left( 1 - e^{-a_i(q_i-q_{e,i})} \right)^2 \] (5.15)

In this classical approach, we are interested in determining the impact of anharmonic couplings on the invariant tori of the system. For a system of \( N \) Morse oscillators, the \( N \) dimensional tori are defined by a set of \( N \) actions \( I = \{ I_1, I_2, \cdots I_N \} \) and angles
$n = 0$
$n = 1$
$n = 3$ 
$n = 4$
$n = 5$
$n = 6$
$n = 7$
$n = 8$
$n = 9$

Figure 5.2: Plot of the Morse and Harmonic potentials curves with their corresponding bound state quantized energy levels. The Morse potential describes a vanishing force at long distance, where the Harmonic potential describes increasing attraction with increasing bond distance.
\[ \phi = \{ \omega_1 t + \phi_0, \omega_2 t + \phi_0, \ldots \omega_N t + \phi_0 \} \]. The action variable for a single Morse oscillator at energy \( E \), \(^{39}\)

\[
I_j = \int_C p_j dq_j = \int_{q_-}^{q_+} \sqrt{2m_i} \left[\frac{E - D_{e,j} \left(1 - e^{-a_j(q_j - q_{e,j})}\right)}{a_j}\right]^2 dq_j = \frac{\sqrt{2m_j D_{e,j}}}{a_j} \left[1 - \sqrt{1 - \frac{E}{D_{e,j}}} \right] \tag{5.16}
\]

where \( q_{j,\pm} = q_{e,j} + \frac{1}{a_j} \ln \left[\frac{D_{e,i+}\sqrt{D_{e,i+E}}}{D_{e,i-E}}\right] \). This expression can be inverted to express the Morse Hamiltonian (equation 5.15) in terms of the action,

\[
H_0(I_j) = \omega_0 I_j \left(1 - \frac{I_j}{2I_{b,j}}\right) \tag{5.17}
\]

where \( I_{b,j} = \frac{\sqrt{2mD_{e,j}}}{a_j} \) is the action at the dissociation energy and \( \omega_{0,j}^2 = \frac{2D_{e,i}}{m} \). The canonically conjugate angle variable is thus, \(^{39}\)

\[
\phi_j = \frac{\partial S}{\partial I_j} = \frac{\partial}{\partial I_j} \int_{q_{j,-}}^{q_j} p_j(E, I_j, q'_j) \ dq'_j = \sin^{-1} \left[\frac{(1 - \frac{I_j}{I_{b,j}})e^{a_j q_j} - 1}{\sqrt{(2 - \frac{I_j}{I_{b,j}}) \frac{I_j}{I_{b,j}}}}\right] + \frac{\pi}{2} \tag{5.18}
\]

The angle evolves in time \( \phi_j = \omega_j t + \phi_0 \), where

\[
\omega_j(I_j) = \frac{\partial H_0,I_j}{\partial I_j} = \omega_{0,j} \left(1 - \frac{I_j}{I_{b,j}}\right) \tag{5.19}
\]
and the action is a constant of motion, \( I_j = \text{const} \). The relationship between the original variables and the action-angle variables,

\[
q_j(I_j, \phi_j) = \frac{1}{a_j} \ln \left[ \frac{1 - \sqrt{1 - \lambda_j^2 \cos \phi_j}}{\lambda_j^2} \right] \tag{5.20}
\]

\[
p_j(I_j, \phi_j) = \frac{\partial S}{\partial q_j} = \frac{m_j \omega_0 \lambda_j}{a_j} \sqrt{1 - \lambda_j^2 \sin \phi_j} \frac{1 - \sqrt{1 - \lambda_j^2 \cos \phi_j}}{1 - \sqrt{1 - \lambda_j^2 \cos \phi_j}} \tag{5.21}
\]

where \( \lambda_j = \left(1 - \frac{I_j}{I_{b,j}}\right) \).

### 5.6.1 Classical Model for a General Triatomic Molecule

A triatomic molecule with only stretch modes can be modeled by two identical Morse oscillators with a kinetic coupling, \(^{89,90,91,15}\)

\[
H(I, \phi) = H_0(I_1) + H_0(I_2) - \epsilon p_1(I_1, \phi_1)p_2(I_2, \phi_2) \tag{5.22}
\]

where \( \epsilon \) is the strength of the coupling and the momentum in action-angle variables is given by equation 5.21. In the absence of the perturbation, the system is completely integrable, the 3D constant energy hypersurface is foliated by 2D invariant tori. The kinetic coupling is a complicated function of actions and angles. However, it can be expanded into a Fourier series in orders of smallness of \( \frac{I_1}{I_{b,1}} \) and \( \frac{I_2}{I_{b,2}} \),

\[
\epsilon p_1(I_1, \phi_1)p_2(I_2, \phi_2) = \frac{2 \epsilon D \alpha_1 \lambda_2 \sqrt{1 - \lambda_1^2} \sqrt{1 - \lambda_2^2 \sin \phi_1 \sin \phi_2}}{(1 - \sqrt{1 - \lambda_1^2 \cos \phi_1})(1 - \sqrt{1 - \lambda_2^2 \cos \phi_2})} = \epsilon \sum_{n_1,n_2} f_{n_1,n_2}(I_1, I_2) \cos(n_1 \phi_1 + n_2 \phi_2) \tag{5.23}
\]
where we set \( m = 1, \omega_{0,1} = \omega_{0,2} = 1, h = 1, \) and \( a = \frac{1}{\sqrt{2Dc}}. \) The action-dependent Fourier coefficients \( f_{n_1,n_2}(I_1, I_2) \) decreases in amplitude as the order of the resonance, \( n = |n_1| + |n_2|, \) increases.\(^{92} \) To the smallest order in action, \( O(\sqrt{I_1I_2}) \),

\[
\epsilon p_1(I_1, \phi_1)p_2(I_2, \phi_2) = 2\epsilon \sqrt{I_1I_2} \left[ \cos(\phi_1 + \phi_2) + \cos(\phi_1 - \phi_2) \right]
\]  

(5.24)

The molecule dissociates in the limit \( \omega_{1,2} \to 0, \) and the \( \cos(\phi_1 + \phi_2) \) term will not be resonant over the action domain \( W_a = \{(I_1, I_2) \in \mathbb{R}^2 \mid \omega(I_1) \geq 0, \omega(I_2) \geq 0\}. \) However, the \( \cos(\phi_1 - \phi_2) \) terms will be resonant over \( W_a. \) Specifically it will be a \((1,1)\) resonance for \( \omega_1(I_1) = \omega_2(I_2) \to I_1 = I_2. \) When the other Fourier term is either averaged out or eliminated via Lie Series Expansion, the Hamiltonian takes the simple form,

\[
H(I, \phi) = \sum_{j=1,2} I_j \left( 1 - \frac{I_j}{4D} \right) - 2\epsilon \sqrt{I_1I_2} \cos(\phi_1 - \phi_2)
\]  

(5.25)

where \( I_b = 2D \) given our choice of parameters. The Hamiltonian greatly simplifies when we use the following canonical transformation \( C : (I, \phi) \to (J, \psi), \)

\[
J_1 = (I_1 - I_2)
\]  

(5.26)

\[
J_2 = (I_1 + I_2)
\]  

(5.27)

\[
\Psi_1 = \frac{1}{2}(\phi_1 - \phi_2)
\]  

(5.28)

\[
\Psi_2 = \frac{1}{2}(\phi_1 + \phi_2)
\]  

(5.29)
where \( J_2 = I_1 + I_2 \) describes the total action, and \( J_1 = I_1 - I_2 \leq J_2 \) describes the difference in action.

\[
H(J, \Psi) = J_2 - \frac{J_2^2}{8D} - \frac{J_1^2}{8D} - \frac{\epsilon}{2} \sqrt{J_2^2 - J_1^2} \cos 2\psi_1
\]  

(5.30)

The Hamiltonian is cyclic in \( \Psi_2 \), which means the action \( J_2 \) is a constant of motion. This means that the total action is conserved, which quantum mechanically relates to the conservation of polyad. We elaborate further on this point in Section 5.7. The nature of the phase space structures depend on the value of \( J_2 \). Hamilton’s equations for \((J_1, \Psi_1)\),

\[
\dot{\Psi}_1 = \frac{\partial H}{\partial J_1} = -\frac{J_1}{4D_e} + \frac{J_1 \epsilon \cos 2\Psi_1}{2\sqrt{J_2^2 - J_1^2}}
\]

(5.31)

\[
\dot{J}_1 = -\frac{\partial H}{\partial \Psi_1} = -\sqrt{J_2^2 - J_1^2} \epsilon \sin 2\Psi_1
\]

(5.32)

which shows there will be fixed points at \( J_1 = 0, \Psi_1 = 0, \pi, \frac{3\pi}{2}, 2\pi \). The nature of these fixed points can be determined by finding the eigenvalues of the stability matrix at each of these fixed points. For \( J_2 < J_{2B} = 2\epsilon D_e \), all of the fixed points are elliptic. At \( J_{2B} \), the system undergoes a bifurcation. For \( J_2 > 2\epsilon D_e \), the fixed points at \( J_1 = 0, \Psi_1 = 0, \pi, 2\pi \) become hyperbolic, and a separatrix emerges. This behavior is shown in figures 5.3(a) and 5.3(b), which show a phase-space portrait in the \((J_1, \Psi_1)\) plane for \( J_2 < 2\epsilon D_e \) and \( J_2 > 2\epsilon D_e \) respectively.

