COHERENT CONTROL, QUANTUM CHAOS, AND DECOHERENCE IN MOLECULAR DYNAMICS

By

Jiangbin Gong

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Graduate Department of Chemistry

University of Toronto

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Coherent Control, Quantum Chaos, and Decoherence in Molecular Dynamics

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Abstract of Thesis

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2001
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Abstract

Extensive coherent control of quantum chaotic diffusion in periodically kicked dynamics is demonstrated in both a paradigm of quantum chaos and molecular systems in pulsed microwave fields. The origin of the control in deviations from random matrix theory is identified, and the survival of the control in the presence of decoherence effects is studied.

Next, a fundamental principle in quantum physics with regard to indistinguishability and interference between multiple pathways to the same final state is applied to the significant field of coherent control. Later, coherent control of diatom-diatom elastic and inelastic scattering of identical molecules is demonstrated by revealing an intriguing role of quantum entanglement in coherent control problems.

Finally, quantum classical correspondence in conservative chaotic systems is carefully examined using a distribution function strategy. Further, the role of decoherence in improving the correspondence is computationally studied from several complementary perspectives.
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Jiangbin Gong

The University of Toronto

June 2001
Dedicated to my parents
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Chapter 1

Introduction
CHAPTER 1. INTRODUCTION

This thesis describes work on three topics: coherent control, quantum chaos, and decoherence. At first glance, these three areas appear unrelated to one another. However, all of these areas are relevant to an understanding of the quantum dynamics of atomic and molecular systems. For instance, (1) decoherence, i.e., the loss of quantum coherence due to uncontrollable noise or quantum entanglement, is an inevitable concern in the design of coherent control experiments, (2) decoherence may be crucial in understanding quantum classical correspondence in classically chaotic systems, (3) coherent control may provide methods for overcoming decoherence, and (4) quantum chaos may prove to be a significant challenge to control of molecular systems, etc. Indeed, new perspectives into each of these areas could be awarded when their overlap is emphasized.

Coherent control of molecular and atomic processes has been a fascinating and rapidly developing research area. Absent from our traditional understanding of chemistry, the key observation in coherent control is that the constructive or destructive quantum interference effects between multiple pathways to the same target state can be engineered to enhance or suppress the yield of desired or undesired product. Many theoretical and experimental studies in coherent control have been done, demonstrating our ability of active control of chemical processes by introducing different quantum interference effects. In this sense, we have witnessed the emergence of a new branch of chemistry: coherence chemistry.

In order to help experimentalists find and design laboratory parameters to achieve different control objectives, an essential part of the theoretical work on co-
herent control is to explore new quantum interference effects in molecular dynamics, to provide insights into various quantum coherence phenomena, and to reveal the role of decoherence effects in various problems. In particular, this thesis is motivated to (1) open up some new directions of coherent control, such as the control of periodically kicked chaotic dynamics and the control of diatom-diatom scattering, etc., (2) advance our understanding of the quantum interference phenomena in various coherent control scenarios in the literature, and (3) provide new insights into quantum classical correspondence in conservative chaotic systems, as a preparation for the study of coherent control of complex molecular dynamics (e.g., coherent control of intramolecular vibrational relaxation) which is typically nonlinear and chaotic. Below we introduce this work, in an effort to briefly describe the literature, motivation, and results associated with each chapter of this thesis.

Quantum chaos has been a rapidly developing area for two decades. The focus of much of the literature on quantum chaos is on quantum manifestations of classical chaos, such as the Random-Matrix-Theory statistical behavior of eigenvalues and eigenfunctions, time-dependent characteristics of wavepacket evolution, and signatures of classical unstable periodic orbits, to name a few. The central issue of this field is to understand quantum classical correspondence (QCC) in classically chaotic systems. In such systems, the classical dynamics is characterized by exponential sensitivity to initial conditions, with the exponential divergence rate of two nearby trajectories given by the Lyapunov exponent. By contrast, for any quantum bounded system, the quantum dynamics is necessarily quasi-periodic due to the dis-
creteness of the spectrum. Hence, QCC presents many serious theoretical problems for classically chaotic systems. Of most fundamental importance is the unresolved question as to whether the macroscopic chaotic classical world is a simple limit of quantum mechanics. The issue is of importance to atomic and molecular systems as well, insofar as it is still unclear to what extent one can use classical chaos language to describe nonlinear systems which may be neither extremely quantal nor perfectly classical.

It is thus not surprising that most quantum chaos studies to date have focused on quantum interference effects solely in terms of quantum dynamics and have avoided considering input coherence effects on the dynamics. This is in sharp contrast to the studies on coherent control, where both input quantum coherence (e.g., the initial quantum phases introduced by a laser pulse) and quantum interference in the ensuing dynamics are essential. Thus, we are naturally led to the question as to whether it is possible to coherently control quantum chaotic dynamics by actively introducing different quantum coherence effects into the system of interest.

To answer this question, we present in Chap. 2 our study of coherent control of quantum chaotic diffusion, using the kicked rotor model, the paradigm for both classical and quantum chaos. In particular, we show ample evidence that extensive coherent control of quantized chaotic dynamics can be achieved, provided that the quantum system is not close to the semiclassical limit. The origin of such control is identified as statistical deviations from Random-Matrix-Theory. Thus, the importance of initial quantum phases in quantum chaotic dynamics surfaces for the first
CHAPTER 1. INTRODUCTION

time. Moreover, we consider decoherence effects on coherent control of quantum chaotic dynamics, using two different models simulating the system-environment interaction. This enriches our understanding of decoherence effects on quantum chaos and coherent control. In Chap. 3, we consider coherent control of quantum chaotic dynamics in diatomic molecular systems periodically kicked with microwave pulses. Results in Chap. 3 constitute a successful extension of the study in Chap. 2. New directions for both areas of quantum chaos and coherent control are thus opened. We anticipate that results in Chaps. 2 and 3 could be experimentally realized in the near future.

Having demonstrated some intriguing and useful quantum interference effects in molecular dynamics, in Chap. 4 we turn to a deep and thorough understanding of quantum interference in the context of coherent control. In doing so, we address a fundamental principle regarding to the relationship between quantum interference and indistinguishability of multiple pathways to the same target state. That is, multiple pathways to the same target state interfere with one another only if they are indistinguishable. With this principle, several typical coherent control scenarios in the literature (such as two-pulse control, incoherent interference control, and \("\omega_1 + \omega_2\) vs. \("\omega_2 + \omega_1\) control, etc.) are carefully examined. We show that, if there exists significant undesired quantum entanglement, then the which-pathway information leaks out and coherent control is lost. It turns out that it is usually the classical properties of light fields that could guarantee the coherence transfer from light fields to molecular systems without suffering from any entanglement-induced decoherence.
effects. Having demonstrated that, the crucial role of laser-matter interaction in coherent control becomes clear. Further, we reveal a fundamental difference between laser-phase sensitive and laser-phase insensitive coherent control scenarios.

Our work in Chap. 2 and Chap. 3 and most studies in the literature on coherent control focus on unimolecular processes. By contrast, active control of both nonreactive and reactive bimolecular collisions is currently under preliminary investigation and presents a big challenge. Chapter 5 is devoted to a novel consideration of the coherent control of bimolecular collisions between identical molecules. Specifically, Chap. 5 presents an intriguing interference manipulation scenario which is related to molecular entanglement and constitutes new theoretical progress towards the coherent control of bimolecular scattering. In particular, using the scattering of \textit{para} $H_2 + \textit{para} H_2$ as a computational example, we show that subtle quantum interference effects can have dramatic effects on both differential and total cross sections in elastic and inelastic diatom-diatom scattering of identical molecules. We also discuss the extension and experimental realization of our theoretical control results.

Our results in Chaps. 2 and 3 seem to suggest that the coherent control approach may also be promising in manipulating much more complicated molecular dynamics, such as the intramolecular vibrational energy flow which typically involves many degrees of freedom and is classically chaotic. However, much work remains to be done along this direction. In particular, we believe that a crucial step is to gain more insights into QCC and decoherence effects in conservative chaotic dynamics. This motivates us to return to the topic of quantum chaos in Chaps. 6 and 7.
A very promising distribution function approach was proposed recently in order to attack the problem of QCC in chaotic systems. This approach circumvents the difficulty caused by the absence of a trajectory description of the quantum dynamics (within the orthodox interpretation of quantum mechanics). Rather, it takes advantage of the similarity between the von-Neumann equation and the classical Liouville equation. Chapter 6 applies this approach. In particular, we study the quantum analogue of a measure of classical phase space structure, whose exponential increase rate gives rise to classical Lyapunov exponent. The correspondence and discrepancy between quantum and classical chaotic dynamics with regard to this measure is then examined in detail, shedding much light on the issue of QCC. Studies in Chap. 6 are also relevant to understanding the decoherence rate in terms of the entropy production rate in classical statistical mechanics. In addition, Chap. 6 shows that QCC from the viewpoint of phase space structure is closely related to the stability properties of some classical trajectories, and that QCC from the perspective of ensemble expectation values may assume a completely different nature.

Unfortunately, the results in Chap. 6 based on the distribution function strategy can not help in the understanding of the emergence of chaotic trajectories from quantum mechanics. To see the seriousness of this issue, let's imagine a macroscopic quantized chaotic Hamiltonian system starting its time evolution with a minimum-uncertainty-product wavepacket. Due to the underlying classical chaotic motion, the wavepacket would rapidly smear over a considerable part of the phase space such that its central motion will no longer satisfy Newton's equation after an unusually
short time scale. Thus, it is clear that chaotic trajectories can not emerge from within quantum dynamics of closed systems. This motivates our study in Chap. 7, which focuses on an unraveling of the master equation of the distribution function into quantum trajectories, in order to understand environment-induced decoherence effects on quantized chaotic systems. In doing so, we deliberately choose a strongly chaotic system for which there is extensive competition between decoherence effects and chaos-induced quantum interference effects. We show that decoherence can lead to significant improvement in QCC in ensemble expectation values, i.e., quantum mechanics plus decoherence effects is in far better agreement with the classical mechanics plus decoherence effects than is the analogous comparison in the absence of decoherence. We further show that it is possible to observe the emergence of chaotic classical trajectories from open quantum systems. The results in Chap. 7 constitute the first computational study of decoherence effects in conservative chaotic systems, from both the ensemble and the trajectory point of view.

In summary, this thesis explores some new problems relevant to three significant research areas, namely, coherent control, quantum chaos, and decoherence. In addition to several independent contributions to each of these areas, a considerable part of this thesis is devoted to the exploration of some novel physics resulting from their overlap. Of considerable significance is that this thesis (1) pioneers the study of coherent control of quantum chaotic dynamics, (2) reveals for the first time the subtle role of quantum entanglement in coherent control problems, and (3) substantially enriches our understanding of quantum classical correspondence and decoherence effects.
in conservative chaotic systems.
PART I

COHERENT CONTROL
OF CHAOTIC DIFFUSION
Chapter 2

Coherent Control of Quantum Chaotic Diffusion
Chapter Summary:

Extensive coherent control over quantum chaotic diffusion using the kicked rotor model is demonstrated. Further, the extent of control in the presence of external decoherence is established using two simple decoherence models. The results are relevant to the areas of both quantum chaos and coherent control.
Chapter 2. COHERENT CONTROL OF QUANTUM CHAOTIC DIFFUSION

2.1 Introduction

The observation that quantum interference and hence molecular dynamics can be altered via experimentally controllable parameters motivated the exciting field of coherent control (CC) of molecular processes [1]. The essence of several scenarios of CC of molecular processes consists of three steps: (1) prepare the molecular system in a superposition state composed of several basis states, (2) control the relative phases of these basis states, and (3) subject the molecular system to external fields which allow for multiple coherent pathways to the same target state. Successful control results when the yield of particular target states can be extensively altered by changing the relative phases in the second step. Studies of this kind include, for example, the original contribution on CC [2], two-pulse control schemes applied to various problems [3], and the CC of molecular scattering [4].

Traditional studies in CC typically deal with regular model systems in which very few energy levels are involved in the dynamics. By contrast, the majority of molecular systems are very complex: the quantum dynamics may involve many energy levels and the underlying classical dynamics may be strongly chaotic. For this reason consideration of control for chaotic systems is of general interest and importance.

Classical chaotic systems, the subject of this chapter, display intrinsic stochasticity generated by the dynamics itself [5]. Thus, even without any external noise, a classical chaotic system loses memory of the initial state exponentially fast. Considering the quantum-classical correspondence principle in quantized chaotic systems, one would expect that various manifestations of classical chaos in the quantum system
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should occur when the relevant actions are much larger than Planck's constant [6]. With this perspective, one intuitively believes that quantum phases embedded in initial states play a minor role in classically chaotic systems, and controlling quantized chaotic dynamics in the semiclassical regime could be just as difficult as controlling classical Hamiltonian chaos [7]. Nevertheless, coherent control over quantum chaotic dynamics far from the classical limit should be feasible. There beliefs are examined quantitatively, below.

The kicked rotor and its classical limit, the standard map, have long served as paradigms for classical and quantum chaos [8]. The classical dynamics shows characteristic diffusive energy growth whereas the quantum dynamics shows similar chaotic short time behavior, followed by the suppression of diffusion at longer times. In this chapter, we demonstrate that the quantum features of the chaotic kicked rotor allow for extensive coherent control [1, 2, 3, 4] over quantum chaotic diffusion, even in the presence of modest decoherence. In particular, we show that quantum relaxation dynamics in the kicked rotor model is sensitive to the coherence characteristics of the initial state, and that altering these characteristics allows for control over the energy diffusion. The extent of the controlled behavior is vast, from strong suppression to strong enhancement of diffusion.
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2.2 The Kicked Rotor Model

Consider the kicked rotor whose Hamiltonian is given by

\[ H(\hat{L}, \theta, t) = \frac{j^2}{2I} + \lambda \cos(\theta) \sum_n \delta(t/T - n), \]  

where \( \hat{L} \) is the angular momentum operator, \( \theta \) is the conjugate angle, \( I \) is the moment of inertia, \( \lambda \) is the strength of the "kicking field", and \( T \) is the time interval between kicks. The quantum time evolution operator \( \hat{F} \) for times \((N - 1/2)T \) to \((N + 1/2)T \) is given by [8]

\[ \hat{F} = \exp[i\tau \frac{\partial^2}{4 \partial \theta^2}] \exp[-ik \cos(\theta)] \exp[i\tau \frac{\partial^2}{4 \partial \theta^2}], \]

with dimensionless parameters \( \tau = \hbar T/I \) and \( k = \lambda T/\hbar \). The classical limit [8] of this quantum map is given by the standard map, which, when expressed in terms of dimensionless variables \( \theta \) and the scaled c-number angular momentum \( \tilde{L} = L \tau/\hbar \), takes the following form,

\[ \theta_N = \theta_{N-1} + (\tilde{L}_N + \tilde{L}_{N-1})/2, \]
\[ \tilde{L}_N = \tilde{L}_{N-1} + \kappa \sin(\theta_{N-1} + \tilde{L}_{N-1}/2), \]

where \( \kappa = k\tau \), and \((\tilde{L}_N, \theta_N)\) represents the phase space location of a classical trajectory after \( N \) kicks. An essential difference between quantum and classical maps is that the former has two characteristic parameters \( \tau \) and \( k \), while the latter depends only on their product. As we decrease the magnitude of \( \tau \) and fix the value of \( \kappa \), quantum dynamics will become closer and closer to the semiclassical limit.
Figure 2.1: The Poincaré surfaces of section for the standard map described by Eq. (2.3). (a) $\kappa = 0.5$, (b) $\kappa = 1.0$, (c) $\kappa = 2.5$ and (d) $\kappa = 5.0$. Note that the structure for the entire phase space is also periodic in $L$ with the period $2\pi$.