For librational trajectories, the difference in action, \( J_1 \), will vary from positive to negative values along a single trajectory. This corresponds to energy being exchanged between the two modes during one period. This behavior correspond to normal modes of the molecule. For rotational trajectories, \( J_1 \) will either be positive or negative. This
Figure 5.3: Phase Space portraits in the \((J_1, \Psi_1)\) plane for unitless parameters \(D_e = 10\), \(\epsilon = 0.08\) and \(J_{2B} = 1.6\). In figure (a), \(J_2 = 1 < J_{2B}\), and all of the fixed points are elliptic. In figure (b), \(J_2 = 7 > J_{2B}\), and the fixed points at \(J_1 = 0, \Psi_1 = 0, \pi, 2\pi\) will be hyperbolic.
corresponds to energy being localized in a single bond, \( I_1 \) or \( I_2 \) respectively. The rotational trajectories therefore correspond to local modes of the molecule.\(^{39,89,90,91}\)

To find the corresponding quantum energies, the classical actions of the individual Morse Oscillators are first EBK quantized, \( I_1 = n_1 + \frac{1}{2} \) and \( I_2 = n_2 + \frac{1}{2} \), where \( n_1, n_2 \in \mathbb{Z} \) are the quantum number of each oscillator. This makes the total action \( J_2 = n_1 + n_2 + 1 = n + 1 \) and action difference \( J_1 = n_1 - n_2 = m \). The corresponding quantum matrix elements can be found as described in Chapter 2, Section 2.3, and the full Hamiltonian (equation 5.30) can be diagonalized to find the eigenvalues and eigenfunctions. Alternately, the semiclassical splitting between local modes can be found using a tunneling integral along a path in which connects the modes through the separatrix.\(^{21} \dagger\). In doing so, one can show that the (1,1) resonance weakly couples the local modes, and the level splitting \( \Delta \) between them decreases as their classical trajectories get further from the separatrix.\(^{21,89}\) In the next section, we will discuss how resonances assist in dynamical tunneling.

As \( J_2 \) increases, the single resonance approximation no longer is valid, and \( J_2 \) no longer is a constant of motion. The system therefore becomes chaotic, and the nonresonant Fourier terms \( \cos(n_1\phi_1+n_2\phi_2) \), \( n_1, n_2 > 0 \) must be retained in the interaction.\(^{91}\)

5.7 Classical Quantum Correspondence

The classical-quantum correspondence between creation-annihilation operators and action-angle variables,

\[
a_j^\dagger \rightarrow \sqrt{I_j} e^{i\phi_j} \quad (5.33)
\]

\[
a_j \rightarrow \sqrt{I_j} e^{-i\phi_j} \quad (5.34)
\]

\(^{\dagger}\)See Chapter 3, Section 3.3 for an overview of the method
In CPVT, an anharmonic perturbation for a system of \(N\) oscillators has the form,

\[
V_q \sim (a_1^\dagger)^{q_1^+} (a_1)^{q_1^-} (a_2^\dagger)^{q_2^+} (a_2)^{q_2^-} \cdots (a_n^\dagger)^{q_n^+} (a_n)^{q_n^-} + \text{h.c.} \tag{5.35}
\]

where \(q = \{q_1^+, q_2^+, \cdots, q_N^+\}\) and the coefficients for the \(j\)-th oscillator are either \(q_j^+ > 0\), \(q_j^- = 0\) or \(q_j^+ = 0\), \(q_j^- > 0\). We define a resonance vector for \(q\),

\[
k_q = \{q_1^+ - q_1^-, q_2^+ - q_2^-, \cdots, q_N^+ - q_N^-\} \tag{5.36}
\]

For example, the resonance vector for the coupling, \(V_{2,1} \sim (a_1^\dagger)^2 (a_2) + \text{h.c.}\), is \(k = (2, -1)\). The corresponding polyad vectors, \(p_k\), are orthogonal to \(k\). The Polyad number,

\[
P_k = p_k \cdot \{\hat{n}_1, \hat{n}_2, \cdots, \hat{n}_N\},
\]

is a constant of motion.93

We verify this by considering the general coupling, \(V_{m,l} \sim (a_i^\dagger)^m (a_j)\) + h.c. with resonance vector \(k = m\hat{e}_i - l\hat{e}_j\).‡ For a single coupling in a \(N\) DOF system, there are \(N - 1\) possible Polyad vectors that are orthogonal to \(k\). We show the conservation of Polyad number for a nontrivial Polyad vector, \(p_k = l\hat{e}_i + m\hat{e}_j\), for demonstrative purposes. The commutation of the number operators for the \(i\)-th and \(j\)-th modes with the coupling,

\[
[\hat{n}_i, (a_i^\dagger)^m (a_j)\] = [a_i^\dagger a_i, (a_i^\dagger)^m (a_j)\] = a_i^\dagger [a_i, (a_i^\dagger)^m (a_j)\]

\[
= a_i^\dagger [m(a_i^\dagger)^{m-1}] (a_j)\] = m(a_i^\dagger)^m (a_j)\] \tag{5.37}
\]

\[
[\hat{n}_j, (a_i^\dagger)^m (a_j)\] = [a_j^\dagger a_j, (a_i^\dagger)^m (a_j)\] = (a_i^\dagger)^m [a_j^\dagger, (a_j)\] a_j \]

\[
= (a_i^\dagger)^m [-l(a_j)\] = -l(a_i^\dagger)^m (a_j)\] \tag{5.38}
\]

‡ Here \(\hat{e}_{i,j}\) are unit vectors corresponding to \(i\)-th and \(j\)-th component of \(k\).
\[ [\hat{n}_i, (a_i^\dagger)^m(a_j)^l] = [a_i^\dagger a_i, (a_j^\dagger)^l(a_i)^m] = -m(a_j^\dagger)^l(a_i)^m \quad (5.39) \]

\[ [\hat{n}_j, (a_i^\dagger)^m(a_j)^l] = [a_j^\dagger a_j, (a_j^\dagger)^l(a_i)^m] = l(a_j^\dagger)^l(a_i)^m \quad (5.40) \]

where we used the commutation identity \([a_i, a_j^\dagger] = \delta_{ij}\). The conservation of the Polyad number \(P = l\hat{n}_i + m\hat{n}_j\), can now be shown using the commutation relations above,

\[
\frac{dP}{dt} = \frac{1}{i\hbar} [P, V_{lm}] = (lm - ml)(a_i^\dagger)^m(a_j)^l + (-lm + ml)(a_j^\dagger)^m(a_j)^l = 0 \quad (5.41)
\]

The conservation of the other \(N - 2\) Polyad numbers, \(P = \hat{n}_k\) for \(k \neq i, j\), for this coupling can easily be shown as \([a_i, a_k^\dagger] = 0\). The corresponding classical expression for \(V_{m,l}\) in action angle variables,

\[
V_{ml}(I_i, I_j, \phi_i, \phi_j) \sim \sqrt{(I_i)^m(I_j)^l} \cos(m\phi_i - l\phi_j) \quad (5.42)
\]

where the nontrivial classically conserved Polyad is \(P_c = lI_i + mI_j\).

For \(M\) linearly independent resonance vectors, there will be \(N - M\) conserved polyad numbers. Quantum Mechanically, this means that Hamiltonian will block diagonalize according to states with the same set of Polyad numbers. Classically, this corresponds to reducing the effective degrees of freedom from \(N\) to \(M\). In order to find the reduced canonically conjugate action-angle variables, we can use a canonical transformation, \(C : (I, \phi) \to (J, P_1, P_2 \cdots P_{N-M}, \psi, \theta_1, \theta_2 \cdots \theta_{N-M})\) with
$(J, \psi) \in \mathbb{R}^M \times \mathbb{T}^M,$

$$
\begin{pmatrix}
J_1 \\
\vdots \\
P_{N-M-1} \\
P_{N-M} \\
\psi_1 \\
\vdots \\
\theta_{N-M-1} \\
\theta_{N-M}
\end{pmatrix} =
\begin{pmatrix}
A_{N \times N} & 0 \\
0 & B_{N \times N}
\end{pmatrix}
\begin{pmatrix}
I_1 \\
\vdots \\
I_{N-1} \\
I_{N-1} \\
\phi_1 \\
\vdots \\
\phi_{N-1} \\
\phi_{N}
\end{pmatrix}
$$

(5.43)

Here $A$ and $B$ are $N \times N$ matrices with the requirement, $AB^T = BA^T = I_N$ in order to be a symplectic transformation. The first $M \leq N$ rows of $A$ are given by the resonance vectors between the modes. The last $N - M$ rows of $B$ are given by the $N - M$ polyad vectors. The remaining portion of the coefficients are not unique.$^{94}$

One can then use this classical-quantum correspondence to study by the quantum spectroscopic Hamiltonian and the corresponding classical Hamiltonian.
6

Dynamical Tunneling Versus Fast Diffusion For a Non-convex Hamiltonian

6.1 **Introduction**

An unresolved question in the physical chemistry community is the nature of the 0.01-0.10 cm$^{-1}$ peak splittings that have been observed in high-resolution IR spectra of polyatomic molecules.\textsuperscript{15,95,96,97,98,99} These splittings are indicative of energy flow in the phase space of the molecule, induced by weak residual anharmonic couplings, and contain information on the long-time dynamics of the molecules. One hypothesis has been that the mechanism for this peak splitting is due to dynamical tunneling, though
no definitive proof has yet been given. Part of the problem in elucidating the mechanism of Intramolecular Vibrational Redistribution (IVR) is that it is first necessary to define a set of structures between which the energy redistribution occurs. One of the landmark papers in this field was a computational study by Stuchebrukhov and Marcus, in which they used empirical data to construct vibrational potential energy surfaces to determine the fine peak splittings in specific polyatomics. However, by working in a harmonic basis, they were required to diagonalize states within a 50 cm\(^{-1}\) window or larger in order to converge the calculations. Thus, while they were formally able to account for the 0.01-0.10 cm\(^{-1}\) peak splittings, they were required to invoke the concept of a “superexchange” mechanism between zeroth-order states of greatly differing energies. The harmonic basis therefore suffers from the opposite problem of the eigenbasis in attempting to define a reference point for IVR. Namely, while in the eigenbasis there is no IVR at all, in the harmonic basis there is too much IVR. Although the “superexchange” mechanism is formally correct, it is a basis-dependent notion and therefore somewhat unphysical. However, the superexchange mechanism can be more naturally understood in the context of dynamical tunneling in zeroth-order anharmonic Hamiltonians. 

A natural basis from which to define energy redistribution is given by the classical invariant tori of the Hamiltonian. The vibrational Hamiltonians of polyatomics are given by harmonic oscillators plus anharmonic terms. The anharmonicities are small in the low quantum number regime, which is generally the regime probed by experimentalists in IR spectroscopy. Thus, the KAM Theorem assures that almost all of the phase-space is filled with invariant tori. Semiclassically, one may associate quantum-mechanical wave functions with the invariant tori of actions \(I_1, \ldots, I_D\) =
\[ h(n_1 + \alpha_1/4, \cdots, n_D + \alpha_D/4) \]. Here the \( n_i \) are nonnegative integers, and the \( \alpha_i \) are the Maslov indices, which are usually equal to 2. The semiclassical energy spectrum is then obtained by setting \( E(n_1, \cdots, n_D) = H(I_1, \cdots, I_D) \), where \( H \) denotes the Hamiltonian. The method just described is the Einstein-Brillouin-Keller (EBK) quantization method, and the point is that, even for nearly integrable systems, it is still possible to semiclassically find a set of good quantum numbers \((n_1, \cdots, n_D)\) characterizing the energy spectrum. Spectroscopists attempt to determine the functional form of the energy dependence on the quantum numbers by fitting the spectral peaks to an Dunham-like expansion,\(^{87}\)

\[
E(n_1, \cdots, n_D) = E_0 + \sum_{i=1}^{D} a_i n_i + \sum_{i \leq j} a_{ij} n_i n_j + \sum_{i \leq j \leq k} a_{ijk} n_i n_j n_k \cdots \quad (6.1)
\]

What happens for medium-sized polyatomics is that energy flow between the tori destroys the good quantum numbers and leads to spectroscopically unassignable peaks. The peak splittings are sufficiently narrow that they are the result of long-time dynamics, on the order of thousands to hundreds of thousands of vibrational periods of the molecule. One possible culprit is mode mixing, whereby the peak splittings are the result of the formation of new “normal” modes. The relative strength of the different peaks is a measure of the relative contribution of the different “local” modes to the overall “normal” modes. In the language of classical mechanics, one would say that the peak splittings indicate that the vibrational dynamics reside on invariant tori lying inside resonance zones generated by the Hamiltonian. The main problem with this analysis is that these peak splittings are ubiquitous, and are already seen at low quantum numbers (3 and often less). At such low quantum numbers the anharmonicities in the vibrational Hamiltonian are sufficiently small that the resonance zones
should occupy only a small fraction of the total phase-space volume. Thus, it is improbable that invariant tori residing in the resonance zones could support a significant fraction of the vibrational eigenstates.

By similar reasoning, classical chaos is likely also an insufficient mechanism accounting for the peak splittings. While such a mechanism would be expected to dominate for large quantum numbers, the nearly integrable regime is the regime of interest in this paper. The remaining mechanism accounting for the peak splittings is slow between the invariant tori residing outside the resonance zones. Because the splittings are indicative of long-time dynamics, they are believed to be quantum-mechanical in nature, i.e., dynamical tunneling. For systems with $N = 2$ degrees of freedom, KAM tori act as barriers in phase space and prevent diffusion over the entire energy hypersurface. However, quantum mechanically a system can access classically disconnected regions of phase space via dynamical tunneling.\(^{15}\)

For systems $N > 2$ degrees of freedom, the resonance structure of the Hamiltonian forms a dense network in phase space known as the Arnol’d Web. In principle, a trajectory can ergodically traverse the entire energy hypersurface in the nearly-integrable regime by navigating the Arnol’d Web.\(^{103,70,102}\) For a general nonlinear system, the diffusion is expected to be exponentially slow, with a diffusion coefficient that scales as $e^{-c|\omega_{m,n}|/\sqrt{\lambda}}$. Here $\lambda$ denotes the perturbation strength, and $\omega_{m,n} \neq 0$ is known as the resonance detuning.\(^{70}\) This is referred to as Arnold Diffusion\(^{103}\) and has been observed in various systems.\(^{104,105,106,107,108,109}\) A few works have started to explore the impact of the Arnol’d Web in IVR.\(^{22,110,23}\) However, Arnold Diffusion can be extremely hard to detect numerically as a result of the errors that accumulate over exponentially long time segments.\(^{111,112}\)

Non-convex Hamiltonians are a special class of Hamiltonian functions in which the
diffusion along the resonance network is expected to be fast, where the rate of diffusion $O(\lambda)$. Given that dynamical tunneling generally occurs over long time periods, fast diffusion would be a worst case scenario as a viable competitor to dynamical tunneling. The question then arises on whether tunneling even plays a significant role in the rate of energy transfer in these types of systems. In this paper, we consider this worst case scenario. We show that tunneling still dominates classical transport in the nearly-integrable regime for a non-convex Hamiltonian, when the diffusion is expected to be fast.

It should be emphasized here that comparisons between dynamical tunneling and fast diffusion must be made in the few quantum-number regime. The reason for this is that for sufficiently high quantum numbers, quantum effects become unimportant, so classical transport would be expected to dominate any tunneling effects. For IR studies on polyatomic molecules, the few quantum-number regime is exactly the regime being probed. It is expected that quantum effects are important for these types of systems, and so a comparison between dynamical tunneling and classical diffusion rates is warranted.

However, in comparing quantum and classical energy flow rates, two key issues need to be properly addressed. First of all, does one include zero-point energy into the classical calculations? The problem is that in order to have a proper semiclassical simulation, zero-point energy must be taken into account. However, for a sufficiently large number of vibrational degrees of freedom, the zero-point energy may be so large that classically the molecule can dissociate, even in its ground state. Secondly, it is necessary to develop a criterion which can distinguish between genuine transport along the web and energy flow which is simply due to mode mixing. This is not necessarily a trivial point, since realistic systems have such a large density of states that it
becomes difficult to track which resonances are active at any given time. The solution to both problems is the construction of a synthetic Hamiltonian which does not classically dissociate with the inclusion of the zero-point energy, and which has an easily constructible Arnol’d Web, making it a simple matter to detect diffusion along the web.

In this paper we present numerical studies on a such a Hamiltonian, which support the consensus view that dynamical tunneling is likely significantly faster than classical diffusion in the nearly-integrable regime, even when the classical diffusion is expected to be fast. Hence tunneling is the main cause of the fine peak splittings observed in IR spectra. Though constructed by hand, the Hamiltonian we present has a number of characteristics in common with vibrational Hamiltonians.

This paper is organized as follows: In Section 6.2 we present the Hamiltonian which we will use for our subsequent calculations, describe its action space geometry and its consequences, and show how to construct its Arnol’d Web. In Section 6.3 we describe both the classical and quantum calculations, and how we compare dynamical tunneling and classical rates with the results of the calculations. In Section ?? we present our results for $\hbar = 1$ and in the classical limit $\hbar \to 0$. We conclude in Section 6.6.

6.2 The Model

We will work with the D-dimensional Hamiltonian given in action-angle variables,

$$H(I, \phi) = H_0(I) + \lambda V(I, \phi)$$  \hspace{1cm} (6.2)
with \((\mathbf{I}, \phi) \in \mathbb{R}^D \times \mathbb{T}^D\). Here \(H_0\) resembles nearly a Morse oscillator Hamiltonian,

\[
H_0(\mathbf{I}) = \sum_{i}^{D} (\alpha_i I_i - \beta_i I_i^2)
\]

with parity dependent parameters \(\alpha_j\) and \(\beta_j\)

\[
\alpha_{2j-1} = \omega + \frac{\omega^2}{2D_e} I_0
\]

\[
\alpha_{2j} = \omega - \frac{\omega^2}{2D_e} (I_0 + \Delta I)
\]

\[
\beta_j = -(-1)^j \frac{\omega^2}{4D_e}
\]

and \(\Delta I\) and \(I_0\) are constants to be chosen. Here \(\omega\) and \(D_e\) correspond to the harmonic frequency and dissociation energy of the oscillators, respectively. The interaction \(V\) features a nonlinear coupling with a 1-1 resonance between local modes,

\[
V(\mathbf{I}, \phi) = \sum_{i<j} \gamma_{ij}(I_i, I_j) \cos(\phi_i - \phi_j)
\]

Low order resonances are characteristic of few quantum number regimes. We choose a single \((m:n)\) resonance here for simplicity, though in general a molecule can have several different resonances between two or more modes. Here we consider three different forms for the coupling \(\gamma_{ij}\). We start by defining

\[
\gamma(I_i, I_j) = \left(1 - e^{-I_i/I_c}\right)\left(1 - e^{-I_j/I_c}\right)
\]

Coupling Scheme I features an interaction between nearest neighbors, which is defined by setting \(\gamma_{ij}(I_i, I_j) = \gamma(I_i, I_j)\) if and only if \(|i - j| = 1\). Coupling Scheme II features
an interaction between modes with different parity, with \( \gamma_{ij}(I_i, I_j) = \gamma(I_i, I_j) \) if and only if \( i + j \) is odd. Finally, Coupling Scheme III features an interaction between all modes, with \( \gamma_{ij}(I_i, I_j) = \gamma(I_i, I_j) \) for all \( i \neq j \). In Table 6.1, the coupling schemes are summarized for \( D = 3, 4 \) and 5 modes. For all coupling schemes, the perturbation conserves the total polyad number \( P_c = \sum_{j=1}^{D} I_j \), \( \frac{dP_c}{dt} = 0 \).