Figure 2.1 displays the poincaré surfaces section for the standard map for $\kappa = 0.5, 1.0, 2.5$ and 5.0. For small $\kappa$ shown in Fig. 2.1a, there are some Kolmogorov-Arnold-Moser (KAM) curves extending over the entire range of $\theta$. These KAM curves characterize the local integrable motions and act as dynamical barriers forbidding the classical trajectories to go from the low $L$ regions to high $L$ regions. It is well known that the last global KAM curve is broken for $\kappa > \kappa_\text{cr} = 0.9716...$. This is
illustrated in Fig. 2.1b for $\kappa = 1.0$. Figures 2.1c and 2.1d show that the classical system becomes more and more chaotic with increasing $\kappa$. As the classical dynamics becomes chaotic, the unbounded chaotic diffusion into the entire energy space arises. The resultant diffusion constant can be defined as the absorption rate of the average scaled rotational energy $\tilde{E} \equiv \langle \tilde{E}^2 \rangle / 2$.

Comparing classical and quantum dynamics for typical initial classical states shows that quantum dynamics displays significant suppression of the classical chaotic diffusion, i.e., the external field can only excite a finite number of unperturbed energy levels [9]. This number, characterized by the so-called dynamical localization length, can be shown by statistical considerations to be related to the classical diffusion constant [9]. Thus, there is a marked difference between the classical and quantum dynamics manifest in qualitatively different energy absorption behavior.

### 2.3 Phase Control Results

The fact that the rotor is a Hamiltonian system and the kick is coherent implies that the system maintains its quantum phase throughout the evolution. If this is the case then the system should be controllable via coherent control [1], i.e., by using quantum interference phenomena to affect the dynamics. To demonstrate this, and to examine the extent of possible control, we consider the dynamics of states which are initially comprised of superpositions of two arbitrary angular momentum eigenstates, $|m\rangle = \exp(i m \theta) / \sqrt{2\pi}$ and $|n\rangle = \exp(i n \theta) / \sqrt{2\pi}$. Each of these eigenstates is classically allowed, with a corresponding classical distribution function given by
\rho_{m}^{c}(\theta, \vec{L}) = \delta_{L/\tau,m}/2\pi \text{ and } \rho_{n}^{c}(\theta, \vec{L}) = \delta_{L/\tau,n}/2\pi, \text{ respectively } [10].

To show that changing the coherent characteristics of the initial state significantly alters the subsequent dynamics, we consider the dynamics of states given initially by the superposition \( |\psi\rangle = \cos(\alpha)|m\rangle + \sin(\alpha)\exp(i\beta)|n\rangle \). Typical results, culled from numerous cases of varying \( \alpha, \beta, k \) and \( \tau \) are shown below and correspond to a weaker and stronger chaotic case, and to two values of \( \beta \), i.e., \( \beta = 0 \), and \( \beta = \pi \). Specifically, we display below results for case (a) \( |\psi_{a}^{\pm}\rangle = (|+2\rangle \pm |-1\rangle)/\sqrt{2} \), with \( \tau = 0.5, k = 5.0 \) and for case (b) \( |\psi_{b}^{\pm}\rangle = (|+1\rangle \pm |+2\rangle)/\sqrt{2} \), with \( \tau = 1.0, k = 5.0 \). Note that neither the basis states nor the superposition states are eigenstates of the parity operator.

Figure 2.2 shows \( \tilde{E} \) for each of these two systems and for each of the values of \( \beta \). Figure 2.2a, for example, displays \( \tilde{E} \) for \( |\psi_{a}^{-}\rangle \) (dashed curve) and for \( |\psi_{a}^{+}\rangle \) (solid curve). Clearly, the initial state \( |\psi_{a}^{-}\rangle \) gives clear diffusive behavior during the first 40 kicks whereas energy absorption in the case of \( |\psi_{a}^{+}\rangle \) is completely suppressed. As a result, \( \tilde{E}(t = 40T) = 9.6 \) for the \( |\psi_{a}^{-}\rangle \) case, while \( \tilde{E}(t = 40T) = 1.6 \) for propagation from the initial state \( |\psi_{a}^{+}\rangle \). Note (1) that this huge difference is achieved solely by changing the initial relative phase \( \beta \) between the two participating states \(|+2\rangle \) and \(|-1\rangle \) in the initial superposition, and (2) that by contrast, each of \(|+2\rangle \) or \(|-1\rangle \) individually would behave similarly to one another with respect to energy absorption, giving \( \tilde{E}(t = 40T) = 5.4 \) and 6.0, respectively. Hence, the observed control is due entirely to changing the coherent properties of the initial superposition state.

Similar control persists for the more chaotic case shown in Fig. 2.2b. Here
Figure 2.2: The expectation value of the dimensionless scaled rotational energy \( \tilde{E} = \langle \hat{L}^2 \rangle / 2 \hbar^2 \) versus time (in units of \( T \)). (a) Solid and dashed lines are for the initial states \( |\psi_+^+\rangle \) and \( |\psi_-^-\rangle \), respectively, \( \tau = 0.5, k = 5.0 \). (b) Solid and dashed lines are for the initial states \( |\psi_+^+\rangle \) and \( |\psi_-^-\rangle \), respectively, \( \tau = 1.0, k = 5.0 \).

\( |\psi_+^+\rangle \) (solid line) shows extensive chaotic diffusion (i.e., compare ordinates scale for Figs. 2.2a and 2.2b) for up to 45 kicks, giving \( \tilde{E}(t = 45T) \) far higher than the value of 70.4 and 77.1 reached by propagating either of the basis functions \( | +1 \rangle \) and \( | +2 \rangle \).

Further, and by contrast, there is essentially no quantum diffusion after \( t = 4T \) for \( |\psi_-^-\rangle \) (dashed line).

These differences are also reflected in the details of the evolving wavefunctions. For example, Fig. 2.3 shows the probability \( P(m) \) of finding the system in the state \( |m\rangle \) at \( t = 60T \). For case (a), \( P(m) \) for \( |m| \geq 10 \) is 15.8% and 3.4% for \( \beta = \pi \) and for \( \beta = 0 \), respectively. Similarly, for case (b) \( P(m) \) differs by a factor of 5.4 for the two \( \beta \) values (3.2% vs. 17.2%) in the probability of exciting the rotor to high-energy
rotational states $|\alpha\rangle$, $|\beta\rangle \geq 20$. In both Figs. 2.3a and 2.3b it is evident that the difference in final populations resulting from the evolution of the two superpositions is an erratic function of $m$ with few evident trends.

Figure 2.3: Probability $P(m)$ of finding the system in the state $|\alpha\rangle$ at $t = 60T$. Results are for the cases shown in Fig. 2.2.

The behavior shown in Fig. 2.2 is in sharp contrast to that which would be observed for the same initial distributions propagated classically. These computations are shown in Fig. 2.4 and result from classical propagation of the initially non-positive-definite Wigner function $\rho^W(\theta, \bar{L})$ associated with the wavefunction $\cos(\alpha)|\alpha\rangle + \sin(\alpha)\exp(i\beta)|\beta\rangle$. That is, we classically propagate

$$\rho^W(\theta, \bar{L}) = \cos^2(\alpha)\rho_m^\alpha(\theta, \bar{L}) + \sin^2(\alpha)\rho_n^\beta(\theta, \bar{L})$$

$$+ \frac{1}{2\pi} \sin(2\alpha) \cos[\beta - (m - n)\theta] \delta_{L/\tau, (m+n)/2}. \quad (2.4)$$

for each of $|\psi^\pm\rangle$ and $|\psi^0\rangle$. In all cases, the classical results show [Fig. 2.4] strong
Figure 2.4: As in Fig. 2.2 except that $\tilde{E}$ is calculated by classically propagating the initial non-positive-definite Wigner function in Eq. (2.4).

diffusion, characteristic of the chaotic dynamics of the standard map. In particular, (1) for the strong chaos case [Fig. 2.4b], after several kicks the classical diffusion rate of $|\psi_0^+\rangle$ is identical with that of $|\psi_0^-\rangle$, indicating that the classical dynamics rapidly loses its memory of the initial-state information; (2) for the weak chaos case [Fig. 2.4a], there are only small differences in the $\tilde{E}$ diffusion between $|\psi_\alpha^+\rangle$ and $|\psi_\alpha^-\rangle$.

Thus, the extensive phase control results illustrated in Fig. 2.2 is not a simple result of initial state coherence. Rather, it is based on the interplay of initial-state coherence and coherent quantum dynamics.

It is interesting to discuss the origin of the small differences in the diffusion rate between $|\psi_\alpha^+\rangle$ and $|\psi_\alpha^-\rangle$ shown in Fig. 2.4a. They can be understood in terms of the interference term in Eq. (2.4) with connection to the classical phase space structure (see Fig. 2.1c). In the weak chaos case, there are some stable islands in the phase
space. Thus, classical trajectories initially located on the stable islands contribute nothing to the chaotic diffusion, whereas classical trajectories initially located on the chaotic sea will contribute quite uniformly to the chaotic diffusion. As a result, if the positive region of the interference term in Eq. (2.4) overlaps largely with the chaotic sea and its negative region overlaps largely with the stable islands, it will enhance the classical diffusion; and if its negative region overlaps largely with the chaotic sea and its positive region overlaps largely with the stable islands, it will suppress the classical diffusion.

Figure 2.5: The expectation value of the dimensionless scaled rotational energy $\tilde{E} = \langle \tilde{L}^2 \rangle r^2 / 2h^2$ versus time (in units of $T$). Solid and dashed lines are for the initial states $|\psi^+\rangle$ and $|\psi^-\rangle$, respectively. (a) $\tau = \pi / 3$, $k = 5.0$, (b) $\tau = \pi / 2$, $k = 4.0$.

To end this section, it should also be noted that the kicked-rotor model can assume some extremely fast energy absorption behavior which does not have a classical analogue. This happens when the parameter $\tau$ is given by $(m/n)\pi$, where $m$
and \( n \) are integers. Under such conditions the free motion of the rotor is in resonance with the kicking field, and the corresponding energy absorption behavior is called quantum-resonance diffusion. Undoubtedly, it is also of great interest to examine the significance of phase control in quantum resonance cases. Figure 2.5 displays two computational examples of phase control of quantum resonance diffusion. It is seen that control is also possible, but somewhat less extensive than the chaotic diffusion cases shown before.

### 2.4 Origin of Phase Control

Consider the origins of coherent control of chaotic systems in the quantum dynamics, and the behavior in the classical limit. To this end we diagonalize the quantum map operator \( \hat{F} \) by a unitary operator \( \hat{U} \), i.e., \( \langle i | \hat{F} | j \rangle = \sum_k e^{-i\phi_k} U^*_k U_{kj} \), where \( U_{ij} \equiv \langle i | \hat{U} | j \rangle \), \( j = 1, 2, \ldots \) is the eigenvector with eigenphase \( \phi_i \). After the initial superposition state \( |\psi\rangle = \cos(\alpha)|m\rangle + \sin(\alpha)\exp(i\beta)|n\rangle \) is kicked \( N \) times, we have

\[
\frac{2\tilde{E}}{\tau^2} = \cos^2(\alpha) \sum_{ijj'} l^2 U^*_{jm} U^*_{j'n} U_{jl} U_{j'm} \exp[iN(\phi_j - \phi_{j'})] \\
+ \sin^2(\alpha) \sum_{ijj'} l^2 U^*_{jn} U^*_{j'n} U_{j'l} U_{j'm} \exp[iN(\phi_j - \phi_{j'})] \\
+ \left\{ \frac{1}{2} \sin(2\alpha) \exp(-i\beta) \sum_{ijj'} l^2 U^*_{jm} U_{j'n} U_{jl} U_{j'l} \exp[iN(\phi_j - \phi_{j'})] \right\} + \text{c.c.}, \tag{2.5}
\]

where c.c. denotes the complex conjugate of the immediately preceding term within the brackets. The total term in brackets corresponds to interference effects due to
initial-state coherence. For large $N$ only the $j = j'$ terms will survive in the summations due to rapid oscillations of $\exp[iN(\phi_j - \phi_{j'})]$. Hence the last two terms reduce to $1/2 \sin(2\alpha) \exp(-i\beta) \sum_i l^2 \sum_j |U_{ij}|^2 U_{jm}^* U_{jn} + c.c.$

As further discussed in detail in the next chapter, if there is no structure in $|U_{ij}|^2$ and the eigenvector components $U_{jm}^*$ and $U_{jn}$ are perfectly independent, as expected from Random-Matrix-Theory [11], then $\sum_j |U_{ij}|^2 U_{jm}^* U_{jn}$ is small and the fluctuation of the interference term is $1/\sqrt{D}$ times smaller than that of the incoherent terms (where $D$ is the effective dimension of the Hilbert space), interference vanishes and control is lost. Thus, the coherent control of quantum chaotic diffusion relies upon the residual statistical correlations between eigenvector components $\{U_{ij}\}$. Indeed, in this system the matrix $\langle i| \hat{P}^\dagger |j \rangle$ is known to display a band structure with the bandwidth $2k$ where the quantity $k^2/N$, where $N$ is the size of the banded random matrices, provides a measure of the statistical deviations from Random Matrix Theory [12]. Numerical results show that $k^2/N < 0.2$ is sufficiently small for control to persist. This being the case, we obtain a necessary condition to ensure the significance of the interference term, namely, $k < 0.2N_\kappa/\kappa$ or $\tau > \kappa^2/(0.2N_\kappa)$, where $N_\kappa$ is the minimum grid size for accurate FFT calculations with $\tau = 1$. Numerical studies indicate that, for $\kappa < 10.0$, $N_\kappa \approx 256$, implying that we require $k < 50/\kappa$ or $\tau > \kappa^2/50$ for control. This makes clear that as one approaches the classical limit (by increasing $k$ or decreasing $\tau$ with fixed $\kappa$), coherent control is lost.
2.5 Decoherence Effects

The dynamics of the kicked rotor in the presence of decoherence effects has also been examined both experimentally [13] and theoretically [14]. The survival of control in the presence of decoherence is of interest both in general, and for this particular case. To examine this issue we first introduce a very simple decoherence model. Here, the quantum map operator between \((N - 1/2)T\) and \((N + 1/2)T\) is taken as \(\hat{R}\hat{F}\), where \(\hat{R}\) introduces random phases into the system. Specifically,

\[
\hat{R}|m\rangle = \exp[i2\pi r \xi(m, N)]|m\rangle,
\]

where \(m = 0, \pm 1, \pm 2, \ldots\), and \(\xi(m, N)\) takes on random values that are distributed uniformly between 0 and 1 for each different \(m\) or \(N\). The interesting aspect about this model is that its \(r \to 1\) limit corresponds to momentum-measurement-induced quantum diffusion [15].