**Table 6.1:** Coupling Schemes

<table>
<thead>
<tr>
<th>Modes</th>
<th>Scheme I</th>
<th>Scheme II</th>
<th>Scheme III</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td><img src="image1.png" alt="Diagram" /></td>
<td>Same as Scheme I</td>
<td><img src="image2.png" alt="Diagram" /></td>
</tr>
<tr>
<td>4</td>
<td><img src="image3.png" alt="Diagram" /></td>
<td><img src="image4.png" alt="Diagram" /></td>
<td><img src="image5.png" alt="Diagram" /></td>
</tr>
<tr>
<td>5</td>
<td><img src="image6.png" alt="Diagram" /></td>
<td><img src="image7.png" alt="Diagram" /></td>
<td><img src="image8.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

The motivation for the form of \( \gamma_{ij} \) is as follows: We want the resonance structure of the full Hamiltonian to be essentially dictated by the zeroth-order Hamiltonian. This will allow us to understand the role of dynamical tunneling versus fast diffusion when the dynamics are nearly integrable. Thus, we want \( \dot{\phi} \approx \nabla I H_0 \), which means that we need \( \nabla I V \approx 0 \). At the same time, we want the dynamics to be such that \( I_i \geq 0 \) at all times. Thus, we want \( \dot{I}_i = 0 \) if \( I_i = 0 \). Note that \( \gamma(I_i, I_j) \) satisfies
these requirements. If $I_i, I_j \gg I_c$, then $\gamma(I_i, I_j) \approx 1$, so $\nabla I V \approx 0$, while if $I_i$ or $I_j$ are equal to 0, then $\gamma(I_i, I_j) = 0$ so that $\dot{I}_i = 0$. By choosing $I_c$ sufficiently small compared to the characteristic actions of our simulations, we can make the region of phase-space whose resonance structure is dictated by the zeroth-order Hamiltonian as large as possible.

6.2.1 Convexity

Consider a nondegenerate, quasi-integrable Hamiltonian as in equation 6.2 that satisfies KAM-Theorem for a sufficiently small perturbation strength $\lambda$. Nekhoroshev’s Theorem\textsuperscript{113} concerns the stability of solutions that are in the complement set to the set of KAM-tori. This complement set forms a network of resonant surfaces called the Arnol’d Web. The a priori estimate of the stability of these solutions is $t << \frac{1}{\lambda}$.

However, Nekhoroshev’s Theorem places a bound on the rate of Arnold Diffusion depending on the steepness properties of the Hamiltonian.\textsuperscript{113,70,37} Nekhoroshev’s Theorem guarantees that a system will be stable up to an exponentially long time $T \sim \mathcal{O}(\exp[1/\lambda])$ if the Hamiltonian is steep. To be specific, given the initial condition $I(0) \in \mathbb{R}^D$,

$$|I(t) - I(0)| < r_0 \lambda^\alpha$$

$$T = t_0 \exp \left( \frac{\lambda_0}{\lambda^\beta} \right)$$

for $t \in [0, T]$. Here $\alpha, \beta, r_0, t_0, \lambda_0$ are constants that depend on specific properties of $H_0$. Convex functions– a specific class of steep functions, produce the best stability estimates for $D$ DOF with $\alpha = \beta = \frac{1}{2D}$.\textsuperscript{114,115,37}

Consider the Hessian of the Hamiltonian $H_0(I)$, $A(I) = \nabla^2 H_0$. $H_0$ is convex if it
satisfies,

\[ u^T A(I) u = 0 \Rightarrow u = 0 \]  
(6.11)

for \( I \in \mathcal{W}_a \) for domain \( \mathcal{W}_a \subseteq \mathbb{R}^D \). This condition is satisfied for a Hamiltonian with a sign-definite Hessian. An example of a convex function is \( H_0(I_1, I_2) = \frac{I_1^2}{2} + \frac{I_2^2}{2} \). Quasi-convexity requires convexity only along the direction of the resonance surfaces.

The direction of fast drift, \( \dot{I} = \nabla_\phi H \sim \lambda k \), is parallel to \( k \) with speed \( \propto \lambda \), where \( k \in \mathbb{Z}^D \). For a convex function, the direction of fast drift is always perpendicular to the resonance surface \( k \cdot \nu(I) = 0 \), where \( \nu_j(I) = \frac{\partial H_0}{\partial I_j} \), and causes diffusion across the resonance surface. Diffusion along the resonance surface only occurs through the nonresonant harmonics in the perturbation, which can be eliminated successively via canonical transformations to an exponential small remainder.\(^{116} \)

For a non-convex function, which is nonsteep, the direction of fast drift is parallel the resonance surface. Consequently, solutions \( I(t), \phi(t) \) can be found for \( H_0 \) that feature fast drift, \( I(t) = f(\lambda t) \). An example of a non-convex function is \( H_0 = \frac{I_1^2}{2} - \frac{I_2^2}{2} \). In Section 6.2.2 we discuss the differences between these two cases for \( D = 2 \) in further detail, as well as the case where diffusion for a non-convex Hamiltonian can slow.

Our model Hamiltonian (equation 6.2) is non-convex. This is clear when we examine its Hessian for resonance vector \( u = \{u_1, u_2 \cdots u_N\} \),

\[ u^T A(I) u = \sum_{i} D - \beta_i u_i^2 = \sum_{i} (-1)^i |\beta_i| |u_i|^2 = 0 \]  
(6.12)

which is true for various \( u \in \mathbb{Z}^D \setminus 0 \) on an action domain defined by the entire energy hypersurface. In Section 6.2.3, we show explicitly for \( D = 3 \) and Coupling Scheme...
I that two interacting modes in our model feature fast diffusion along a given resonance surface at a rate $I(t) \sim \pm \lambda t$. This has been more generally shown for non-convex Hamiltonian functions in reference 109. In a particular domain for $\mathcal{W}_a = \{I \in \mathbb{R}^D | I_{2j} = \text{constant}, \ j \leq D/2\}$, the Hamiltonian in equation 6.2 is steep because it is ellipsoidal in the remaining coordinates. This yields different drift rates depending on the direction of the resonance surface on the energy hypersurface.

6.2.2 Convexity and the Direction of Fast Drift

Here we discuss how convexity impacts the direction of fast drift in greater detail.

Consider the following integrable Hamiltonians,

\begin{align*}
H_C(I_1, I_2) &= \frac{1}{2}(I_1^2 + I_2^2) \\
H_{NC}(I_1, I_2) &= \frac{1}{2}(I_1^2 - I_2^2)
\end{align*}

(6.13)

(6.14)

which are convex and non-convex, respectively. The canonical vector fields are,

\begin{align*}
\dot{\phi} &= D_1 H_0 = \omega_C(I_1, I_2) = (I_1, I_2) \\
\dot{\phi} &= D_1 H_0 = \omega_{NC}(I_1, I_2) = (I_1, -I_2) \\
\dot{I}_C &= \dot{I}_{NC} = -D_\phi H_0 = 0
\end{align*}

(6.15)

(6.16)

(6.17)

as shown in Figure 6.1(a) and Figure 6.1(b).

By adding the perturbation, $V_{int} = \epsilon \cos(\phi_1 \pm \phi_2)$, the actions are no longer constants of motion,

\begin{align*}
\dot{I}_C &= \dot{I}_{NC} = -D_\phi V_{int} = \epsilon \sin(\phi_1 \pm \phi_2)(1, \pm 1)
\end{align*}

(6.18)
and evolve in the $k_{\pm} = (1, \pm 1)$ direction in action space. Each resonance surface is defined by, $M = k \cdot \omega(I) = 0$. For the convex Hamiltonian, the resonance surface $M_{\pm} = I_1 \pm I_2 = 0$ is perpendicular to the direction of fast drift. For $D = 2$, the resonance surfaces only intersect each constant energy surface at two points, which means the system cannot diffuse along the resonance surface, i.e. stay in resonance, for $D < 3$ DOF. For the non-convex Hamiltonian, the resonance surface $M_{\pm} = I_1 \mp I_2 = 0$ is parallel to the direction of fast drift and embedded in the two constant energy hypersurfaces that pass through $(I_1, I_2) = (0, 0)$. This allows an initial state starting on anywhere $M_{\pm}$ to diffuse along the resonance surface $M_{\pm}$. Figures 6.2(a) and 6.2(b) summarize this.

For the general nonconvex Hamiltonian, $H_0(I) = c_1 I_1 - c_2 I_2$, there will only be fast diffusion iff $\frac{c_1}{c_2} \in \mathbb{Q}$. Otherwise, $\exists k \in \mathbb{Z}^2$ that satisfy the condition $k^T \nabla^2 I H_0 k = 0$ except for $k = 0$. This is referred to as rational convexity and generalizes to higher
Figure 6.2: Plot of the resonance surfaces $\mathcal{M}_\pm$ in red for (a) a convex Hamiltonian (Equation 6.13) and (b) a non-convex Hamiltonian (Equation 6.14). The contour lines correspond to energy hypersurfaces. For the convex Hamiltonian, the direction of fast drift is perpendicular to the resonance surface and will not diffuse along the resonance surface. For the non-convex Hamiltonian, the direction of fast drift is parallel to the resonance surface and will diffuse along the resonance surface.

6.2.3 Rate of Fast Diffusion

As a result of the conserved polyad Number, $P_c = I_1 + I_2 + I_3$, the effective Hamiltonian can be reduced to 2 DOF via a canonical transformation, $\mathcal{C} : (\mathbf{I}, \phi) \rightarrow (\mathbf{J}, P_c, \psi, \phi_c)$ using the generating function,

$$F(\mathbf{J}, P_c, \phi) = (\phi_1 - \phi_2)J_1 + (\phi_2 - \phi_3)J_2 + \phi_3 P_c$$  \hspace{1cm} (6.19)
with \((\mathbf{J}, \psi) \in \mathbb{R}^2 \times \mathbb{T}^2\). The new and old coordinates are related by \(\psi_n = \frac{\partial F}{\partial J_n}\) and \(I_n = \frac{\partial F}{\partial \phi_n}\). The transformed Hamiltonian becomes,

\[
H_0(\mathbf{J}, \psi) = A + B \left( J_1 - J_2 \right) + CJ_2 - DJ_1J_2
\]

(6.20)

\[
V(\mathbf{J}, \psi) = \gamma_{12} \cos \psi_1 + \gamma_{23} \cos \psi_2
\]

(6.21)

where \(A, B, C, D \in \mathbb{R}\) are constants. Here the \(\mathbf{J}\)-dependence was dropped from \(\gamma_{ij}\) because it is nearly constant \((\approx 1)\) over the action domain \(\mathcal{W}_a \subseteq \mathbb{R}^2\) in consideration. The perturbation features two Fourier terms that are resonant for \(\nu_1 = \frac{\partial H_0}{\partial J_1} = 0\) and \(\nu_2 = \frac{\partial H_0}{\partial J_2} = 0\), respectively. The corresponding resonance vectors in the transformed coordinates are \(k_1 = (1, 0)\) and \(k_2 = (0, 1)\).