The density matrix \(\hat{\rho}\) for the dynamics governed by \(\hat{R}\hat{F}\) can then be obtained as an average over many realizations of \(\xi(m, N)\). We take the linear entropy \(S \equiv Tr \hat{\rho}^2\) as a useful additional measure of the purity of quantum states, and hence of the effect of decoherence. Numerical studies show that for \(r < 0.05\), coherent control of quantum diffusion is hardly affected by the decoherence. For stronger decoherence, e.g. \(r = 0.15\), phase control is essentially lost. Examination of the corresponding values of \(S(t = 60T)\) shows that this is consistent with maintenance of control when the decoherence is sufficiently small so that \(S(t = 60T) > 0.4\). In parallel with the phase control results shown in Fig. 2.2 for the closed system case, Figs. 2.6 and 2.7
Figure 2.6: Same as Fig. 2.2 but in the presence of modest decoherence using the first decoherence model described by Eq. (2.6) with $r = 0.05$.

displays the time dependence $\tilde{E}$ versus the time in the presence of small decoherence [Fig. 2.6, $r = 0.05$] and of appreciable decoherence [Fig. 2.7, $r = 0.15$]. Comparison of Fig. 2.6 with the decoherence-free dynamics in Fig. 2.2 shows that control is still significant, but decoherence is beginning to have an effect insofar as $\tilde{E}$ at $t = 60T$ is larger in Fig. 2.6 than in Fig. 2.2. That is, the results show a slight tendency towards the classical behavior. In the case of stronger decoherence [Fig. 2.7] phase control is greatly reduced and long time linear diffusive growth of $\tilde{E}$ is observed. A careful examination of Figs. 2.7b suggests that phase control persists until $t \approx 15T$ when the slopes of the dashed and solid curve become virtually identical. However, the slopes of these curves are still significantly less than those in Fig. 2.4, suggesting that quantum coherence is still maintained at these longer times. In essence, it appears that phase control over the diffusion rate vanishes before quantum coherence
is completely destroyed.

![Graph](image)

Figure 2.7: Same as Fig. 2.2 but in the presence of strong decoherence using the first decoherence model described by Eq. (2.6) with \( r = 0.15 \).

To further show that coherent control of quantum chaotic diffusion could be substantially degraded by decoherence, the quantum state diffusion technique is applied here to establish a second decoherence model (for the details on the quantum state diffusion approach to decoherence, see Chap. 7). In this model, the time evolution of the state vector is described by the following stochastic Schrödinger equation

\[
|d\psi\rangle = \frac{-i}{\hbar} H|\psi\rangle dt + \sqrt{\gamma} (\cos(\theta) - \langle \cos(\theta) \rangle)|\psi\rangle d\xi - \gamma (\cos(\theta) - \langle \cos(\theta) \rangle)^2 |\psi\rangle dt, \tag{2.7}
\]

where \( \langle \cos(\theta) \rangle \) is given by \( \langle \psi | \cos(\theta) | \psi \rangle / \langle \psi | \psi \rangle \), and \( d\xi \) is a complex differential random
variable with the mean properties:

\[
\begin{align*}
\langle d\xi \rangle &= 0, \\
\langle \Re(d\xi)\Im(d\xi) \rangle &= 0, \\
\langle \Im(d\xi)\Im(d\xi) \rangle &= dt, \\
\langle \Re(d\xi)\Re(d\xi) \rangle &= dt. 
\end{align*}
\tag{2.8}
\]

Clearly, decoherence here is due to system-environment interaction via \(\cos(\theta)\), or continuous measurement of \(\cos(\theta)\), rather than momentum-measurement in the first decoherence model. Nevertheless, similar results with regard to quantum diffusion have been obtained. Figure 2.8 shows the control results in the presence modest

![Figure 2.8: Same as Fig. 2.2 but in the presence of weak decoherence using the second decoherence model described by Eq. (2.7) with \(\gamma = 0.02\).](image)

decoherence with \(\gamma = 0.02\). In Fig. 2.8 it is seen that, for case (a), phase control over the diffusion rate is largely unaffected; whereas for case (b), the phase control seems
somewhat more sensitive to decoherence and decreases to a larger extent. Figure 2.9 shows the control results in the presence of strong decoherence with $\gamma = 0.10$. Clearly, with the introduction of strong decoherence, phase control in both the weak chaos case [Fig. 2.9a] and the strong chaos case [Fig. 2.9b] essentially vanishes, confirming the previous results based on a completely different decoherence model. Further, similar to the results in Fig. 2.7, results in Fig. 2.9 show that phase control over the diffusion rate disappears before the quantum diffusion rate with decoherence gets very close to the classical diffusion rate.

Figure 2.9: Same as Fig. 2.2 but in the presence of strong decoherence using the second decoherence model described by Eq. (2.7) with $\gamma = 0.10$.

2.6 Discussion

There has been some concern addressed as to whether the observed control is due to parity issues. This is not the case. First of all, the extensive phase control is not
Figure 2.10: The expectation value of the dimensionless scaled rotational energy $\tilde{E} = \langle \tilde{L}^2 \rangle \tau^2 / 2\hbar^2$ versus time (in units of $T$). Solid and dashed lines are for the initial states $[\sin(\theta) + \sin(2\theta)]/\sqrt{2\pi}$ and $[\sin(\theta) - \sin(2\theta)]/\sqrt{2\pi}$, respectively. (a) $\tau = 0.5$, $k = 5.0$, (b) $\tau = 1.0$, $k = 5.0$. Results here can be compared with those in Figs. 2.2 and 2.11.

Based on parity conservation in the kicked rotor model. Indeed, one can readily check that similar control can be obtained if a parity-breaking kicking potential such as $\cos(\theta + \pi/10)$ is used. More significantly, the possibility of control persists if the basis states comprising the initial superposition state have the same parity. Of particular interest are the positive parity real basis states $\cos(m\theta) / \sqrt{\pi}$ and the negative parity real basis states $\sin(m\theta) / \sqrt{\pi}$, which make up two invariant subspaces (positive parity subspace and negative parity subspace) for the kicked rotor model. Amazingly, as shown in Figures 2.10 and 2.11, extensive phase control can also be obtained by adding together either states $\sin(m\theta) / \sqrt{\pi}$ or by adding together states $\cos(m\theta) / \sqrt{\pi}$.
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In particular, it is seen that (1) the relative phase between basis states $\sin(\theta)/\sqrt{\pi}$ and $\sin(2\theta)/\sqrt{\pi}$ induces drastically different diffusive behavior for both the weak chaos case ($\tau = 0.5$ and $k = 5.0$, Fig. 2.10a) and the strong chaos case ($\tau = 0.5$ and $k = 5.0$, Fig. 2.10b), and (2) whereas the relative phase between states $\cos(\theta)/\sqrt{\pi}$ and $\cos(2\theta)/\sqrt{\pi}$ give rise to coherent control for the strong chaos case ($\tau = 1.0$ and $k = 5.0$, Fig. 2.11b), but not the weak chaos case ($\tau = 0.5$ and $k = 5.0$, Fig. 2.11a).

Figure 2.11: The expectation value of the dimensionless scaled rotational energy $\tilde{E} = \langle \hat{L}^2 \rangle \tau^2 / 2\hbar^2$ versus time (in units of $T$). Solid and dashed lines are for the initial states $[\cos(\theta) + \cos(2\theta)]/\sqrt{2\pi}$ and $[\cos(\theta) - \cos(2\theta)]/\sqrt{2\pi}$, respectively. (a) $\tau = 0.5$, $k = 5.0$, (b) $\tau = 1.0$, $k = 5.0$. Results here should be compared with those in Figs. 2.2 and 2.10.

Evidently, the general superposition state $|\psi\rangle = \cos(\alpha)|m\rangle + \exp(i\beta)\sin(\alpha)|n\rangle$ discussed before can be expressed in terms of the real basis states, i.e.,

$$|\psi\rangle = [\cos(\alpha)\cos(m\theta) + \sin(\alpha)\exp(i\beta)\cos(n\theta)]$$
From Eq. (2.9) it is seen that the dynamics emanating from $|\psi\rangle$ involves both the negative and positive parity subspaces. However, due to parity conservation, these two subspaces can never mix with each other so that their contributions to energy absorption will add incoherently. This point affords even more insights into coherent control of quantum diffusion. Comparing Figs. 2.10 and 2.11 with Fig. 2.2, one sees that (1) phase control in Fig. 2.2a is due to the second component in Eq. (2.9) evolving in the negative-parity subspace, whereas the positive-parity subspace essentially contributes nothing, and (2) phase control in Fig. 2.2b is due to both the first and second components in Eq. (2.9), evolving within the negative parity and positive parity subspaces, respectively. Further, because real basis states are time-reversal invariant states and the kicked-rotor Hamiltonian has the time-reversal symmetry, one can prove that for each definite-parity subspace the relative phase $\beta$ between the real basis states has to be either 0 or $\pi$ to give best control (Chap. 3 includes such a proof). This nicely explains the previous choice of $\beta$ to have best control.

More interestingly, since the states $\sin(m \theta)/\sqrt{\pi}$ satisfy the boundary condition of an infinitely deep square-well potential $V(\theta)$ with $V(0) = V(2\pi) = +\infty$ and since the dynamics of a kicked particle in a well is similar to the kicked rotor for similar initial states [16], results in Fig. 2.10 indicate that one can also demonstrate coherent control of chaotic diffusion using superpositions of Hamiltonian eigenstates of a kicked particle in a potential well.
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A number of possible experimental demonstrations of the proposed control scenario are evident. For example, as discussed in the next chapter, the kicked diatomic molecule CsI [17] is a promising molecular system for demonstrating controlled quantum chaotic diffusion. In this case, preliminary controlled laser excitation could be used to prepare the desired initial superposition state (which are here superpositions of $|J, M\rangle$ and $|J', M\rangle$, where $J$ and $J'$ are the angular momentum and $M$ is their projection on the $z$ axis) and to vary $\beta$. Alternatively, one can utilize the square well analogy described above to experimentally study kicked dynamics of a particle in a well. By contrast, implementation of an atom-optics approach [18] to studies of control may be more difficult, insofar as it is necessary to prepare initial quantum superposition states, a considerable extension of previous work [19].

2.7 Summary

In summary, we have shown that quantum chaotic dynamics in systems such as the kicked rotor may be controlled by varying, in accord with coherent control, the coherent characteristics of the initial state. In particular, preparing even a simple superposition state comprising two basis states allows a wide range of control over the diffusive dynamics. The control persists in the presence of weak decoherence, but, as expected, is lost with increasing decoherence strengths. The predicted range of control is extensive, providing results of broad theoretical and experimental interest.
Bibliography


Chapter 2. COHERENT CONTROL OF QUANTUM CHAOTIC DIFFUSION


Chapter 3

Coherent Control of Quantum Chaotic Diffusion: Diatomic Molecules in a Pulsed Microwave Field
Chapter Summary:

Extensive phase control of quantum chaotic diffusion is demonstrated in diatomic molecules periodically kicked with microwave pulses. In particular, complete suppression of chaotic diffusion as well as its enhancement can be achieved by varying the phase of the initial superposition state. The origin of this control in deviations from random matrix theory is also discussed. The results should motivate experiments, that are relevant to both coherent control and to quantum chaos.
3.1 Introduction

In Chap. 2 it is computationally demonstrated that extensive phase control of quantum chaotic diffusion is achievable using the delta-kicked planetary rotor (DKPR) model. In particular, preparing even a simple superposition state comprising two basis states allows for a wide range of control over the ensuing diffusive dynamics. Further, the control was found to persist in the presence of weak decoherence and diminished, as expected, with increasing decoherence strength. This result opened an interesting direction for coherent control, overlapping with fields such as quantum chaos and chaos control.

In this chapter, we extend our previous study of the DKPR model to the case of kicked molecular systems in an effort to motivate experimental coherent control studies of quantum chaotic diffusion. Indeed, experimental studies of microwave-pulse-kicked diatomic molecules are feasible today and may be easier to realize than, for example, atomic physics approaches, e.g., kicked atoms in a single quantum well, or ultracold atoms in a periodic standing wave of near-resonant light [1, 2].

This chapter is organized as follows. In section 3.2, both the classical dynamics and quantum dynamics for diatomic systems kicked by periodic microwave pulses are considered in detail. In section 3.3, representative phase control results are presented, followed by detailed discussions on the mechanism of phase control. Conclusions and a summary comprise section 3.4.
3.2 Microwave Kicked Diatomic Molecules

The proposal to use microwave kicked diatomic molecules as a molecular analog of the DKPR was advanced more than a decade ago [3]. In particular, with the vibrational degree of freedom frozen, the Hamiltonian for the rotational motion of diatomic molecules subject to periodic microwave pulses resembles that of the DKPR. That is, if the orientation of a diatomic molecule is described by two angles $\theta$ and $\phi$ [4], then the corresponding Hamiltonian is

$$\hat{H} = \frac{j^2}{2I} + \mu E_0 \cos(\theta) \sum_n \Delta(\frac{t}{T} - n), \quad (3.1)$$

where $\hat{J}$ is the angular momentum operator in three dimensions:

$$j^2 = -\hbar^2 \left\{ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} [\sin(\theta) \frac{\partial}{\partial \theta}] + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right\}, \quad (3.2)$$

$\mu$ is the molecular electric dipole moment, $E_0$ is the amplitude of the driving field whose polarization direction defines the $z$ direction, $I$ is the moment of inertia of the molecule about an axis perpendicular to the symmetry axis, and $\Delta(t/T - n)$ is the pulse shape function simulating the delta kicking in the DKPR model. Microwave pulses may be realized by an array of phase-locked microwave generators, and following Blümel et al. [3], we first assume $\Delta$ takes the form

$$\Delta(\frac{t}{T} - n) = 1 + 2 \sum_{m=1}^{m=7} \cos[2m\pi(\frac{t}{T} - n - 1/2)]. \quad (3.3)$$

The kicked $\text{CsI}$ molecule appears to be an excellent candidate [3] for experimental studies of chaotic rotational excitation by microwave pulses since: (1) it has a large dipole moment, thus dramatically increasing the molecule-field coupling
strength, and (2) the excitation energy of the first vibrational energy level in CsI corresponds to that of the 71th rotational energy level, so that vibrational excitation and rotation-vibration coupling can generally be neglected. Blümel et al. also estimated [3, 4] that for CsI, $\tau \equiv \hbar T/I = 1.0$ translates into a driving frequency of $T^{-1} \approx 9$ GHz, and that $k \equiv \mu E_0 T/\hbar = 5.0$ translates into the relatively moderate field amplitude $E_0 \approx 1$ kV/cm.

Since the projection of the angular momentum onto the $z$ direction is a constant, we choose it to be zero. As a result, the second term in Eq. (3.2) gives zero contribution, and the kicked diatomic molecule has only one relevant degree of freedom ($\theta$). Nonetheless, there remain important differences between the DKPR model and the kicked diatomic systems. First, the kicking microwave field can only approximate the delta kicks. Second, $\theta$ ranges from 0 to $2\pi$ in the DKPR model, whereas it ranges from 0 to $\pi$ for a three-dimensional rotor. Third, the Hilbert space for the kicked molecule case is spanned by the basis states $|j, 0\rangle$, where 0 denotes the zero-projection of the angular momentum onto the $z$ axis, and $j$ is the rotational quantum number; while in the DKPR model rotational quantum numbers $m$ can be both positive and negative, representing two possible directions of the angular momentum of the planetary rotor. Fourth, in the DKPR model, the matrix elements of the coupling potential $\cos(\theta)$ are given by

$$\langle m|\cos(\theta)|m'\rangle = \frac{1}{2}(\delta_{m',m-1} + \delta_{m',m+1}),$$

(3.4)

while in the kicked molecule case, we have

$$\langle j, 0|\cos(\theta)|j', 0\rangle = C_j\delta_{j',j-1} + C_{j+1}\delta_{j',j+1},$$

(3.5)
where

\[ C_j \equiv \frac{j}{\sqrt{(2j-1)(2j+1)}}. \]  \hspace{1cm} (3.6)

Given these differences, it is necessary to independently examine the possibility of phase control of quantum diffusion in kicked diatomic systems.