Here we consider \(\mathcal{W}_a\) that includes only the \(\nu_1\)-resonance and is sufficiently far away from the \(\nu_2\)-resonance. We can therefore eliminate the \(\psi_2\) harmonic term using a canonical transformation,\(^{117}\) \(\mathcal{C} : (\mathbf{J}, \psi) \rightarrow (\mathbf{J}', \psi')\) via a Lie-generating function \(L_{\chi_1} = \{ \cdot, \chi_1 \}\),

\[
\begin{align}
(\mathbf{J}, \psi) &= \left\{ \exp(L_{\chi_1})\mathbf{J}', \exp(L_{\chi_1})\psi' \right\} \quad (6.22) \\
H'_0 &= \exp(L_{\chi_1})H_0 = H_0 + L_{\chi_1}H_0 + \frac{1}{2} L_{\chi_1}^2 H_0 + \cdots \quad (6.23)
\end{align}
\]

Choosing \(\chi_1(\mathbf{J}', \psi') = \frac{1}{\nu_2(\mathbf{J})} \sin \psi'_2\) eliminates the \(\psi_2\) harmonic term to \(\mathcal{O}(\lambda^2)\). The transformed Hamiltonian becomes,

\[
H'(\mathbf{J}', \psi') = H_0(\mathbf{J}') + \lambda \cos \psi'_1
\]

(6.24)

This solutions for the transformed Hamiltonian can easily be found since \(J'_2\) is constant of motion. The general solutions,
\[
\begin{align*}
\left( J'_1(t), J'_2(t) \right) &= \left( J'_1(0) - \frac{\lambda}{\Omega} \cos \psi'_1(t), \text{const} \right) \\
\left( \psi'_1(t), \psi'_2(t) \right) &= \left( \Omega t + \psi'_{10} - \frac{\omega^2}{2D_e} \left[ (I_0 - J'_1(0))t + \frac{\lambda}{\Omega^2} \sin \psi'_1(t) + \psi'_{20} \right] \right)
\end{align*}
\] (6.25) (6.26)

where the frequency of \( \psi'_1 \) is 
\( \Omega = B - D J'_2 = \frac{\omega^2}{2D_e} \left( 2I_0 + \Delta I - J'_2 \right) \). For the initial conditions \( \psi'_{1,0} = -\frac{\pi}{2} \) and \( J'_1(0) \),
\[
\begin{align*}
J'_1(t) &= J'_1(0) - \frac{\lambda}{\Omega} \sin(\Omega t) \\
\psi'_1(t) &= \Omega t - \frac{\pi}{2}
\end{align*}
\] (6.27) (6.28)

In the limit of \( \Omega \to 0 \), \( J'_2 = 2I_0 + \Delta I \) and the solution for \( J'_1 \) drifts linearly in time at rate \( \lambda \), \( J'_1(t) = J'_1(0) - \lambda t \) and \( \psi'_1 = \frac{\pi}{2} \). Similarly can be done for the second resonance to yield \( J'_1 = I_0 \) and \( J'_2(t) = J'_2(0) - \lambda t \). Figure 6.3 is a contour plot of the transformed Hamiltonian with the constant energy solution in black, as given by equation 6.28.

The solutions evolve along a curve where the convexity of \( H_0 \) is zero. This is to be expected as the Hamiltonian is non-convex, and hence nonsteep. The direction of fast drift is along these lines, which corresponds to along the \( k_1, k_2 \) resonances. The arrow designates motion along the \( k_1 = (1,0) \) resonance.

The general fast drift solution for \( \Omega \to 0 \), \( |J'_2 - \Delta I - 2I_0| < \sqrt{\lambda} \), and arbitrary \( \psi'_{1,0} \),
\[
\begin{align*}
J'_1(t) &= J'_1(0) + \lambda \sin(\psi'_{1,0})t \\
J'_2(t) &= 2I_0 + \Delta I
\end{align*}
\] (6.29) (6.30)

Therefore, we generally expect the original actions to diffuse along single resonance.
Figure 6.3: Contour plot of the Hamiltonian described by equation 6.24. The black lines show the solutions along the resonance surfaces \( \mathbf{k} \cdot \nu(P) = 0 \). The arrow designates the direction of fast drift along the \( \nu_1 \) resonance surface, which is parallel to \( \mathbf{k}_1 = (1, 0) \). The nonconvexity of the Hamiltonian causes \( \mathbf{k} \parallel \mathbf{k} \cdot \nu(P) \), and the direction of fast drift with the diffusion rate \( \lambda \) is along the resonance surface.

surface at a rate \( \lambda \sin(\psi'_{1,0}) \).

6.2.4 Arnol’d Web

Arnol’d Web is a network of intersecting 1-fold resonance surfaces defined by \( \mathbf{k} \cdot \nu(I) = 0 \). Let \( \{\hat{e}_1, \cdots, \hat{e}_D\} \) denote the canonical basis of \( \mathbb{R}^D \). The resonance surface created by the coupling between an even and odd mode, with resonance vector \( \mathbf{k} = -\hat{e}_{2m} + \hat{e}_{2n+1} \), is given by

\[
\mathbf{k} \cdot \nu = 2I_0 + \Delta I - (I_{2n+1} + I_{2m}) = 0
\]  

(6.31)

Given the initial condition \( I_{2n+1} = I_0 + \Delta I \) and \( I_{2m} = I_0 \), the actions will evolve along the resonance surface according to \( I_{2n+1} = I_0 + \Delta I - I(t) \) and \( I_{2m} = I_0 + I(t) \)
until $\Delta I$ units of action have been transferred from the odd mode to the even mode.

In contrast, the resonance surface created by the coupling between same parity modes has the simple condition, $I_{2n+1} = I_{2m+1}$ or $I_{2n} = I_{2m}$ for $n \neq m$.

To be more specific, $(I_0 + \Delta I - I(t), I_0 + I(t), I_0, \cdots I_0)$ describes the evolution along the $1-1$ resonance between the first and second mode. Thus, starting at $(I_0 + \Delta I, I_0, \cdots I_0)$, the system evolves until $\Delta I$ units of action have been resonantly transferred into mode 2. At this point, the system is in state $(I_0, I_0 + \Delta, I_0, \cdots I_0)$, and the 1-1 resonance between second and third modes are then active. The actions then evolve according to $(I_0, I_0 + \Delta I - I, I_0 + I, I_0, \cdots I_0)$. The system can now proceed to transfer energy to mode 3, in principle evolving to the state $(I_0, I_0, I_0 + \Delta I, I_0, \cdots I_0)$.

This energy transfer from mode 1 to mode 3 is accomplished via transport along the web because the energy transfer occurs first along the resonance between modes 1 and 2. During this resonant energy transfer, $I_1 + I_2$ and $I_3$ is approximately conserved because the resonance surface between modes 2 and 3 is sufficiently far away from the resonant surface between modes 1 and 2. Once $\Delta I$ units of action have been transferred to mode 2, the mode 1 - mode 2 and the mode 2 - mode 3 resonance lines intersect, and then energy transfer can occur from mode 2 to mode 3. During this period, $I_2 + I_3$ and $I_1$ is approximately conserved.

Figure 6.4 shows a sample trajectory with $D = 3$ and Coupling Scheme I with the initial condition on the resonance surface. Note that at any given time, either $I_1 + I_2$ remain nearly constant, or $I_1$ and $I_2 + I_3$ remain nearly constant when sufficiently far away from the junction of the two resonance surfaces. Upon approaching the intersection of two resonance surfaces, all three modes are strongly interacting and $I_1 + I_2$ (or $I_2 + I_3$) is no longer nearly an integral of motion. However, the polyad number $P_c = I_1 + I_2 + I_3$ is conserved at all times, shown in black in figure 6.4(b). Thus, the
system moves onto different resonance surfaces via transport along the web.

![Figure 6.4](image)

**Figure 6.4:** (a) Plot of the classical evolution of the initial state \((I_1, I_2, I_3) = (5.5, 0.5, 0.5)\) and \((\phi_1, \phi_2, \phi_3) = (0, \pi/2, 0)\) under Coupling Scheme 1, where \(I_1\) is in blue, \(I_2\) is in red, and \(I_3\) is in green. When two of the modes are in resonance, their sum \(I_i + I_j\) is nearly constant as shown in figure (b). The diffusion rate at various points in figure (a) are given \((s_1, s_2, s_3, s_4) = (0.0096, 0.0104, 0.011, 0.0096)\), where \(\lambda = 0.01\). Here \(I_1 + I_2\) is in purple and \(I_2 + I_3\) is in orange. The interaction preserves \(P_c = I_1 + I_2 + I_3\) at all times, as shown by the black line.

Coupling Scheme I only allows for sequential resonant energy transfer, where energy can only flow from mode 1 to mode 2 to mode 3, and so on. Coupling Schemes II and III allow for resonant energy transfer between any two modes of opposite par-
ity. Table 6.1 schematically shows the possible networks of resonant energy flow paths given a particular coupling scheme. Note that Coupling Scheme I results in a simple chain, while Coupling Schemes II and III produce an actual web. This web becomes more dense with increasing $D$. To visualize Arnol’d web in action space for $D < 5$, a canonical transformation can be made to reduce the degrees of freedom from $N$ to $N - 1$ as a result of the conserved polyad, $P_c$ (See Section 6.2.3).

Figures 6.5(a) and 6.5(b) show the zeroth order Arnol’d Web for the effective Hamiltonian, $H_0(\mathbf{J}, P_c)$ for $D = 3$ and $D = 4$ degrees of freedom respectively. In both figures, the intersection of the resonance surfaces with $H_0(\mathbf{J})$ are shown in black for resonances between opposite parity modes and in red between same parity modes. The resonance surface created by the $\gamma_{ij}$-coupling is denoted by $k_{ij}$. The initial actions $I(0)$ is represented by the orange dot. For $D = 3$, the constant energy hypersurface of the effective two dimensional Hamiltonian lies along the two resonance surfaces between opposite parity modes. The $k_{1,3}$ resonance surface only intersects the zeroth order energy hypersurface at the point $I_1 = I_3 = I_0$.

For $D = 4$ the constant energy hypersurface of the effective three dimensional Hamiltonian is a surface shown in yellow. The opposite parity resonance surfaces are linear along the hypersurface, which is a characterization of the non-convexity of $H_0$ and will feature fast drift. The same parity resonance surfaces are curved along the surface, which is a characterization of the quasi-convexity of $H_0$ in the direction of these resonances. Consequently, these resonance surfaces feature exponentially slow diffusion. The system will therefore preferentially diffuse along the the opposite-parity resonance surfaces. This means that same-parity coupling mostly serves as a nonresonant perturbation rather than viable path of energy flow between modes. In contrast, the opposite parity couplings create pathways for energy flow between local
modes through the fast diffusion resonance surfaces.

\[ J_1 = I_1, \quad J_2 = I_1 + I_2, \quad J_3 = I_1 + I_2 + I_3, \quad \text{and} \quad P_c = 7 \]

The energy hypersurface of the effective Hamiltonian is shown in yellow.

Care must be taken to choose \( \lambda \) sufficiently small so that the system is indeed quasi-integrable at the energy being studied. If \( \lambda \) is too large, then rapid energy flow becomes possible via nonresonant chaotic dynamics, which can then account for both classical and quantum energy flow. For our simulations, we set \( \lambda = 0.01 \). As figure 6.4(a) shows, there is essentially no non-resonant energy transfer for this value of the perturbation strength. For \( \lambda = 0.1 \) a similar inspection of the classical trajectories reveals some non-resonant energy transfer, but overall this is still small, and fast diffusion remains essentially the only mechanism for energy flow between resonance zones. The main difference between \( \lambda = 0.01 \) to \( \lambda = 0.1 \) is a shortening of the
timescales over which fast diffusion occurs. However, the dynamics becomes chaotic for $\lambda = 1$.

Before concluding this section, it should be also pointed out that restrictions must be placed on $\omega$, $D_e$, $I_0$ and $\Delta I$ to ensure that the frequencies $\nu_j(I) = \frac{\partial H}{\partial I_j} = \alpha_j - 2\beta_j I_j \geq 0$ for a given value of $D$. As mentioned earlier, the interaction conserves the total polyad number and guarantees that $I_i \geq 0$ at all times. It follows that $0 \leq I_i \leq \sum_{j=1}^{D} I_j = \Delta I + DI_0$. Using the definition for $\alpha_i, \beta_i$ in equation 6.6, the requirement for positive frequencies gives

$$j = 2n$$

$$\nu_{2n} = \omega - \frac{\omega^2}{2D_e}(I_0 + \Delta I) \geq 0$$

$$\rightarrow 2D_e \geq \omega(I_0 + \Delta I) \quad (6.32)$$

$$j = 2n - 1$$

$$\nu_{2n-1} = \omega + \frac{\omega^2}{2D_e}I_0 - \frac{\omega^2}{2D_e}(DI_0 + \Delta I) \geq 0$$

$$\rightarrow 2D_e \geq \omega[(D - 1)I_0 + \Delta I] \quad (6.33)$$

6.3 Method

In this section, we describe how we compare quantum and classical energy flow rates, and the way this is translated into a comparison of dynamical tunneling versus classical diffusion. We run our simulations starting from the torus with quantum numbers $m = (5, 0, \cdots, 0)$. We let the angles run from 0 to $2\pi$. The conversion from quantum numbers $m = (m_1, \cdots, m_D)$ to actions $I = (I_1, \cdots, I_D)$ is accomplished via $I_i = \hbar(m_i + \frac{1}{2})$. Thus, we have $I_0 = \hbar/2$ and $\Delta I = 5\hbar$. 

118
For all of our simulations, we took \( \hbar = 1 \), \( \lambda = 0.01 \), \( \omega = 1.0 \), \( D_e = 5.0 \), and \( I_c = 0.1 \). Typical values for the vibrational frequency and interaction strength in medium-sized polyatomic molecules: \( \omega \sim 100 - 1000 \, \text{cm}^{-1} \) and \( V_{\text{int}} \sim 10 - 100 \, \text{cm}^{-1} \) with a ratio \( \frac{V_{\text{int}}}{\omega} = 0.01 - 1 \). Thus, \( \lambda = 0.01 \) is a small, but physically relevant strength given \( \omega = 1 \). The condition that we have only bound-state motion becomes (eqn 6.33), \( 10 \geq 5 + (D - 1)/2 \), which gives \( D \leq 11 \). Therefore, we can run calculations up to 11 degrees of freedom without fear of dissociation. By making the time steps sufficiently small, we were able to accurately propagate the trajectories out to a time of 2000, which was sufficient to compare the classical and quantum energy flow rates. For our choice parameters, this would correspond to on the order of hundreds of vibrational periods.

### 6.3.1 Classical Calculations

To determine \( \langle I_i(t) \rangle \) classically, we find the average of \( I_i(t) \) for a swarm of trajectories with actions of the initial torus, but differing initial angles. We considered initial angle vectors \( (\phi_1, \ldots, \phi_D) = (2\pi i_1/N, \ldots, 2\pi i_D/N) \), where each \( i_k = 0, 1, \ldots, N - 1 \) giving \( N^D \) initial trajectories. We then numerically integrate these trajectories using Hamilton’s equations of motions. We chose \( N = (16, 12, 8) \) and for \( D = (3, 4, 5) \) respectively to produce the most convergence results without making the runtime prohibitively slow.

### 6.3.2 Quantum Calculations

As discussed in Chapter 2, Section 2.3, the classical analog of the quantum matrix elements is given by the \( k = (m - n) \) th Fourier component of the classical hamiltonian
evaluated at the average of quantized actions,

\[ H^{CA}_{m,n} = H_{k=m-n} \left( \frac{I_m + I_n}{2} \right) \quad (6.34) \]

The Hamiltonian block diagonalizes by the conserved quantum polyad number
\[ P^Q_c = \sum_i m_i. \] Therefore, we only need to use the zeroth order basis states from a particular polyad to find the energy eigenvalues and eigenstates within that polyad. For a particular polyad \( P^Q_c = 5 \), there is a subset of zeroth order states that are degenerate with respect to \( H_0(I) \). The states in this subset lie directly on the opposite-parity resonance surfaces in the corresponding classical phase space (Figure 6.5(a)). The connection between classical resonances and quantum near-degeneracies is well known.\(^{118}\) The large degree of degeneracy in this model is typical of non-convex Hamiltonians, such as a system of \( N \) harmonic oscillators with commensurate frequencies, as a result of the linearity of the energy hypersurface.

6.4 Results

We ran numerical calculations for \( D = 3, 4, \) and 5 degree of freedom systems. Five degrees of freedom was the maximum that memory and time constraints permitted. Six degrees of freedom would have required so many trajectories to get reasonably converged calculations (using 8 angles per degree of freedom), that the run time would have taken several months.

6.4.1 Quantum and Classical Diffusion Rates

Figure 6.6(a), shows a plot of \( \langle I_3(t) \rangle \) classical (dashed) versus \( \langle I_3(t) \rangle \) quantum (solid) for Coupling Scheme I. Classical action flow from the first mode into the third mode
can only occur via fast diffusion. Clearly, the quantum flow dominates the classical energy flow, so that by definition, dynamical tunneling is much quicker than classical transport in this example. Coupling Schemes I and II are identical for three degrees of freedom. Figure 6.6(b), $\langle I_3(t) \rangle$ classical (dashed) versus $\langle I_3(t) \rangle$ quantum (solid) for Coupling Scheme III. For Case III, the quantum flow is still faster, but the classical flow is comparable. This result appears to be atypical, since as higher dimensional results will show, the classical diffusion rate is highly suppressed relative to the quantum rate by adding more couplings for $D > 3$.

Figure 6.7(a) shows a plot of $\langle I_3(t) \rangle$ classical (dashed) versus $\langle I_3(t) \rangle$ quantum (solid) for Coupling Scheme I. Once again, dynamical tunneling is dominant. The discrepancy between dynamical tunneling and classical diffusion rates becomes even more apparent in when comparing $\langle I_4(t) \rangle$ classical versus $\langle I_4(t) \rangle$ quantum for Coupling Scheme I. In this case, there is hardly any classical energy flow into $\langle I_4(t) \rangle$ at all.
Both the classical and quantum diffusion rates are suppressed for Coupling Schemes II and III (Figure 6.7(b) and Figure 6.7(c)) in comparison to Coupling Scheme I. However, the rate of dynamical tunneling is much larger than classical transport along the web in all three coupling schemes. This illustrates that dynamical tunnel-
ing is faster than classical diffusion regardless of the structure of the Arnol’d web.

**Figure 6.8:** (a) Plot of $\langle I_3(t) \rangle$, $\langle I_4(t) \rangle$, and $I_5(t)$ for Coupling Scheme I and $D = 5$. Quantum Mechanically, energy can flow from mode 1 to mode 5 for $t \in [0, 2000]$. Classically, energy can only flow into mode 3 within the same time interval. This indicates that dynamical tunneling is faster than fast diffusion. (b) Plot of $\langle I_3(t) \rangle$ for Coupling Scheme II and $D = 5$. $\langle I_5(t) \rangle$ is not shown in this plot because it is quantum mechanically equivalent to $\langle I_3(t) \rangle$ due to the symmetry of the web (See Table 6.1) (c) Plot of $\langle I_3(t) \rangle$ and $\langle I_5(t) \rangle$ for Coupling Scheme III and $D = 5$. As for $D = 4$, the rate of dynamical tunneling is much larger than classical diffusion, regardless of the coupling structure. This supports that the comparable quantum and classical diffusion rates for $D = 3$ and Coupling Scheme III does not generalize for $D > 3$.