### 3.2.1 Classical dynamics

With the vibrational degree of freedom frozen and the projection of the angular momentum onto the polarization vector of the driving field being zero, the classical Hamiltonian \( H_d \) for diatomic molecules kicked by microwave pulses is given by

\[ H_d = \frac{I \dot{\theta}^2}{2} + \mu E_0 \cos(\theta) \sum_n \Delta\left(\frac{t}{T} - n\right). \]  \hspace{1cm} (3.7)

The classical equation of motion for \( \theta \) is then:

\[ I \frac{d^2 \theta}{dt^2} = \mu E_0 \sin(\theta) \sum_n \Delta\left(\frac{t}{T} - n\right). \]  \hspace{1cm} (3.8)

If we define \( \xi \equiv t/T, \bar{J} \equiv \dot{\theta}T \), the above equation can be re-expressed as two canonical equations in \( \bar{J} \) and \( \theta \):

\[
\frac{d\theta}{d\xi} = \bar{J},
\]

\[
\frac{d\bar{J}}{d\xi} = (k \tau) \sin(\theta) \sum_n \Delta(\xi - n). \]  \hspace{1cm} (3.9)
Figure 3.1: The Poincaré surfaces of section for the classical dynamics of the kicked diatomic molecules. (a) $k\tau = 0.5$, (b) $k\tau = 1.0$, (c) $k\tau = 2.5$, (d) $k\tau = 5.0$.

Clearly, $\tilde{J}$ is the counterpart of $\tilde{L}$ in the DKPR model [see Eq. (2.3) in Chap. 2], and the classical dynamics depends only on the product of $k$ and $\tau$. Note also that the quantum counterpart of $\tilde{J}^2$ is $j(j+1)\tau^2$, where $j$ is the rotational quantum number. Figure 3.1 displays the Poincaré surfaces of section for $k\tau = 0.5, 1.0, 2.5$, and $5.0$. The results are obtained by numerical integration of 15 different initial trajectories with $\tilde{J}(0) = 0$ and $\theta(0) = l\pi/16$, $l = 1, 2 \ldots, 15$, for time equal to 720 kicks. It is clear from Fig. 3.1 that when $k\tau \geq 5.0$, the classical dynamics is predominately chaotic in
the entire $\tilde{J}$ region. We focus below on quantum dynamics in this $k\tau$ regime.

### 3.2.2 Quantum dynamics

To solve for the time-evolving wavefunction $|\psi(t)\rangle$ for the kicked molecule, we first expand the wavefunction in the Hilbert space basis

$$|\psi(t)\rangle = \sum_j A_j(t)|j,0\rangle. \quad (3.10)$$

Substituting this expansion into the time-dependent Schrödinger equation and using Eq. (3.5), we have

$$i\hbar\frac{dA_j(t)}{dt} = \frac{j(j+1)\hbar^2}{2I}A_j(t) + \mu E_0 \sum_n \Delta(\frac{t}{T} - n)(C_jA_{j-1}(t) + C_{j+1}A_{j+1}(t)). \quad (3.11)$$

The dynamical equations can be further simplified by working with an interaction picture [4]. Specifically, let $B_j(t) = A_j(t)\exp[i\hbar(j + 1)t/(2I)]$, we finally get

$$i\frac{dB_j(\xi)}{d\xi} = k \sum_n \Delta(\xi - n)\{\exp[i\tau j\xi]C_jB_{j-1}(\xi) + \exp[-i\tau(j + 1)\xi]C_{j+1}B_{j+1}(\xi)\}. \quad (3.12)$$

Clearly, in contrast to classical dynamics, the quantum dynamics of the kicked molecule depends on two parameters, $\tau$ and $k$. Thus, by decreasing the magnitude of $\tau$ with $k\tau$ fixed, we can arbitrarily decrease the quantum effects due to the quantization of angular momentum while keeping the underlying classical dynamics unaffected.

The coupled equations of motion for the expansion coefficients $B_j(t)$ can be readily solved using the fourth order Runger-Kutta method, with a time step of $10^{-4}T$, and with the number of basis states chosen to be $500/\tau$. With these choices, convergence of the results was excellent.
3.3 Phase Control of Quantum Chaotic Diffusion in Kicked Molecules

As clearly seen from Eqs. (3.1) and (3.3), the Hamiltonian of the system considered here is strictly periodic with time. Hence the time evolution operator $\hat{F}$ associated with one period $T$ is of particular interest and will prove useful in the analysis of the results. The formal solution for $\hat{F}$ can be written, with the help of the time-ordering operator $\Gamma$, as

$$\hat{F} = \Gamma\{\exp[-i\frac{\mathcal{H}}{\hbar} \int_0^T dt' \hat{H}(t')]\}, \quad (3.13)$$

where

$$\Gamma[\hat{C}(t)\hat{D}(t')] = \hat{C}(t)\hat{D}(t'), \quad \text{if} \ t > t'$$

$$\Gamma[\hat{C}(t)\hat{D}(t')] = \hat{D}(t')\hat{C}(t), \quad \text{if} \ t < t'. \quad (3.14)$$

Although it is not possible to give an explicit form of $\hat{F}$ in the kicked molecule case, the existence of this formal solution yields a stroboscopic description of the dynamics,

$$|\psi(nT)\rangle = \hat{F}^{n-1}|\psi((n-1)T)\rangle = \hat{F}^n|\psi(0)\rangle. \quad (3.15)$$

More importantly, as we will see below, eigenfunctions and eigenphases of the quantum map operator $\hat{F}$ help provide clear insights on how chaotic rotational excitations may be controlled by manipulating quantum phase in the initial state.
3.3.1 Formal dynamics and initial-state coherence effects

Consider now an initial superposition state prepared as

\[ |\psi(0)\rangle = \cos(\alpha)|j_1, 0\rangle + \sin(\alpha)\exp(-i\beta)|j_2, 0\rangle. \tag{3.16} \]

Here we use only two basis states (more basis states can be considered, providing more adjustable parameters for control). After the molecule is kicked \( N \) times, the quantum state evolves to \( \hat{F}^N|\psi(0)\rangle \). In order to compare quantum results for our case with that for the DKPR model and the classical limit, we define the dimensionless rotational energy \( \tilde{E} \equiv \sum_j P_j(j + 1)r^2/2 \), where \( P_j = |B_j|^2 \) is the occupation probability of the \( |j, 0\rangle \) state. The classical limit of \( \tilde{E} \) is given by \( \langle J^2/2 \rangle \) (where \( \langle \cdot \rangle \) means the average over an ensemble). \( \hat{F} \) can be formally diagonalized by a unitary transformation,

\[
<j_a, 0|\hat{F}|j_b, 0> = \sum_{j_c} \exp(-i\phi_{j_c})U_{j_c,j_a}^* U_{j_c,j_b}.
\tag{3.17}
\]

where \( U_{j_c,j_a} \equiv \langle j_c, 0|\hat{U}|j_a, 0\rangle \) (\( j_a = 0, 1, 2, \ldots \)) is the eigenvector with eigenphase \( \phi_{j_c} \). Moreover, since the basis states \( |j, 0\rangle \) are time-reversal invariant, one can prove that the matrix elements \( U_{j_c,j_b} \) can be chosen as real numbers [5], i.e.,

\[
U_{j_c,j_a}^* = U_{j_c,j_a}, \quad j_a, j_c = 0, 1, 2, \ldots \tag{3.18}
\]

Further, evaluating \( \tilde{E} \) at \( t = NT \) with Eqs. (3.16), (3.17) and (3.18) gives

\[
\frac{2\tilde{E}}{r^2} = \langle \psi(0)|\hat{F}^{-N}\frac{\hat{J}_z^2}{\hbar^2}\hat{F}^N|\psi(0)\rangle
\]

\[
= \cos^2(\alpha) \sum_{j\neq j_b} j(j + 1)U_{j_a,j_b}U_{j_a,j_b}U_{j_b,j_1}U_{j_b,j_1} \exp[iN(\phi_{j_a} - \phi_{j_b})]
\]

\[
+ \sin^2(\alpha) \sum_{j\neq j_b} j(j + 1)U_{j_a,j_b}U_{j_a,j_b}U_{j_b,j_2}U_{j_b,j_2} \exp[iN(\phi_{j_a} - \phi_{j_b})]
\]
\[ + \frac{1}{2} \sin(2\alpha) \{ \exp(-i\beta) \sum_{j_1j_2} j(j + 1)U_{j_1j_2}U_{j_2j_3}U_{j_3j_4} \exp[iN(\phi_{j_2} - \phi_{j_3})] + c.c. \} \]

(3.19)

Evidently, the first two terms are incoherent since they do not depend on the value of \( \beta \). They represent quantum dynamics associated with each of the states \( |j_1, 0\rangle \) and \( |j_2, 0\rangle \) independently. The last two terms represent interference effects due to initial-state coherence between \( |j_1, 0\rangle \) and \( |j_2, 0\rangle \). Below we show that quantum diffusion over the energy space can be extensively controlled by manipulating the initial quantum phase described by \( \beta \), which corresponds to manipulating the interference term in Eq. (3.19).

### 3.3.2 Phase control results

In Fig. 3.2 we present two representative examples (\( \tau = 1.0, k = 5.0 \) in Fig. 3.2a and \( \tau = 1.2, k = 4.8 \) in Fig. 3.2b) to illustrate phase control of quantum chaotic diffusion in kicked diatomic molecules. In both examples the underlying classical dynamics of rotational excitation is strongly chaotic, as shown in Fig. 3.1. We choose \( j_1 = 1 \) and \( j_2 = 2 \) to create the initial superposition state \( (|1, 0\rangle \pm |2, 0\rangle)/\sqrt{2} \), i.e., \( \alpha = \pi/4 \) and \( \beta = 0, \pi \) in Eq. (3.16) (Reasons for choosing \( \beta \) to be 0 or \( \pi \) will be explained in the next subsection). As seen in Fig. 3.2, the phase control is striking. For both examples, \( (|1, 0\rangle - |2, 0\rangle)/\sqrt{2} \) results in almost no diffusion over the energy space whereas \( (|1, 0\rangle + |2, 0\rangle)/\sqrt{2} \) shows extraordinarily fast diffusion (even faster than the semiclassical diffusion shown in Fig. 3.5 later below) before it essentially stops at \( t \approx 10T \). Note (1) that this huge difference is achieved solely by changing the
Figure 3.2: The dimensionless rotational energy of the kicked diatomic molecule $\hat{E} = \sum_j P_j j (j + 1) \tau^2 / 2$ versus time (in units of $T$). Solid line and dashed line are for the initial states $(|1, 0\rangle + |2, 0\rangle)/\sqrt{2}$ and $(|1, 0\rangle - |2, 0\rangle)/\sqrt{2}$, respectively. (a) $\tau = 1.0$, $k = 5.0$. (b) $\tau = 1.2$, $k = 4.8$.

initial relative phase between the two participating states $|1, 0\rangle$ and $|2, 0\rangle$ in the initial superposition state, and (2) that by contrast, each of $|1, 0\rangle$ or $|2, 0\rangle$ individually would give very similar diffusion behavior lying between the solid and dashed lines in Fig. 3.2. In effect, the two participating states $|1, 0\rangle$ and $|2, 0\rangle$ can either constructively or destructively interfere with each other, even though the underlying classical dynamics is strongly chaotic. Details of the respective wavefunctions at $t = 60T$ are shown in Fig. 3.3 in terms of the occupation probability $P_j$ versus $j$. In both Fig. 3.3a and Fig. 3.3b, one sees vividly that changing $\beta$ from 0 to $\pi$ alters the occupation probability of many states by almost an order of magnitude. This further demonstrates the role of the initial quantum phase embedded in the initial nonclassical states in chaotic...
molecular processes.

Figure 3.3: The occupation probability $P_j$ versus the rotational quantum number $j$ at $t = 60T$. Solid line and dashed line are for the initial states $(|1,0⟩ + |2,0⟩)/√2$ and $(|1,0⟩ - |2,0⟩)/√2$, respectively. (a) $\tau = 1.0, k = 5.0$. (b) $\tau = 1.2, k = 4.8$.

In an effort to gain insights into the nature of this control we examined the evolving wavefunctions in the $\theta$ representation. Figure 3.4 displays $|⟨θ|\psi⟩|^2 \sin(θ)$ versus $θ/π$ at times $t = 0T, 2T, 10T$ and $20T$, for the case of $\tau = 1.0, k = 5.0$ and for $ψ(0) = (|1,0⟩ + |2,0⟩)/√2$ or $(|1,0⟩ - |2,0⟩)/√2$. Note that due to wavefunction normalization $\int_{0}^{\pi} |⟨θ|\psi⟩|^2 \sin(θ)dθ = 1$. At $t = 0$ [Fig. 3.4a], the relative phase between the basis states $|1,0⟩$ and $|2,0⟩$ is manifest as a difference in molecular orientation. In particular, for the initial state $(|1,0⟩ - |2,0⟩)/√2$, the highest of three significant peaks of $⟨θ|\psi⟩|^2 \sin(θ)$ is at $θ_0 \approx 0.15π$, whereas for $ψ(0) = (|1,0⟩ - |2,0⟩)/√2$ the peak is at $π - θ_0 \approx 0.85π$. However, since the kicking force is proportional to $\sin(θ)$ and since $\sin(θ_0) = \sin(π - θ_0)$, such orientation effects can not be the direct origin
Figure 3.4: $|\langle \theta | \psi \rangle|^2 \sin(\theta)$ versus $\theta / \pi$ at times (a) $t = 0T$, (b) $t = 2T$, (c) $t = 10T$, and (d) $t = 20T$. Solid line and dashed line are for the initial states $(|1,0\rangle + |2,0\rangle)/\sqrt{2}$ and $(|1,0\rangle - |2,0\rangle)/\sqrt{2}$, respectively. $\tau = 1.0$, $k = 5.0$.

of our phase control. Indeed, after only two kicks [Fig. 3.4b], it becomes very hard to see any significant difference between the two evolving wavefunctions in the $\theta$ representation, although their energy absorption behavior afterwards (see Fig. 3.2a continues to be completely different. Also of interest is the comparison in Fig. 3.4c and Fig. 3.4d between the evolving wavefunctions at times $t = 10T$ and $20T$ (at those times the energy absorption shown in Fig. 3.2 has stopped). We find that, in the suppressed diffusion cases, the wavefunction displays fairly smooth behavior over
the entire range of $\theta$, whereas in the enhanced diffusion cases the magnitude of the wavefunction drastically oscillates with $\theta$. However, the wavefunctions in Fig. 3.4c and Fig. 3.4d for both the suppressed and the enhanced cases show similar behavior on the average. Hence, the $\theta$ dependence of the wavefunction sheds little light on the origins of the observed phase control. Indeed, gaining insights into the origins of the control is difficult insofar as it is a nonresonant multiphoton absorption process.

![Graph](image)

Figure 3.5: As in Fig. 3.2 except that the effective Planck constant $\tau$ is 50 times smaller. (a) $\tau = 0.02$, $k = 250$. (b) $\tau = 0.024$, $k = 240$.

To further appreciate that the results in Fig. 3.2 are based on quantum effects, we show in Fig. 3.5 the results after reducing the effective Planck constant $\tau$ by 50 times, while keeping $kr$ constant. As discussed below, when the system is closer to the semiclassical limit, one expects the extent of phase control to decrease. This is confirmed in Fig. 3.5. For both the case of $\tau = 0.02$ and $k = 250$ in Fig. 3.5a and the case of $\tau = 0.024$ and $k = 240$ in Fig. 3.5b, the energy diffusion only shows slight
dependence on \( \beta \). In essence, phase control disappears in both cases. This confirms the expectation that quantum chaotic dynamics in the classical limit is insensitive to initial-state coherence.