Figure 6.8 shows the quantum and classical diffusion for $D = 5$ for the three different coupling schemes. Figure 6.8(c) shows that classically $\langle I_5(t) \rangle$ increases slightly
faster than \( \langle I_3 \rangle \), which is mostly likely a result of sampling only 8 angles per each \( \phi_i \) for \( D = 5 \). Overall, these figures show the same trends as for \( D = 4 \) (See Figure 6.7). Specifically, dynamical tunneling is faster than classical diffusion regardless of the structure the Arnol’d Web and the presence of more couplings suppresses the rate of energy flow.

The first finding is quite unexpected because classically the system starts in the neighborhood of a resonance surface, which is expected to feature fast diffusion. For a single resonance, the system features fast diffusion with resonance width \( O(\sqrt{\lambda}) \).\(^{116}\) However, for a general perturbation, the system will not remain locked in resonance for \( t > \frac{1}{\lambda} \).\(^{119}\) We can further understand this by expressing the full Hamiltonian in Birkhoff resonant normal form up to \( O(\lambda^2) \),\(^{117}\)

\[
H(J, \psi) = H_0(J) + \lambda Z_1(J, \psi) + \lambda^2 R(J, \psi) \\
= Z_1(J, \psi) + \lambda^2 R(J, \psi) 
\]  

(6.35)

where \( Z_1(J, \psi) \) is the resonant normal form and \( R(J, \psi) \) is the remainder that drives the system away from its normal form. The resonant normal form, \( Z_1(J, \psi) \), describes fast diffusion along the \( k_{12} \) resonance surface. The remainder contains the remaining terms after a canonical transformation to eliminate the nonresonant Fourier terms in the perturbation up to \( O(\lambda^2) \). Equation 6.35 shows that the \( O(\lambda^2) \) remainder drives the system away from fast diffusion, \( Z_1 \). We now show using classical perturbation theory how the system departs from the resonance surface for a subset of initial conditions. Thus, many of the initial states constituting the classical density will not remain on the web long enough to evolve onto the next resonance surface.

The relation between the solutions of the transformed actions \( (J'_1, J'_2) \) to the ac-
tions \( (J_1, J_2) \) is given,\(^{117} \)

\[
J = \exp(L\chi)J = J' + \lambda\{J', \chi_1\} + \frac{\lambda^2}{2}\{\{J', \chi_1\}, \chi_1\} + \mathcal{O}(\lambda^2)
\] (6.36)

We substitute the single-resonance solutions (eqns. 6.26) into equation 6.36 to find how the system evolves over a domain where \( \gamma_{ij} \approx 1 \). Given the initial conditions, \( \phi(0) = (\phi_{1,0}, \phi_{2,0}, \phi_{3,0}) \) and \( \mathbf{I}(0) = (I_0 + \Delta I, I_0, I_0) \), the initial conditions for the transformed variables, \( J_2'(0) = J_2(0) - \delta = 2I_0 + \Delta I - \delta, \ J_1'(0) = J(0) + \frac{\lambda D^2}{\delta \omega} \cos \left( \frac{\psi_1' \omega}{2D_e} \right) \). Here \( \psi_{1,0}' \approx \psi_{1,0} = \phi_{2,0} - \phi_{1,0} \) and \( \delta \) is found by matching the first order perturbation theory expressions with the numerical solution.

Figures 6.9 show the evolution of \( J(t) \) found using perturbation theory for \( \delta = 0.0001, (\psi_1, \psi_2) = (-\frac{\pi}{2}, \frac{\pi}{2}) \) and \( \delta = 0.0157, (\psi_1, \psi_2) = (-\frac{\pi}{5}, \frac{\pi}{5}) \), versus the numerically integrated and fast drift solution (equation 6.30). Figures 6.9(a) and 6.9(b) show fast diffusion for \( \delta = 0.0001 \), and \( J_2(t) \) oscillates about the single-resonance value \( 2I_0 + \Delta I \). However, figures 6.9(c) and 6.9(d) show how the system will not remain locked into resonance for \( \delta = 0.0157 \), even though \( \delta < \sqrt{\lambda} \), and will slightly drift from the single-resonance value \( 2I_0 + \Delta I \). Rather than featuring fast drift, the first action varies as \( J_1(t) \sim \cos \left( \frac{\delta \omega^2 t}{2D_e} \right) + \mathcal{O}(\lambda^2) \) such that the system will never reach the second resonance surface, \( \nu_2(J) = 0, J_1 = I_0 \). This means that a subset of initial states in the classical ensemble will not remain on the resonance surface long enough to reach the resonance surface \( k_{23} \) in order to evolve to \( (I_1, I_2, I_3) = (I_0, I_0, \Delta I + I_0) \). Consequently, the ensemble average of \( \langle I_3 \rangle \) will be much smaller than if all initial states featured fast diffusion down both \( k_{12} \) and \( k_{23} \).

For Coupling Schemes II and III, the presence of more nonresonant Fourier turns will further perturb the system from the fast drift normal form. This is consistent
Figure 6.9: Plots for the time evolution of $J$ with (a-b) $\delta = 0.0001$ for initial conditions $(\phi_{1,0}, \phi_{2,0}, \phi_{3,0}) = (0, \frac{\pi}{2}, 0)$ and (c-d) $\delta = 0.0157$, $(\phi_{1,0}, \phi_{2,0}, \phi_{3,0}) = (0, \frac{\pi}{1}, 0)$ of the exact numerically integrated solution, the first order perturbation theory (FOPT) result (equation 6.36), and the fast drift solution (equation 6.30). For $\delta = 0.0001$, the system features fast drift. However, for $\delta = 0.0157$, the system does not feature fast diffusion.

with the results for $D > 3$, which feature a reduction in the rate of diffusion both classically and quantum mechanically, (See Figure 6.5). Another complication that arises is that the initial conditions lie upon the intersection of two or more resonance surfaces for $D > 3$ and Coupling Scheme II and III, and the collective behavior of both resonances can prevent fast diffusion. Therefore, the classical system is very sensitive to the initial conditions and topology of the Arnol’d Web.

Quantum Mechanically, the resonances enhance the rate of diffusion. As mentioned earlier, a degenerate manifold of states of $H_0$ lie upon the resonance surfaces created
by the couplings between opposite parity modes. Consequently the mixing between degenerate states is much stronger than with states outside the degenerate manifold for \( h = 1 \). The second order correction to energy from coupling with states outside the degenerate manifold goes as \( \sim \frac{x^2}{\Delta E_{ij}} \) where \( \Delta E_{ij} \geq 0.1 \) for \( h = 1 \). This is rather small. The quantum system is therefore more resilient against energy flowing outside the degenerate manifold, and consequently energy transfer between resonant modes will happen faster.

We verify this with the overlap probability between the time-evolving state and each EBK-quantized invariant torus,

\[
|\langle \beta | \Psi(t) \rangle|^2 = |\langle \beta | e^{-iHt/\hbar} | \beta_0 \rangle|^2 = \sum_{n,n'} c_{n\beta} c_{n'\beta}^* c_{n'\beta}^* c_{n\beta} e^{-i(E_n - E_{n'})t/\hbar}
\] (6.37)

Here \( \{ |\beta \rangle \} \) are set of states lying on the degenerate manifold, \( | \beta_0 \rangle = (5, 0, \cdots, 0) \) is the initial state, and \( c_{n\beta} = \langle n | \beta \rangle \) is the overlap coefficient between an EBK-quantized torus, \( | \beta \rangle \), and the \( n \)-th energy eigenstate. The classical analog of the overlap probability,

\[
P_{\beta}(t) = \text{Tr}[\rho_{\beta} \rho(t)]
\] (6.38)

where \( \rho(t) \) is the time-evolving density and \( \rho_{\beta} \) is the density of the EBK-quantized torus. We approximate this density of each torus as \( \rho_{\beta} = \theta(d - |I_\beta - I|) \), where \( d \) is the threshold distance away from \( I_\beta \).

Figure 6.10(a) shows the overlap probability of the time-evolving state with the tori along the resonance surface for \( D = 3 \) and Coupling Scheme I. At \( t = 0 \), the time-evolving state begins at \( | \beta_0 \rangle = (5, 0, 0) \rightarrow I_\beta = (5.5, 0.5, 0.5) \), which results in an
overlap probability of unity. The overlap probability decreases with each sequential state on the degenerate manifold up until \( t = 1300 \text{ s} \). Here there is a large overlap with the symmetric \((I_1 \leftrightarrow I_3)\) state \(|\beta\rangle = (0, 0, 5)\). Figure 6.10(b) shows the classical overlap probability for \( D = 3\), Coupling Scheme I with a very generous threshold distance \( d = 0.1 \). The overlap probability between the time-evolving density and all states following \( I_\beta = (1.5, 4.5, 0.5) \) are not shown because the overlap with each of these states is negligible. The decreasing overlap with states on the resonance surface verifies that the classical system does not stay on the resonance surface for long in comparison to the quantum system.

The quantum diffusion rate for Coupling Scheme I is also enhanced by the sequential energy flow between states on the degenerate manifold. When comparing Coupling Schemes I and III, figure 6.11 shows that the addition of another resonance surface decreases the overlap probability starting in the neighborhood of the intersection of all three resonant surfaces (See Figure 6.5(a)) around \( t \sim 700 \text{ s} \). Coupling Scheme III directly couples the two EBK-quantized tori \(|\beta\rangle = (1, 4, 0)\) and \(|\beta'\rangle = (0, 4, 1)\), which lie on the first and second resonance surface respectively. This allows the time-evolving state to either reverse its direction to return to the first surface or continue down the second surface. Consequently the overlap probability will be nonzero for states on both resonance surfaces. Physically, this corresponds to energy simultaneously flowing into many different vibrational modes.