We have also examined the stability of the results in Fig. 3.2 for \( \tau \) far from resonance. We have checked that control in Fig. 3.2a (Fig. 3.2b) remains essentially the same when \( \tau \) is changed from 1.0 to 0.99 to 1.01 or from 1.2 to 1.19 to 1.21. This insensitivity may be important for experimental studies, suggesting that extensive control of quantum diffusion should be robust to small fluctuations of the frequency of the periodic kicking field.

It should be noted that for periodically kicked systems, the dynamics can be very sensitive to the exact value of \( \tau \). For example, when \( \tau = p\pi/q \), where \( p, q \) are integers, the free evolution of the kicked system is in resonance with the kicking field, and the corresponding quantum diffusion can be extremely fast [5, 6]. Indeed, when the resonance condition is satisfied, the spectrum of the system assumes a completely different form (for example, in the DKPR model, the spectrum is continuous at resonance). Here we have examined cases of \( \tau \) far from resonance since the uncontrolled dynamics for the case of resonant \( \tau \) is still poorly understood. Nevertheless, it should be noted that the possible range of quantum diffusion rates due to phase control, as shown in Fig. 3.2, is comparable to, or even larger than, that induced by quantum resonances in kicked diatomic systems. For \( \tau \) near or on resonance, we also observed extensive phase control in many cases. Figure 3.6 shows two examples of phase control of quantum resonant diffusion, for \( \tau = \pi/2, k = 4.5 \) [Fig. 3.6a] and \( \tau = 2\pi/5 \).
$k = 5.0$ [Fig. 3.6b]. However, due to the sensitivity of the dynamics to $\tau$, the phase control for $\tau$ near or on resonance is also very sensitive to $\tau$.

Figure 3.6: The dimensionless rotational energy of the kicked diatomic molecule $\tilde{E} = \sum_j P_j (j + 1) \tau^2 / 2$ versus time (in units of $T$). Solid line and dashed line are for the initial states $(|1, 0 \rangle + |2, 0 \rangle)/\sqrt{2}$ and $(|1, 0 \rangle - |2, 0 \rangle)/\sqrt{2}$, respectively. (a) $\tau = \pi/2$, $k = 4.5$. (b) $\tau = 2\pi/5$, $k = 5.0$.

Finally, we examine the pulse-shape dependence of our phase control. Our previous calculations have used the microwave pulse given by Eq. (3.3), which needs seven consecutive harmonically related microwave frequencies. Although this case is indeed very close to delta-kicked dynamics, it could be challenging experimentally since one has to phase-lock so many different microwave fields. Fortunately, we found that similar phase control can be observed using only three consecutive harmonically related microwave fields. Figure 3.7 displays the somewhat less extensive phase
control results, where the pulse shape function $\Delta(t/T - n)$ in Eq. (3.1) is replaced by

$$\Delta'(t/T - n) = 1 + 2 \sum_{m=1}^{m=3} \cos[2m\pi(t/T - n - 1/2)].$$

(3.20)

It is clear that the main characteristics of the phase control results in Fig. 3.2 are also observed in Fig. 3.7. Thus, utilizing Eq. (3.20) should significantly reduce technical difficulties in experimental studies of phase control of quantum chaotic diffusion.

Figure 3.7: As in Fig. 3.2 except that the pulse shape function is given by Eq. (3.20).

### 3.3.3 Discussion

The results obtained for $CsI$ are similar to those observed in the DKPR model, despite the fact that there are several differences between the DKPR model and the kicked molecule case. This suggests that the mechanism for phase control of microwave kicked diatomics may be the same as that for the DKPR model. Below we discuss the fact that phase control is based upon, and is a manifestation of, strong statistical deviations from random matrix theory (RMT).
Chapter 3. COHERENT CONTROL OF QUANTUM CHAOTIC...

One of the main results of the study of quantum chaos is that statistical properties of eigenfunctions and eigenvalues of the quantum map operator $\hat{F}$ (or the Hamiltonian operator for conservative systems) tend to be well described by RMT if the underlying classical dynamics is chaotic [5]. Indeed, statistical behavior close to RMT predictions are regarded as clear signatures of classical chaos. In particular, RMT claims that eigenvector components of $\hat{F}$ are random and obey universal statistical laws. However, in the case of the DKPR model and the kicked diatoms, deviations from RMT are observed in the suppressed quantum diffusion [6]. Here we demonstrate that quantum control is another strong manifestation of the deviation from RMT.

To do so we first note that Eq. (3.19) can be further simplified, for relatively large $N$, by making a fairly good approximation. That is, the factor $\exp[iN(\phi_{j_a} - \phi_{j_b})]$ tends to oscillate so rapidly that essentially only those terms with $j_a = j_b$ contribute to the sum over $j_a$ and $j_b$. We then obtain

$$\frac{2\tilde{E}}{\tau^2} = \cos^2(\alpha) \sum_j j(j + 1) \sum_{j_a} |U_{j_a}|^2 |U_{j_a + 1}|^2$$
$$+ \sin^2(\alpha) \sum_j j(j + 1) \sum_{j_a} |U_{j_a}|^2 |U_{j_a + 1}|^2$$
$$+ \sin(2\alpha) \cos(\beta) \sum_j j(j + 1) \sum_{j_a} |U_{j_a}|^2 U_{j_a + 1} U_{j_a + 2}. \quad (3.21)$$

Evidently, the last term in Eq. (3.21) arising from quantum interference is proportional to $\cos(\beta)$, and would be most effective when $\beta = 0$ or $\beta = \pi$. This explains our previous choice of $\beta = 0$, $\pi$ for the demonstration of extensive phase control.

Consider then RMT applied to the statistics of the eigenvectors $U_{j_a j_a}$ in Eq. (3.21). Suppose the effective dimension of the Hilbert space is $D \propto 1/\tau$, $\tau$ being the
effective Planck constant. We then assume that $U_{ja1}$, $U_{ja2}$, and $U_{ja3}$ are independent random numbers with mean value 0 and variance $1/D$, in accord with RMT. With this statistical description, we are now ready to compare the magnitudes of the interference term and the incoherent terms in Eq. (3.21). Consider first the interference term. As an approximation, $\sum_{ja} |U_{ja}|^2 U_{ja1} U_{ja2} \approx 1/D \sum_{ja} (U_{ja1} U_{ja2})$, where high order correlations between $|U_{ja}|^2$ and $U_{ja1} U_{ja2}$ are neglected. Note that the ensemble average of $U_{ja1} U_{ja2}$ $(j_1 \neq j_2)$ is zero. Hence the the standard deviation of $1/D \sum_{ja} (U_{ja1} U_{ja2})$ is given by $1/\sqrt{D}$ times the standard deviation of $U_{ja1} U_{ja2}$ (which is of the order of $1/D$). It follows that the standard deviation of $\sum_{ja} (U_{ja1} U_{ja2})$ from zero is of the order of $1/\sqrt{D}$. On the other hand, for the incoherent terms, say, the first term, $\sum_{ja} |U_{ja}|^2 |U_{ja1}|^2 \approx 1/D \sum_{ja} |U_{ja1}|^2 = 1/D$. Thus, according to RMT, the interference term is zero statistically, and the magnitude of the fluctuation of the interference term is $1/\sqrt{D}$ times smaller than that of the incoherent term. That is, RMT predicts that phase control of quantum diffusion is bound to fail. Further, since $D$ scales with $1/\tau$, we have that the magnitude of the fluctuations of the quantum interference term in Eq. (3.21) scales with $\tau^{3/2}$. As the system approaches the classical limit by decreasing the effective Planck constant $\tau$, initial state coherent effects, and thus phase control necessarily vanish.

Thus, our phase control results presented in the last subsection imply that RMT is not a good statistical description when the periodically kicked molecular system is not close to the semiclassical limit. Indeed, quantum localization occurs in the kicked molecule case as well [4]. Just as in the DKPR model, when quantum
effects are large, the \( \hat{F} \) matrix and thus the \( \hat{U} \) matrix are banded matrices \cite{7} in representation of angular momentum eigenstates. This band structure causes strong statistical deviations from what might be expected from RMT. Particularly, in the sum \( \sum_{ja} |U_{j,i}^a|^2 U_{ja1} U_{ja2} \), only those terms with \(|j - ja|\) less than the band width of the \( \hat{U} \) matrix (or the localization length of the eigenvector \( U_{j,i} \)) will contribute, i.e., the number of contributing terms in the sum will be much less than \( D \), the effective dimension of the Hilbert space. This directly leads to enhanced fluctuations of \( \sum_{ja} |U_{j,i}^a|^2 U_{ja1} U_{ja2} \), i.e., the interference term in Eq. \((3.21)\) can be comparable to the first two incoherent terms. As a result, extensive phase control of quantum chaotic diffusion becomes possible.

Based on the observation that statistical deviations from RMT are responsible for control, in the previous chapter a necessary condition has been suggested for extensive phase control. Specifically, in the DKPR model, we require \( k < 50/\kappa \) or \( \tau > \kappa^2/50 \) for control. The essence of this condition is evident. That is, larger quantum effects induce more phase control. It is thus very natural to conjecture that this condition could also apply to the model of periodically kicked molecules. Indeed, (1) under this condition, for numerous cases of varying \( \alpha, \beta, k \) and \( \tau \), we have obtained extensive phase control results similar to those in Fig. 3.2, and (2) outside that domain, phase control is not extensive in general.
3.4 Conclusion and Summary

The results of this chapter should impact strongly on two research areas, that of quantum chaos and that of coherent control. The focus of traditional studies in quantum chaos is quantum-classical correspondence, i.e., the conditions under which quantum and classical dynamics agree, and how this agreement breaks down with time as a result of quantum interference effects. In order to understand interference effects, most studies have used classical initial states and have avoided using nonclassical initial states. As such, the literature of quantum chaos rarely considers initial-state coherence effects [8]. Rather, people often take the semiclassical view that the classical chaotic dynamics leads to a randomization of the phase in quantum evolution, and that the quantum dynamics is insensitive to the form of the initial condition [9]. By contrast, studies in coherent control [10] emphasize the significance of quantum phases, both in the initial state and the ensuing dynamics.

Our study clearly demonstrates the importance of initial-state coherence in quantized chaotic dynamics. Specifically, we have demonstrated that initial-state coherence can dramatically alter the dynamics of quantum diffusion when the system is far from the semiclassical limit. This sensitivity is lost as the system approaches the classical limit. This phase control is based on, and is a manifestation of, strong statistical deviations from RMT. Further, it is distinct from other studies of control in diatomic excitation [12, 13], which can essentially be described classically [14].

Having theoretically shown that initial-state coherence can be used to control chaotic rotational excitation of diatomic molecules, the only remaining issue is the
experimental preparation of initial superposition states such as $(|1,0\rangle \pm |2,0\rangle)/\sqrt{2}$, or, more generally, the generation of rotational coherence before the periodic kicking field is turned on. Note that STIRAP [15] provides a natural choice for such superposition state preparation. In particular, in the tripod-STIRAP scheme [16], an additional laser couples the intermediate level (through which the initial and final state are radiatively connected via the pump and Stokes-laser) with another unpopulated state. Depending on the overlap in time of the interaction of the additional laser with that of the pump and Stokes-laser, any coherent superposition of the initial and final state can be created.

In summary, the general principle of coherent control has been successfully applied to chaotic rotational excitation of diatomic molecules. Corresponding experimental studies on the kicked CsI system are of interest to both areas of quantum chaos and coherent control.
Bibliography


Chapter 3. COHERENT CONTROL OF QUANTUM CHAOTIC ...  


PART II

INDISTINGUISHABILITY, INTERFERENCE, AND ENTANGLEMENT IN COHERENT CONTROL
Chapter 4

Indistinguishability and Interference in Coherent Control
Chapter Summary:

Interference occurs only when independent pathways to the same target state are indistinguishable. Due to this indistinguishability requirement, bimolecular collisions in general cannot create useful molecular coherence in collision products for subsequent use as initial states in coherent control. By contrast, laser-matter interaction can create useful molecular coherence for coherent control. In particular, the most classical (coherent) states of light can create and utilize molecular coherence without leaking out any which-way information, whereas quantum states of light may provide some which-way information and thus destroy interference in coherent control. Further, the difference between phase sensitive and phase insensitive control scenarios is explained in terms of the nature of indistinguishability between multiple excitation pathways. Finally, the possibility of creating useful molecular coherence in photodissociation processes is discussed.
4.1 Introduction

Interference, which is ubiquitous in classical wave phenomena, constitutes one of the most mysterious aspects of quantum mechanics. Specifically, when one target state is accessible by two or more independent coherent pathways, we must add the corresponding probability amplitudes rather than the probabilities. The observation that the resulting constructive or destructive interference terms can be altered via experimentally controllable parameters motivated the field of “coherent control” [1]. Considerable theoretical and experimental work has been done in this field, demonstrating our ability of active control over molecular processes by manipulating quantum interference [2, 3].

Despite the fact that quantum interference allows for active manipulations, the mystery it contains, however, admittedly remains [4, 5]. This becomes very clear if we consider the role of Young’s double-slit interference experiment for atoms or electrons, introduced during the early days of quantum mechanics. Traditional understandings of the double-slit experiment are based largely on Bohr’s complementarity, or the wave-particle duality. That is, if we can measure the recoiling slits and successfully determine which slit a particular particle goes through, then the interference will be necessarily washed out due to the position uncertainty of the double-slit plate introduced by measurement. As a result, the wave-like property and the particle-like property can not be observed simultaneously. Modern quantum optical tests further support Bohr’s claim [6]. For example, in the double-slit experiments for atomic beams, micromaser detectors can determine which pathway the particle has followed,
without affecting the atomic spatial wavefunction, by use of the atomic internal degrees of freedom. Doing so, however, causes loss of interference as a consequence of the available which-way information contained in the entanglement between the particles and the measuring apparatus. Other one-photon and two-photon interference experiments [7] further demonstrated that quantum interference should be understood as the physical manifestation of the intrinsic indistinguishability of multiple independent pathways, and that once there is some way, even in principle, of distinguishing between independent quantum routes to the same target state, the corresponding probabilities should be added and quantum interference vanishes.

There exist some useful quantitative treatments of the relationship between quantum interference and indistinguishability of various pathways [8, 9, 10, 11]. Although they are not the focus of this chapter, here we would like to briefly introduce one of them, that will be used below. Let $|\psi_1\rangle$ and $|\psi_2\rangle$ denote the final states arising from two different pathways. A measure for distinguishing between these two states can be described by a complete set of commuting orthogonal projection operators $\{P_n \equiv |\xi_n\rangle\langle\xi_n|\}$. The degree of indistinguishability can then be defined as

$$U_{P_n}(\psi_1, \psi_2) = \sum_n \sqrt{\frac{\langle\psi_1|P_n|\psi_1\rangle\langle\psi_2|P_n|\psi_2\rangle}{\langle\psi_1|\psi_1\rangle\langle\psi_2|\psi_2\rangle}},$$

(4.1)

where $U_{P_n}(\psi_1, \psi_2) = 1$ represents maximum indistinguishability (e.g., when $|\psi_1\rangle$ differs from $|\psi_2\rangle$ by a phase factor only), and $U_{P_n}(\psi_1, \psi_2) = 0$ represents perfect distinguishability. On the other hand, the degree of interference power of $|\psi_1\rangle$ and $|\psi_2\rangle$, for
a complete set of orthogonal projection operators \( \{ P_i = |\eta\rangle\langle \eta | \} \), is defined as

\[
I_{P'}(\psi_1, \psi_2) = \sum \frac{|\langle \psi_1 | P'_i | \psi_2 \rangle|^2}{\sqrt{\langle \psi_1 | \psi_1 \rangle \langle \psi_2 | \psi_2 \rangle}},
\]

(4.2)

It has been proved that if \( \{ P_n \} \) and \( \{ P'_i \} \) are commutable, then the degree of interference power is always no larger than that of indistinguishability \([9]\), i.e.,

\[
U_{P_n}(\psi_1, \psi_2) \geq I_{P'}(\psi_1, \psi_2).
\]

(4.3)

Equation (4.3) implies that entangling the initial system wavefunctions \(|1\rangle, |2\rangle\) with measuring apparatus wavefunctions \(|\xi_1\rangle, |\xi_2\rangle\) should significantly affect quantum interference effects of multiple pathways \([12]\). To see this let us assume that the decoupled time evolution of the system and the measuring apparatus is described by the unitary operators \( U_S \) and \( U_M \), respectively. The corresponding final states for the system and the measuring apparatus are given by

\[
|\psi_1\rangle = U_S |1\rangle \otimes U_M |\xi_1\rangle, \quad \text{and} \quad |\psi_2\rangle = U_S |2\rangle \otimes U_M |\xi_2\rangle.
\]

Then, the degree of interference power [Eq. (4.2)] for any measurement \( P'_i \) on the system only is proportional to

\[
|\langle \xi_1 | U_M^\dagger U_M |\xi_2 \rangle| = |\langle \xi_1 | \xi_2 \rangle|.
\]

Hence, when \(|1\rangle\) and \(|2\rangle\) are entangled with orthogonal states \(|\xi_1\rangle\) and \(|\xi_2\rangle\), respectively, there is definitely no interference, since \(\langle \xi_1 | \xi_2 \rangle = 0\). From the viewpoint of indistinguishability, the degree of indistinguishability [Eq. (4.1)] between \(|\psi_1\rangle\) and \(|\psi_2\rangle\) is zero if we choose \( P_1 = |\xi_1\rangle\langle \xi_1 | \) and \( P_2 = |\xi_2\rangle\langle \xi_2 | \). Clearly, this zero indistinguishability is due to the fact that the measurement of \( P_1 \) and \( P_2 \) serves to distinguish between \(|1\rangle\) and \(|2\rangle\), and thus to distinguish between the two independent pathways \(|1\rangle \rightarrow |\eta\rangle\) and \(|2\rangle \rightarrow |\eta\rangle\), where \(|\eta\rangle\) are the target states about the system only. On the other hand, if the states \(|\xi_1\rangle\) and \(|\xi_2\rangle\) are similar (i.e., their overlap is considerable), then
such entanglement between the system and the measuring apparatus is weak enough to allow for quantum interference, because the measurement of $P_1$ and $P_2$ will not provide much information about the system.

In considerations of coherent control, our understanding of the role of interference far exceeds our appreciation of fundamental issues on the origins of interference. In particular, in laser control of chemical reactions, a laser pulse is usually employed to prepare a superposition state for the subsequent generation of multiple coherent pathways, which then play the same role as the beam splitter in the double-slit experiment. Several fundamental questions then naturally arise. Do laser pulses provide the only way to create molecular coherence for subsequent coherent control? Is there any which-way information extractable from the light field after the light-matter interaction is finished? Are those independent pathways indeed largely indistinguishable so as to ensure interference? Further, in the light of indistinguishability between multiple excitation pathways, how do we understand the well-known fact that, on one hand traditional coherent control scenarios are extremely phase-sensitive, and on the other hand there are also some phase-insensitive interference control scenarios?

The purpose of this chapter is to examine the issue of indistinguishability and interference within the context of coherent control. The chapter is organized as follows. Section 4.2 includes rather formal considerations on the possibility of creating molecular coherence by bimolecular collisions. It is shown that, due to the indistinguishability requirement, bimolecular collisions can not, in most instances, create useful molecular coherence for subsequent control. Thus, as the first step in most
coherent control scenarios, creating a superposition state comprising nondegenerate states is done by coherent laser irradiation of molecules. In section 4.3, we (1) compare a fully quantized theory of two-pulse coherent control scenario with a semiclassical treatment, in order to understand conditions under which molecule-photon collisions can create molecular coherence without leaking out which-way information; and (2) analyze the differences between phase sensitive and phase insensitive control scenarios in terms of the nature of indistinguishability of multiple excitation pathways. The creation of quantum coherence in photodissociation processes is discussed in section 4.4, with special attention to quantum entanglement between photodissociation fragments. A summary is given in section 4.5.

4.2 Bimolecular Collisions Cannot Create Useful Molecular Coherence

In several important coherent control scenarios [1, 2, 3], the first step is to create a superposition state which is then used to generate multiple coherent pathways to the same target state. Thus, it is of considerable interest to examine the possibility of preparing useful quantum superposition states via bimolecular collisions. To see that this is a rather fundamental issue, let us first consider a typical molecular crossed-beam experiment. Because the interaction time $\delta t$ in the crossed-beam experiment is very short, in effect each beam is subject to a "pulsed" interaction due to the other beam. It would then appear that such a molecular process is an analog of pulsed laser-
molecule interaction, and may be able to generate useful quantum superposition states with the characteristic energy coherence width given by $\hbar/\delta t$. However, as we will see below, this is not the case, even when the total system is perfectly isolated from the environment. In short, this is because different energy or momentum components of the quantum state of the particle of interest are distinguishable by measuring the quantum state of other products.

Consider the following bimolecular collision,

$$A + B \rightarrow C + D,$$

(4.4)

where $A, B, C, D$ are, in general, molecules of mass $m_A, m_B, m_C$ and $m_D$. Their free internal Hamiltonians are $H_A^0, H_B^0, H_C^0$ and $H_D^0$. Here $C$ and $D$ can be identical to $A$ and $B$ (nonreactive scattering) or can differ from $A$ and $B$ (reactive scattering).

For a molecule denoted by $X$, the momentum eigenket (in the laboratory frame) is denoted by $|K_X\rangle$ with the wave vector $K_X$, and the internal eigenstate is represented by $|\phi_{EX, n_X}\rangle$, where $E_X$ is the internal energy of particle $X$ and $n_X$ is a set of good quantum numbers accounting for degeneracies. As to the relative motion and the center of mass of motion of two molecules denoted by $X$ and $Y$, their eigenkets are represented by $|K_{XY}^{E_X, E_Y}\rangle$ and $|K_{XY}\rangle$, respectively. Now suppose that the preparation of a superposition state of the molecule $C$ is of particular interest. Then other channels not including $C$ can be neglected, without loss of any generality [13]. Thus, states $|\phi_{EC, n_C}^C\rangle \otimes |\phi_{ED, n_D}^D\rangle \otimes |K_{CD}^{E_C, E_D}\rangle \otimes |K_{CD}\rangle$ form a complete basis set of the Hilbert space of interest.

A collision between molecules $A$ and $B$ can readily produce a superposition
state consisting of different translational and/or internal quantum states, in the entire product Hilbert space. To see this let us assume that initially both $A$ and $B$ are in pure quantum states $|\phi_{E_A,n_A}^A\rangle$ and $|\phi_{E_B,n_B}^B\rangle$, respectively. In addition, under normal circumstances their translational states can be taken as momentum eigenstates if they are created in a molecular beam machine [14]. Thus, before the collision the quantum state is

$$|\Psi(-\infty)\rangle = |\phi_{E_A,n_A}^A\rangle \otimes |\phi_{E_B,n_B}^B\rangle \otimes |k_{AB}^{E_A,E_B}\rangle \otimes |K_{AB}\rangle,$$

(4.5)

where

$$k_{AB}^{E_A,E_B} = (m_B k_A - m_A k_B)/(m_A + m_B), \quad K_{AB} = k_A + k_B.$$

(4.6)

After the collision this initial state is scattered as $|\Psi_{\text{prep}}\rangle$ into the product channel $C + D$.

Given the initial and final free molecular Hamiltonians:

$$H_{AB}^{\text{free}} = \frac{\hbar^2 \dot{k}_{AB}^2}{2(m_A + m_B)} + \frac{(m_A + m_B)\hbar^2 \dot{k}_{AB}^2}{2m_A m_B} + H_A^0 + H_B^0,$$

$$H_{CD}^{\text{free}} = \frac{\hbar^2 \dot{k}_{CD}^2}{2(m_C + m_D)} + \frac{(m_C + m_D)\hbar^2 \dot{k}_{CD}^2}{2m_C m_D} + H_C^0 + H_D^0,$$

(4.7)

and the total Hamiltonian $H = H_{AB}^{\text{free}} + V_{AB} = H_{CD}^{\text{free}} + V_{CD}$, $|\Psi_{\text{prep}}\rangle$ can be formally obtained via the scattering operator $\hat{S}$ [15]:

$$|\Psi_{\text{prep}}\rangle = \hat{S}|\Psi(-\infty)\rangle = \lim_{t_1 \to \infty, t_2 \to -\infty} e^{iH_{CD}^{\text{free}}t_1} e^{-iH_{CD}^{\text{free}}t_2} e^{iH_{AB}^{\text{free}}t} |\Psi(-\infty)\rangle.$$
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By the completeness of all channel states mentioned above, one obtains

\[
|\Psi_{\text{prep}}\rangle = \int dK_{CD} \int dK_{CD} \sum_{E_{C:D}, E_{D:D}} \sum_{E_{C:D}, E_{D:D}} 
\left[ (|\phi_{E_{C:D}}^C| \otimes |\phi_{E_{D:D}}^D| \otimes (K_{CD}|H|^0)) \right] 
\times (|\phi_{E_{C:D}}^C| \otimes |\phi_{E_{D:D}}^D| \otimes |K_{CD}|). 
\]

(4.9)

Some integrals in the above equation can be easily done due to the conservation of total momentum and total energy. Let \( \hat{S} \) be the corresponding reduced scattering operator after integrating out these two delta-functions in Eq. (4.9). Then we have

\[
|\Psi_{\text{prep}}\rangle = \int d\Omega \sum_{E_{C:D}, E_{D:D}} \sum_{E_{C:D}, E_{D:D}} \left( (|\phi_{E_{C:D}}^C| \otimes |\phi_{E_{D:D}}^D| \otimes (K_{CD}|H|^0)) \right) 
\hat{S}(K_{AB}, K_{CD}) \otimes |\phi_{A:B}^A| \otimes |\phi_{B:B}^B|) 
\times (|\phi_{E_{C:D}}^C| \otimes |\phi_{E_{D:D}}^D| \otimes |K_{CD}|). 
\]

(4.10)

where \( \Omega \) represents the direction of \( K_{CD} \), and

\[
K_{CD} = K_{AB},
\]

\[
\frac{(m_C + m_D)h^2}{2m_Cm_D} |K_{CD}|^2 = \frac{(m_A + m_B)h^2}{2m_am_b} |K_{AB}|^2 
+ E_A + E_B - E_C - E_D. 
\]

(4.11)

Equation (4.10) explicitly shows the well-known result that \( |\Psi_{\text{prep}}\rangle \) resulting from a collision is a quantum superposition state due to the presence of multiple channels.

The next step is to examine the possibility of using the \( C \) superposition state for coherent control in a second chemical reaction, i.e., we propose to use \( C \) as a
reactant in a subsequent step. Thus, the specific quantum state composition of $C$ is of interest. For notational convenience, we define

$$S_{AB\rightarrow CD}(E_C, n_C; E_D, n_D|\Omega)$$

$$\equiv \langle \phi^C_{E_{C,D}} \rangle \otimes \langle \phi^D_{E_{D,D}} \rangle \otimes \langle k^{E_{C,D}}_{CD} | S | k^{E_{A,B}}_{AB} \rangle \otimes | \phi^A_{E_{A,B}} \rangle \otimes | \phi^B_{E_{B,B}} \rangle.$$  \hspace{0.5cm} \text{(4.12)}$$

Noticing that

$$|k^{E_{C,D}}_{CD}\rangle \otimes |K_{CD}\rangle = |K_C\rangle \otimes |K_D\rangle,$$  \hspace{0.5cm} \text{(4.13)}$$

where

$$K_C = \frac{m_C}{m_C + m_D} K_{AB} + k^{E_{C,D}}_{CD};$$

$$K_D = \frac{m_D}{m_C + m_D} K_{AB} - k^{E_{C,D}}_{CD},$$  \hspace{0.5cm} \text{(4.14)}$$

one can rewrite $|\Psi_{\text{prep}}\rangle$ as

$$|\Psi_{\text{prep}}\rangle = \int d\Omega \sum_{E_{C,D} n_C} \sum_{E_{D,D} n_D} S_{AB\rightarrow CD}(E_C, n_C; E_D, n_D|\Omega)$$

$$\times |\phi^C_{E_{C,D}}\rangle \otimes |K_C\rangle \otimes |\phi^D_{E_{D,D}}\rangle \otimes |K_D\rangle.$$  \hspace{0.5cm} \text{(4.15)}$$

Equation (4.15) shows that, in general, both the translational and the internal states of $C$ and $D$ are entangled. As such, even if there is no clue on how to precisely measure the $D$ states, entanglement between $C$ and $D$ can, in principle, provide which-state information about the molecule $C$. Indeed, if we have obtained the values of $K_D$ and $E_D$ by measuring $D$ only, then (a) from Eq. (4.14) we can infer the value of $K_C$ and $k^{E_{C,D}}_{CD}$; and (b) from Eq. (4.11) we can infer the value of $E_D$. Hence, a natural set of projection operators $\{P_{K_D,E_D,n_D}\}$ for distinguishing between different $C$ states, and
thus distinguishing between different pathways associated with these states, are given by

\[ P_{K_D, E_D, n_D} = |\Psi_D\rangle \langle \phi_D_{E_D, n_D}| \langle \phi_D_{E_D, n_D}| \langle K_D|. \quad (4.16) \]

As one can easily see, the corresponding degree of indistinguishability between the \( C \) states with different \( E_C \) or \( K_C \) is zero. As a result, the interference power of the \( C \) states has to be zero, i.e., the \( C \) states with different \( E_C \) or \( K_C \) can not be used for coherent control in a second reaction which does not involve the product \( D \).

This result, in some sense, is very counter-intuitive. It implies that, if two molecules (\( C \) and \( D \)) have once interacted with each other, they will never be separable \([16]\). It is this nonseparability that makes which-state information about one molecule available. The availability of the which-state information about \( C \) rules out bimolecular collisions as a rational means to create indistinguishable multiple pathways associated with \( C \) to the same target state.