In contrast to the usual resonance-assisted tunneling, the enhancement of the quantum rate over the classical rate in this system features a new kind of dynamical tunneling. Specifically, the resonance surfaces are dynamical structures that create a large degeneracy in the quantum system, which consequently enhance the rate of diffusion over the corresponding classical system.
Figure 6.10: Plot of the overlap probability with all states lying on the resonance surface for
$D = 3$ Coupling Scheme I (a) in the quantum and (b) classical system. The system begins in
state $|β_0⟩ = (5, 0, 0) → I_β = (5.5, 0.5, 0.5)$ at $t = 0$ (solid blue line). Figures (a)-(b) show that
the quantum system stays on the resonance surface longer than the classical system, and the
quantum system has a large overlap with $I_β = (0.5, 0.5, 5.5)$ (dashed blue line).
\[ D = 3, \text{ Scheme III} \]

\[ |\langle \beta | \Psi(t) \rangle|^2 \]

\[ D = 3, \text{ Scheme III} \]

\[ I_{\beta} = (5.5, 0.5, 0.5) \]
\[ I_{\beta} = (4.5, 1.5, 0.5) \]
\[ I_{\beta} = (3.5, 2.5, 0.5) \]
\[ I_{\beta} = (2.5, 3.5, 0.5) \]
\[ I_{\beta} = (1.5, 4.5, 0.5) \]
\[ I_{\beta} = (0.5, 5.5, 0.5) \]
\[ I_{\beta} = (0.5, 4.5, 1.5) \]
\[ I_{\beta} = (0.5, 3.5, 2.5) \]
\[ I_{\beta} = (0.5, 2.5, 3.5) \]
\[ I_{\beta} = (0.5, 1.5, 4.5) \]
\[ I_{\beta} = (0.5, 0.5, 5.5) \]

**Figure 6.11:** Overlap Probability for Coupling Scheme III and \( D = 3 \) in the quantum system. Comparing shows that additional resonance surfaces allow energy to be transferred into several different modes at once, leading to a reduction of the quantum diffusion rate.

### 6.5 Classical Limit

In the classical limit, Planck’s constant \( \hbar \rightarrow 0 \) or equivalently the quantum number \( n \rightarrow \infty \). In this limit the system fully recovers its classical dynamics. Tunneling is a classically forbidden process and is suppressed in the classical limit. Studying the classical limit in our system will further support that tunneling enhances the rate of energy flow between local modes.

In taking \( \hbar \rightarrow 0 \), we fix the classical action \( I \) of the initial state in order to preserve the structure of phase space,

\[ m = \left( \frac{I_{1,i}}{\hbar} - \frac{1}{2}, \frac{I_{2,i}}{\hbar} - \frac{1}{2}, \cdots \frac{I_{D,i}}{\hbar} - \frac{1}{2} \right) \]  

(6.39)

which must obey the following conditions: \( m \in \mathbb{Z}^D \) and \( I_i = \left( I_0 + \Delta I, I_0, \cdots I_0 \right) \). The only values of \( \hbar \) that satisfy both are \( \hbar = \frac{1}{2l+1} \) where \( l \in \mathbb{Z} \). Figure 6.12 shows the
location of quantum states by points in the classical action space for $D = 3$ using the reduced actions $J_1$ and $J_2$ and the relation $I = \hbar(m_1 + \frac{1}{2}, m_2 + \frac{1}{2}, m_3 + \frac{1}{2})$. The blue points correspond to degenerate manifold of states for $H_0(J_1, J_2)$.

\[ \begin{align*}
J_1 &= I_1 \\
J_2 &= I_1 + I_2 \\
\hbar &= \frac{1}{3}
\end{align*} \]

\[ \begin{align*}
J_1 &= I_1 \\
J_2 &= I_1 + I_2 \\
\hbar &= \frac{1}{5}
\end{align*} \]

**Figure 6.12**: Plot of the location of quantum states in action space for $D = 3$ for $\hbar = 1, \frac{1}{3}$, and $\frac{1}{5}$ for $D = 3$ using the reduced actions $J_1$ and $J_2$. The blue points correspond to the degenerate manifold of states for $H_0(J_1, J_2)$. The coarse graining of phase space decreases with $\hbar$, and density of states on or nearby the resonance surface increases. The states in the neighborhood of the resonance surface become nearly degenerate to the states within the degenerate manifold.

The Hamiltonian is diagonalized as described in Section 6.3.2 for the total polyad number $P^Q_c = \sum_i m_i$ for $m$ defined by equation 6.39. Figures 6.13(a) and 6.13(b) show $\langle I_3 \rangle$ for $D=3$ Coupling Scheme I and Coupling Scheme III, respectively for $\frac{1}{7} \leq \hbar \leq 1$. For $h < \frac{1}{7}$, the calculation of $\langle I_3 \rangle$ became numerically intractable due to the large number of basis states in $P^Q_c$, even when a truncated basis set was used. Nevertheless, both figures 6.13(a) and 6.13(b) clearly show $\langle I_3 \rangle$ approaching the classical limit as $\hbar$ decreases.

Reducing $h$ decreases the coarse graining in action space. This increases the number of states on or nearby the classical resonances, and several states become nearly degenerate to the states lying on the resonance. The second order correction to energy due to coupling with states outside the degenerate manifold goes as $\Delta_2 \sim \frac{\lambda^2}{h}$. 

131
This becomes increasingly significant in the limit $\hbar \to 0$, and the degenerate states will mix with states outside the degenerate manifold. Consequently, this leads to energy flow away from resonance surface and reduces the flow rate along the resonance surface.

![Scheme I](a)

![Scheme III](b)

**Figure 6.13:** Plot of semiclassical limit for D=3 with $\frac{1}{7} \leq \hbar \leq 1$ for (a) Coupling Scheme I and (b) Coupling Scheme III. For both couplings, $\langle I_3 \rangle$ approaches the classical average as $\hbar$ is decreased.
6.6 Conclusion

We have studied the classical transport rates and compared them to dynamical tunneling rates using a relatively simple, yet physically motivated, Hamiltonian with a readily constructible Arnol’d Web. Our results show that dynamical tunneling occurs at a significantly faster rate than classical transport. Classically, the system is extremely sensitive to initial conditions and topology of the Arnol’d Web. A portion of the initial states do not remain on the resonance surface for $t > \frac{1}{\lambda}$ and will not diffuse along the web. Consequently, the entire classical density does not feature the expected fast drift.

Quantum Mechanically, the system is more resistant to energy flow outside the resonance surface for $h = 1$ and features a significant enhancement over the classical rate of energy flow, regardless of the coupling structure. The only major exception is a three degree of freedom run using the Coupling Scheme III. Even for this run, however, the dynamical tunneling was still dominant. The results also suggest that with higher degrees of freedom and an increasingly dense Arnol’d Web, the rate of energy flow is suppressed both classically and quantum mechanically. Examining the tunneling rate for $D = 3$ in the semiclassical limit further illustrated robustness of the analogous quantum system against flow off the resonance surface in the few quantum number regime ($h = 1, P_c = 5$).

The results in this paper support the claim that dynamical tunneling is a prime culprit for the fine low-energy peak splittings observed in IR spectra of medium-sized polyatomic molecules. If dynamical tunneling is faster than fast diffusion, it very likely that it would be faster than Arnol’d Diffusion in which takes place on exponentially long timescales. While our model does not sample the entire parameter space.
for determining whether or not dynamical tunneling is faster than fast diffusion, this is impossible to do in any event. Although we studied a specific non-convex Hamiltonian in this paper, our model is not completely nongeneric because Hamiltonians that are quadratic in action must be sign-definite in order to be steep. Therefore, the results and findings in this paper can possibly be applied to a variety of other physical systems.

In addition, future research will need to determine the roles that classical chaos and mode mixing play in vibrational energy flow at low quantum numbers. As discussed in the Introduction, these mechanisms are believed to be unimportant, but it would be useful to directly test this assumption with numerical and even experimental studies. Future work will also need to compare the rate of dynamical tunneling versus Arnol’d Diffusion for an actual molecule in order verify that dynamical tunneling causes the 0.01-0.1 cm$^{-1}$ peak splittings, as observed in high-resolution IR spectra of polyatomic molecules.
In this thesis, the classical-quantum correspondence of polyatomic molecules was discussed in two separate limits: (1) completely rigid asymmetric top molecules and (2) molecules with purely vibrational behavior. The motivation of the first part was to study the behavior of two rigid structural isomers, \textit{para}-aminobenzonitrile (PABN) and \textit{ortho}-aminobenzonitrile (OABN). Determining the degree of ergodicity brought great insight into their behavior in MBD experiments. Specifically, the results show that the dynamics of each molecule depends on the region of phase space of the initial rotational state, the asymmetry of the molecule, and the direction of the dipole. A larger portion of phase space was chaotic for OABN than for PABN, which is a likely cause for the experimental discrepancies as observed in reference 1.
Future work needs to be done in the general case, where a polyatomic molecule has both vibration and rotational degrees of freedom. The system becomes incredibly complicated once vibrational degrees of freedom are introduced, and a statistical approach is used to describe non-rigid molecules. However, a non-statistical description for a semi-rigid rotor could be made by adding a single vibrational mode along a rotational axis. In this limit, one can study how a single vibrational degree of freedom impacts deflection and work up to the limit where all vibrational modes are present.

The motivation of the second part was to consider the impact of dynamical tunneling in IVR and compare it to classical diffusion. The quantum and classical energy-flow rates were found for a non-convex Hamiltonian, which encapsulated the essential characteristics of a polyatomic molecule with purely vibrational behavior. The results show that the quantum rate of energy-flow is much faster than the classical rate, even though the classical system was expected to feature fast diffusion. The results rule out Arnol’d Diffusion as a viable mechanism for the $0.01 - 0.1 \text{ cm}^{-1}$ peak splittings in high-resolution IR spectra, as dynamical tunneling would likely be faster.

Future work needs to consider the impact of dynamical tunneling in IVR for a convex Hamiltonian, which is ideally derived from a spectroscopic Hamiltonian. This could be done using the methods discussed in Chapter 5, Section 5.7. This could provide further insight, beyond conjecture, on the role of dynamical tunneling in the ubiquitous $0.01$-0.1 cm$^{-1}$ splittings in IR spectra and how it compares to other speculated mechanisms, such as trapping near resonance junctions.
References


[8] Breidung, J.; Thiel, W. Handbook of High-resolution Spectroscopy 2011,