It remains to examine whether or not there are useful coherence effects between degenerate internal states of \( C \). To clearly address this issue, and to further understand the relationship between interference and indistinguishability, we use below a density matrix approach. Consider the density operator \( \hat{\rho}_{\text{prep}} \) in the \( C + D \) arrangement after the preparation collision,

\[ \hat{\rho}_{\text{prep}} = |\Psi_{\text{prep}}\rangle \langle \Psi_{\text{prep}}| \]

\[ = \int \int d\Omega d\Omega' \sum_{E_C, n_C} \sum_{E_D, n_D} \sum_{E'_C, n'_C} \sum_{E'_D, n'_D} S_{AB \to CD}(E_C, n_C; E_D, n_D|\Omega) S_{AB \to CD}(E'_C, n'_C; E'_D, n'_D|\Omega') \]

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\[ x|\phi_{E_C,n_C}^C \rangle \otimes |K_{E_C,E_D}^{E,C,E_D} \rangle \otimes |\phi_{E_D,n_D}^D \rangle \otimes |K_{E_D}^{E,C,E_D} \rangle \]
\[ \times \langle K_{E_D}^{E,C,E_D} | \otimes \langle \phi_{E_D,n_D'}^{F} | \otimes \langle (K_{E_D}^{E,C,E_D})^{E_D} | \otimes \langle \phi_{E_C,n_C'}^{C} |. \] (4.17)

Then consider a second collision

\[ C + F \rightarrow \text{products}, \] (4.18)

where \( F \) can be an atom, a molecule or photon. The total initial density operator \( \hat{\rho} \) of the second collision is a product of the density operator prepared in the first collision and the density operator \( \hat{\rho}_F \) of the particle \( F \), i.e.,

\[ \hat{\rho} \equiv \hat{\rho}_{\text{prep}} \otimes \hat{\rho}_F. \] (4.19)

To avoid being involved in the details of the second reaction, we similarly introduce a second scattering operator \( \hat{S}' \). Thus, after the second collision, the total density operator for the entire system, including all particles like \( A, B, C, D, F, \) etc, is given by \( \hat{S}'_t \hat{\rho} \hat{S}' \).

Using Eqs. (4.17) and (4.19), and noticing that in general all bras and kets involving \( D \) only commute with the scattering operator \( \hat{S}' \), we have

\[ \hat{S}'_t \hat{\rho} \hat{S}' = \int \int d\Omega d\Omega' \sum_{E_C,n_C} \sum_{E_D,n_D} \sum_{E_C,n_C'} \sum_{E_D,n_D'} S_{AB \rightarrow CD}(E_C,n_C; E_D,n_D|\Omega)S_{AB \rightarrow CD}(E_C',n_C'; E_D',n_D'|\Omega') \]
\[ |\phi_{E_D,n_D}^D \rangle \otimes |K_{E_D}^{E,C,E_D} \rangle \langle K_{E_D}^{E,C,E_D} | \otimes \langle \phi_{E_D,n_D'}^F | \]
\[ \hat{S}'_t |\phi_{E_C,n_C}^C \rangle \otimes |K_{E_C}^{E,C,E_D} \rangle \langle K_{E_C}^{E,C,E_D} | \otimes \langle \phi_{E_C,n_C'}^C |. \] (4.20)

Suppose the target state is \( |\phi_{\text{target}} \rangle \). This target state is a result of the collision of \( C + F \) and is independent of \( D \). Then the probability of reaching this target is given
by \( P_{\text{target}} = \hat{T}(\hat{S}^{\dagger} \rho \hat{S}|\phi_{\text{target}}\rangle\langle \phi_{\text{target}}|) \), where \( \hat{T} \) represents the trace operator. \( \hat{T} \) can be factorized into two operators \( \hat{T}_D \) and \( \hat{T}'_D \), representing the trace over \( D \) and the trace over all other degrees of freedom. That is,

\[
\hat{T}(\hat{S}^{\dagger} \rho \hat{S}|\phi_{\text{target}}\rangle\langle \phi_{\text{target}}|) = \hat{T}_D \hat{T}'_D (\hat{S}^{\dagger} \rho \hat{S}|\phi_{\text{target}}\rangle\langle \phi_{\text{target}}|).
\]  

Since the target state has nothing to do with the by-product \( D \), the projector onto the target state commutes with all bras and kets solely involving \( D \). Using Eqs. (4.11) and (4.13), one obtains that tracing over those degrees of freedom of \( D \) yields \( \delta_{E_D,E'_D}, \delta_{n_D,n'_D}, \delta_{E_C,E'_C} \) and \( \delta(\Omega - \Omega') \). This gives

\[
P_{\text{target}} = \int d\Omega \sum_{E_C} \sum_{E_D,n_D} \sum_{n_C,n'_C} S_{AB \rightarrow CD}(E_C, n_C; E_D, n_D|\Omega) S_{AB \rightarrow CD}^*(E_C, n'_C; E_D, n_D|\Omega)
\]

\[
\times \hat{T}_D (\hat{S}^{\dagger}|\phi_{E_C,n_C}\rangle \otimes |K_{E,C,E_D}\rangle \langle K_{E,C,E_D}^*| \otimes \langle \phi_{E_C,n'_C}| \otimes \rho \hat{S}^*|\phi_{\text{target}}\rangle\langle \phi_{\text{target}}|)
\]

\[
= \int d\Omega \sum_{E_C} \sum_{E_D,n_D} \sum_{n_C,n'_C} S_{AB \rightarrow CD}(E_C, n_C; E_D, n_D|\Omega) S_{AB \rightarrow CD}^*(E_C, n'_C; E_D, n_D|\Omega)
\]

\[
\times T_{E_C,E_D,n_D}^{n_C,n'_C}(\Omega),
\]  

where we have implicitly defined the expression \( T_{E_C,E_D,n_D}^{n_C,n'_C}(\Omega) \).

Note first that \( T_{E_C,E_D,n_D}^{n_C,n'_C}(\Omega) \) only contains terms diagonal in the translational motion of \( C \). Hence, the translational coherence of \( C \) does not affect the target state. Likewise, the reaction probability is diagonal in representation of the nondegenerate internal states of \( C \). Thus, the product of the \( C + F \) collision is insensitive to the “quantum coherence” between nondegenerate states of \( C \). Clearly, here one should ex-
pect no interference whatsoever between multiple pathways \((E_A, E_B, n_A, n_B, k_{AB}^{E_A,E_B})\) → 
\([E_C(E'_C), n_C, K_C^{E_C,E_D}(K_C^{E_{C'}E_D})] \) → target states.

These results are consistent with the previous observations based on the indistinguishability requirement. Interestingly, in the derivations here the degrees of freedom associated with \(D\) are traced over since \(D\) is not of interest. Thus, quantum coherence effects of the \(C\) states with different momentum or internal energy can not show up in the target state even though we do not make any measurement on \(D\) to distinguish between the \(C\) states. This observation provides more insights into the issue. That is, it makes clear that what is fundamentally important is not that we really distinguish between different \(C\) states by use of the projectors \(P_{K_D,E_D,n_D}\) defined in Eq. (4.16), but simply that there exists the possibility of distinguishing between different \(C\) states. Put another way, what counts is what you can do, not what you actually do.

The which-state information about \(C\) arises as a direct consequence of the conservation laws of total momentum and total energy of \(C\) and \(D\). To “erase” the which-state information contained in quantum entanglement, i.e., to introduce uncertainty in knowing the state of \(C\) from measuring \(D\), it is necessary to introduce some uncertainties in momentum or energy into molecular systems. One approach is to introduce, for example, energy widths through laser excitation. Thus the reason why laser technologies are so important to coherent control is understood by recognizing that multi-channel molecular collision is not a useful means for producing interesting quantum interference effects.
Now we examine whether or not bimolecular collisions may create quantum coherence between *degenerate* molecular states of C. Interestingly, in Eq. (4.22), one sees that for each specified set of $\Omega$, $E_C$, $E_D$, $n_D$ the reaction probability contains the diagonal terms $T_{E_C,E_D,n_D}^{n_C,n_C}(\Omega)$, and the cross terms $T_{E_C,E_D,n_D}^{n_C,n_C'}(\Omega)$ ($n_C \neq n'_C$). The cross terms describe interference effects between the pathways $(E_A, E_B, n_A, n_B, k_{AB}^{E_A,E_B}) \rightarrow [E_C, n_C(n'_C), K_{C}^{E_C,E_D}, n_D, K_{D}^{E_C,E_D}] \rightarrow$ target states. They refer to identical internal and translational states of $D$, consistent with the indistinguishability requirement for multiple interfering pathways arising from the $C$ states. To further ensure such quantum interference, the coefficients associated with these nondiagonal terms $S_{AB\rightarrow CD}(E_C, n_C; E_D, n_D|\Omega) S^{*}_{AB\rightarrow CD}(E_C, n'_C; E_D, n_D|\Omega)$ ($n_C \neq n'_C$) should be nonzero. Since $n_C$ and $n_D$ usually refer to quantities like the parity or the projection of the total angular momentum onto a space-fixed axis, at first glance it may appear that $S_{AB\rightarrow CD}(E_C, n_C; E_D, n_D|\Omega) S^{*}_{AB\rightarrow CD}(E_C, n'_C; E_D, n_D|\Omega) = 0$ for $n_C \neq n'_C$, because either $n_C n_D$ or $n_C + n_D$ should be conserved by the scattering matrix $S_{AB\rightarrow CD}$. However, we note (1) that the conservation laws of parity and angular momentum only require

$$\int d\Omega S_{AB\rightarrow CD}(E_C, n_C; E_D, n_D|\Omega) S^{*}_{AB\rightarrow CD}(E_C, n'_C; E_D, n_D|\Omega) = 0, \quad n_C \neq n'_C, \quad (4.23)$$

and (2) that for any particular direction characterized by $\Omega$ [e.g., the direction strongly preferred by the second reaction via the $\Omega$ dependence of $T_{E_C,E_D,n_D}^{n_C,n_C}(\Omega)$], $S_{AB\rightarrow CD}(E_C, n_C; E_D, n_D|\Omega) S^{*}_{AB\rightarrow CD}(E_C, n'_C; E_D, n_D|\Omega)$ can be nonzero. Hence, bimolecular collision can create a certain kind of useful quantum coherence between degenerate molecular states, but in a very subtle manner. This result may be of
particular interest to some recent considerations on controlling bimolecular reactions [17], where superposition states consisting of degenerate internal states are required. Nevertheless, it should be pointed out that quantum coherence between degenerate states is of limited use.

To end this section, we restate the issue and the conclusions. We have considered the collision of $A + B \rightarrow C + D$ at fixed total energy and total momentum, and asked if the coherence created by this collision in the products is useable in a subsequent collisional step to do coherent control. Specifically, can we use the established coherence in one product molecule. we conclude that (a) bimolecular collisions, such as multi-channel collision $A + B \rightarrow C + D$, can not produce useful molecular translational coherence, (b) bimolecular collisions can not achieve useful coherence between non-degenerate ro-vibrational states, (c) bimolecular collisions can not produce useful coherence between different product states of various translational and ro-vibrational states, and (d) bimolecular collisions, however, can produce certain useful coherence between degenerate molecular states with different parities or projections of the total angular momentum onto a space-fixed axis.

### 4.3 Indistinguishability and Interference in Coherent Radiative Control

In this section let's first take a representative phase-sensitive control scenario, namely, two-pulse control [18], to examine the fundamental issue of indistinguishability and
interference in coherent radiative control of molecular processes. The interesting analyses are then extended to two phase-insensitive interference control scenarios.

4.3.1 The semiclassical two-pulse control theory: classical treatment of the laser fields

Consider a classical linearly polarized electric field $E(t)$ incident on an initially bound molecule. The molecule is assumed to be in an eigenstate $|E_0\rangle$ of the molecular Hamiltonian $H_M$. The overall Hamiltonian, in the dipole approximation, is then given by

$$H = H_M - d[E(t) + E^*(t)],$$

(4.24)

where $d$ is the component of the dipole moment $D$ along the electric field. In the two-pulse control scenario, the external field consists of two separated Gaussian pulses centered at $t = t_2$ and $t_d$, respectively. That is, $E(t) = E_2(t) + E_d(t)$, with the Fourier transform of $E_2(t)$ and $E_d(t)$ denoted as $E_2(\omega)$ and $E_d(\omega)$. The first pulse $E_2(t)$ induces a transition to a superposition of bound excited molecular states and the second pulse dissociates the molecule by further exciting it to the continuum. Both fields are chosen to be sufficiently weak for first-order perturbation theory to be valid.

Assuming that the first pulse only encompasses just two $E_1$ and $E_2$ excited states, the superposition state thus prepared is given by

$$|\phi(t)\rangle = |E_0\rangle \exp(-iE_0t/\hbar) + c_1|E_1\rangle \exp(-iE_1t/\hbar) + c_2|E_2\rangle \exp(-iE_2t/\hbar),$$

(4.25)
where

\[ c_m = \frac{\sqrt{2\pi}}{i\hbar} d_{m,0} E_x(\omega_{E_m E_0}), \quad m = 1, 2, \]  \hspace{1cm} (4.26)

with \( \omega_{E_m E_0} \equiv (E_m - E_0)/\hbar \), and \( d_{m,0} \equiv \langle E_m | d | E_0 \rangle \). This superposition state is subjected to a second pulse after a time delay. When the second-pulse is completed, the system wavefunction is given by

\[ |\psi(t)\rangle = |\phi(t)\rangle + \sum_{n,d} \int dE B(E, n, q|t) |E, n, q^{-}\rangle \exp(-iEt/\hbar), \]  \hspace{1cm} (4.27)

where \( E, n, \text{and} q \) denote the eigenenergy, the quantum numbers other than the energy, and the channel index for the eigenfunction \( |E, n, q^{-}\rangle \) in the continuum. The probability of observing the state \( |E, n, q^{-}\rangle \) in the remote future is given by

\[ P(E, n, q) = \lim_{t \to \infty} \langle \psi(t) | E, n, q^{-}\rangle \langle E, n, q^{-} | \psi(t) \rangle = |B(E, n, q|t = \infty)|^2 = \frac{2\pi}{\hbar^2} | \sum_{m=1,2} c_m \langle E, n, q^{-} | d | E_m \rangle E_d(\omega_{EE_m})|^2 \]

\[ = \frac{2\pi}{\hbar^2} \left\{ |c_1|^2 d_{1,1} |E_d(\omega_{EE_1})|^2 + |c_2|^2 d_{2,2} |E_d(\omega_{EE_2})|^2 \right\} + I_{12}(t_d - t_x), \]  \hspace{1cm} (4.28)

with

\[ \langle E_1 | d | E_0 \rangle \langle E_0 | d | E_2 \rangle \equiv \langle E_1 | d | E_0 \rangle \langle E_0 | d | E_2 \rangle \exp(i\phi), \]  \hspace{1cm} (4.29)

\[ \langle E, n, q^{-} | d | E_i \rangle \langle E_i | d | E, n, q^{-} \rangle \equiv |d_{i,m}(E)| \exp[i\alpha_{i,m}(E)], \]  \hspace{1cm} (4.30)
Clearly, by changing the time delay between the two pulses or the ratio between $c_1$ and $c_2$, one can manipulate the interference term $I_{12}(t_d - t_x)$. Moreover, due to the presence of the molecular phase $\alpha_{1,2}$, the interference may be constructive for one channel while being destructive for other channels. Selectivity can thus be achieved through the manipulation of quantum interference and excellent control has been predicted [18] and observed experimentally.

### 4.3.2 A fully quantized version of the two-pulse control theory

The above classical treatment of light fields has several advantages. For example, it shows, in a very simple manner, the source of the interference and how it can be altered experimentally. It can also be readily extended to cases in which laser incoherence is present. However, as far as fundamental questions are concerned, it is not very satisfactory. Just as the double-slit plate is treated quantum mechanically in Bohr's defense of the consistency of quantum mechanics [5, 8], so too we gain more insight by dealing with quantized fields into the issue of indistinguishability and interference in the context of coherent control. As will become apparent, by quantizing light fields, we can examine molecule-photon entanglement, indistinguishability between
independent pathways, and therefore the difference between bimolecular collisions and photon-molecule collisions.

Consider then a molecule subjected to a quantized electro-magnetic field. The total Hamiltonian including the molecular Hamiltonian $H_M$, the radiation Hamiltonian $H_R$, and the interaction Hamiltonian $H_I$, in the Schrödinger picture, is given by

$$H = H_M + H_R + H_I = H_0 + H_I$$

where the electrical field is assumed to be in the same direction as the molecular dipole moment, $d_{ij} \equiv \langle E_i|d|E_j \rangle$, $a_k$ and $a_k^\dagger$ are the photon creation and annihilation operators for the frequency component $\omega_k$.

Given Eq. (4.32), first-order perturbation theory gives [19]

$$\exp(-iHt/\hbar) = \exp(-iH_0t/\hbar)\left\{ 1 + \frac{1}{\hbar} \sum_k \sum_{ij} d_{ij}|i\rangle\langle j| \sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}} \frac{\exp[i(\omega_{E_j} - \omega_k)t]}{i(\omega_{E_j} - \omega_k - i\epsilon)} \right\}$$

where $\epsilon$ finally goes to $0^+$. We define the time $t = 0$ as that after which the first pulse has completed. Further, in addition to those assumptions in the semiclassical treatment, we assume that the quantum state of the first pulse at $t = 0$ would be given by $|\phi_{\text{photon}}^o\rangle$ if there were no laser-molecule interaction. Then, the wavefunction for the entire system at $t = 0$ is given by (in the rotating wave approximation)

$$|\Psi(t = 0)\rangle = |\phi_{\text{photon}}^o\rangle \otimes |E_0\rangle + \frac{1}{\hbar} (d_{10} \hat{A}_{10} |\phi_{\text{photon}}^o\rangle \otimes |E_1\rangle)$$

$$+ \frac{1}{\hbar} (d_{20} \hat{A}_{20} |\phi_{\text{photon}}^o\rangle \otimes |E_2\rangle),$$

(4.34)
where operators $\hat{A}_{i0}$ are

$$\hat{A}_{i0} \equiv \sum_k \sqrt{\frac{\hbar \omega_k}{2e_0 V}} \frac{1}{i(\omega_{E_i} - \omega_k - i\epsilon)} \hat{a}_k. \quad (4.35)$$

For the second laser pulse, the quantum state of light is assumed to be $|\psi_{\text{photon}}^\phi\rangle$ at $t = 0$. Applying Eq. (4.33) a second time gives rise to the wavefunction $|\psi(t)\rangle$ for the entire system at any time $t \geq 0$. For a straightforward comparison with the semiclassical treatment, it is also assumed that only the $|E_1\rangle$ and $|E_2\rangle$ levels can contribute significantly to the photodissociation probabilities. Then one has

$$\lim_{t \to +\infty} |\psi(t)\rangle = \exp(-iH_0 t/\hbar) |\psi(0)\rangle \nonumber$$

$$- \exp(-iEt/\hbar) \frac{1}{\hbar^2} \sum_{n,q} \int dE |E, n, q^-\rangle \nonumber$$

$$\otimes |d_{E,1}^{n,\phi} d_{10}(\hat{B}_{E,1}|\psi_{\text{photon}}^\phi\rangle) \otimes (\hat{A}_{10}|\psi_{\text{photon}}^\phi\rangle)\nonumber$$

$$+ d_{E,2}^{n,\phi} d_{20}(\hat{B}_{E,2}|\psi_{\text{photon}}^\phi\rangle) \otimes (\hat{A}_{20}|\psi_{\text{photon}}^\phi\rangle), \quad (4.36)$$

where $d_{E,i}^{n,q} \equiv \langle E, n, q^- |d_i|E_i\rangle$, and $\hat{B}_{E,i}$ is given by

$$\hat{B}_{E,i} \equiv \sum_k \sqrt{\frac{\hbar \omega_k}{2e_0 V}} \frac{1}{i(\omega_{E_i} - \omega_k + i\epsilon)} \hat{a}_k. \quad (4.37)$$

Equation (4.36) is the fully quantum analogue of Eq. (4.27).

### 4.3.3 Interference and indistinguishability in two-pulse control

Equation (4.36) shows that the target state is entangled with both the first and the second light fields. It is therefore possible that with this entanglement one can tell by
which excitation pathway the molecule has been dissociated, i.e., by either the route $E_0 \rightarrow E_1 \rightarrow E$ or the route $E_0 \rightarrow E_2 \rightarrow E$. However, contrary to the bimolecular collision case, the photon states entangled with molecular states are usually not orthogonal. This suggests that the two independent excitation pathways can still have a high degree of indistinguishability. Specifically, if we define

$$
|\psi_1\rangle = \frac{\exp(-iEt/\hbar)}{\hbar^2} \int dE \sum_{n,q} |E, n, q^-\rangle \\
\otimes d_{E,1}^a d_{10}^b (\hat{B}_{E,1}|\psi_{\text{photon}}^b\rangle) \otimes (\hat{A}_{10}^a |\psi_{\text{photon}}^a\rangle),
$$

$$
|\psi_2\rangle = \frac{\exp(-iEt/\hbar)}{\hbar^2} \int dE \sum_{n,q} |E, n, q^-\rangle \\
\otimes d_{E,2}^a d_{20}^b (\hat{B}_{E,2}|\psi_{\text{photon}}^b\rangle) \otimes (\hat{A}_{20}^a |\psi_{\text{photon}}^a\rangle),
$$

(4.38)

then the continuum part of $|\Psi(t)\rangle$ is just a superposition of these two states, corresponding to different contributions from independent excitation pathways. The interference of these two states for the measurement of the projector $|E, n, q^-\rangle\langle E, n, q^-|$ is given by

$$
\langle \psi_1|E, n, q^-\rangle\langle E, n, q^-|\psi_2\rangle + \langle \psi_2|E, n, q^-\rangle\langle E, n, q^-|\psi_1\rangle
$$

$$
= \frac{1}{\hbar^4} \sum_n (d_{E,2}^a)^* d_{E,1}^a d_{20}^b d_{10}^b \langle \psi_{\text{photon}}^a |\hat{A}_{20,0}^a \hat{A}_{10,0}^b |\psi_{\text{photon}}^b\rangle \langle \psi_{\text{photon}}^b |\hat{B}_{E,2}^b \hat{B}_{E,1}^a |\psi_{\text{photon}}^a\rangle \\
+ \text{c.c.}
$$

(4.39)

The first observation to be made from Eq. (4.39) is the exact correspondence between semiclassical and quantum treatments under certain conditions. To see this, suppose both $|\psi_{\text{photon}}^a\rangle$ and $|\psi_{\text{photon}}^b\rangle$ are products of coherent states for different fre-
where $\alpha_k$ and $\beta_k$ define the coherent states. One establishes the equivalence between quantum and semiclassical treatments for the interference term [i.e., the equivalence between Eqs. (4.39) and (4.31)] by requiring $E_a(\omega_{E,E_0})$ and $E_b(\omega_{EE_i})$ to be the same as the Fourier components $E_z(\omega_{E,E_0})$ and $E_d(\omega_{EE_i})$ of the classical light field. Of even greater interest is the implication of this correspondence condition for the degree of indistinguishability between the two independent excitation pathways ($E_0 \rightarrow E_1 \rightarrow E$ and $E_0 \rightarrow E_2 \rightarrow E$). Substituting Eq. (4.40) into Eq. (4.38), one sees that $|\psi_1\rangle$ is absolutely indistinguishable from $|\psi_2\rangle$ except for an irrelevant phase factor, i.e., the degree of indistinguishability is one. Thus, subject to the condition in Eq. (4.40), it is absolutely impossible to tell which excitation pathway the molecule has taken, even after making precise measurements of the light fields. In other words, the quantum-classical correspondence condition of Eq. (4.40) here corresponds to the case of maximum degree of indistinguishability between the two excitation pathways $E_0 \rightarrow E_1 \rightarrow E$ and $E_0 \rightarrow E_2 \rightarrow E$. Hence, coherent states of light for both the preparation and the dissociation pulses can first create and then manipulate molecular coherence without leaking out any which-way information.
It then follows that quantum states of light in general may provide some which-way information in a molecular process that allows for multiple excitation pathways. This point may be clearly illustrated by using some limiting cases. Consider a case in which the wavefunction $|\psi_{\text{photon}}^\alpha\rangle$ of the preparation pulse is an eigenstate $|n_k\rangle$ of the photon number operator $\hat{a}_k\dagger\hat{a}_k$ for $\omega_k \approx \omega_{E_1E_0}$ and still a coherent state for other frequency components. Then, one can easily distinguish between the two excitation possibilities $E_0 \rightarrow E_1$ and $E_0 \rightarrow E_2$, by carrying out a measurement of the change in the number of photons with the frequency $\omega_{E_1E_0}$. That is, if the number of photons with the frequency $\omega_{E_1E_0}$ decreases by 1, then the molecule must have been excited to $|E_1\rangle$, otherwise it must have been excited to $|E_2\rangle$. According to the indistinguishability requirement for interference, this zero indistinguishability would completely destroy interference. Indeed, if we choose a complete set of distinguishing projectors $P_k = |n_k\rangle\langle n_k|$, then the corresponding degree of indistinguishability [see Eq. (4.1)] between $|\psi_1\rangle$ and $|\psi_2\rangle$ in Eq. (4.38) is zero; and since $\langle \psi_{\text{photon}}^\alpha | \hat{A}_{30}^\dagger \hat{A}_{10} | \psi_{\text{photon}}^\alpha \rangle = 0$, the interference power for the projectors $|E, n, q^-\rangle\langle E, n, q^-|$ is also zero. Similarly, for the dissociation pulse, if $|\psi_{\text{photon}}^\beta\rangle$ is a photon number eigenstate for one frequency component e.g. $\omega_{EE_1}$, interference will also disappear because we can distinguish between $E_1 \rightarrow E$ and $E_2 \rightarrow E$ by measuring the photon number in the second light field.

One could argue that this example could be intuitively understood in terms of the photon number and photon phase uncertainty relation say, $\delta N \delta \phi \approx 1$. That is, a photon number eigenstate ($\delta N = 0$) gives the largest phase uncertainty ($\delta \phi \approx 2\pi$),
and a large phase uncertainty destroys phase control. However, it should be stressed that the physics here is in fact more complex than is evident from this over-simplified perspective. To see this consider the two well-known quantum states of light, namely, the even coherent states (ECS) \( |\psi^{ECS}\rangle = [2(1 + \exp(-2\alpha^2))]^{-1/2}(|\alpha\rangle + | - \alpha\rangle) \) and the odd coherent states (OCS) \( |\psi^{OCS}\rangle = [2(1 - \exp(-2\alpha^2))]^{-1/2}(|\alpha\rangle - | - \alpha\rangle) \), where \( \hat{a}|\alpha\rangle = \alpha|\alpha\rangle \) and \( \hat{a}| - \alpha\rangle = -\alpha| - \alpha\rangle \) [20]. The photon number distribution \( P_{n}^{ECS} \) for ECS is given by \( P_{n}^{ECS} = [2\alpha^n \exp(-\alpha^2)]/[n!(1 + \exp(-2\alpha^2))] \) if \( n \) is even, and \( P_{n}^{ECS} = 0 \) if \( n \) is odd; whereas the photon number distribution \( P_{n}^{OCS} \) for OCS is given by \( P_{n}^{OCS} = [2\alpha^n \exp(-\alpha^2)]/[n!(1 - \exp(-2\alpha^2))] \) if \( n \) is odd and \( P_{n}^{OCS} = 0 \) if \( n \) is even. Note that such OCS and ECS can typically have \( \delta N \gg 1 \), suggesting that the phase uncertainty could be very small (\( \delta \phi < 1 \)) if the uncertainty relation \( \delta N \delta \phi \approx 1 \) is applied. However, here loss of one photon in OCS (ECS) still causes a dramatic change in the quantum states of light, from only allowing for odd (even) numbers of photons to only allowing for even (odd) numbers of photons. Thus, if the preparation or dissociation pulse is given by an OCS (ECS) for one frequency component (say, \( \Omega_{E_xE_y} \)), one can, in principle, tell whether or not the molecule has absorbed a photon of a certain frequency, by a post-interaction measurement of the even/odd property of the photon number distribution. This implies that in these cases there should not be quantum interference, as a result of complete distinguishability of multiple excitation pathways. Indeed, based on the fact that

\[
\langle \psi^{ECS}|\hat{a}|\psi^{ECS}\rangle = \langle \psi^{OCS}|\hat{a}|\psi^{OCS}\rangle = 0,
\]  

(4.41)

one clearly sees that quantum interference given by Eq. (4.39) has to vanish if either
the preparation or the dissociation pulse is really given by OCS or ECS.

4.3.4 Indistinguishability and interference in incoherent control

The analyses in the previous subsection apply also to other weak-field Brumer-Shapiro control scenarios [e.g., "1 photon + 3 photon" control, "1 photon + 2 photon" control, "ω1 + ω2" vs. "ω3 + ω4" control (ω1(2) ≠ ω3(4))] with minor changes. However, it remains to examine the relevance of the issue of indistinguishability and interference to several incoherent interference control scenarios, where interference between multiple pathways was found to be insensitive to laser phases [21, 22].

Consider first the strong-field Brumer-Shapiro coherent control approach [21] in that scenario, the first pathway is simply a direct excitation from the initial state |1⟩ to the target state |E, n, q−⟩, and the second pathway begins with an excitation from the initial state to the target state, followed by back and forth transitions induced by a strong field between the target state and a third intermediate state |2⟩. Obviously a classification of independent pathways like this is a fiction. That is, during the laser-molecule interaction, there are no "back and forth" transitions. Rather, this physical picture of Brumer-Shapiro strong field coherent control is just an alternative interpretation of the excitation from the initial state to a dressed target state. Given that it is absolutely impossible to distinguish between fictitious pathways, even in principle, the maximum degree of indistinguishability is automatically guaranteed, and so is interference control.
Consider another well-known incoherent interference control scenario, the so-called "\( \omega_1 + \omega_2 \)" vs. "\( \omega_2 + \omega_1 \)" scenario [22]. In this case, the first pathway starts with an excitation from state \( |E_0\rangle \) to an intermediate state \( |E_1\rangle \) by absorbing a photon of frequency \( \omega_1 \), followed by a second excitation from state \( |E_1\rangle \) to the target state \( |E, n, q^-\rangle \) by a second photon of frequency \( \omega_2 \). The second pathway proceeds through another intermediate state \( |E_2\rangle \) by first absorbing a photon, from \( |E_0\rangle \), of frequency \( \omega_2 \) and then exciting \( |E_2\rangle \) to \( |E, n, q^-\rangle \) with a second photon of frequency \( \omega_1 \). Rigorously describing such laser-molecule interaction requires a general resonant two-photon photodissociation theory [23], by which both level shifts and level widths can be explicitly taken into account. Nevertheless, for the purpose here it suffices to apply the second-order perturbation theory with the fully quantized Hamiltonian (4.32). Substituting (4.32) into the following perturbation series

\[
\exp(-iHt/\hbar) = \exp(-iH_0t/\hbar)[1 - \frac{i}{\hbar} \int_0^t \exp(iH_0t_1/\hbar)H_f \exp(-iH_0t_1/\hbar)dt_1 \\
- \frac{1}{\hbar^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \exp(iH_0t_1/\hbar)H_f \exp(-iH_0t_1/\hbar) \exp(iH_0t_2/\hbar) \exp(-iH_0t_2/\hbar)],
\]

neglecting the first-order term (i.e., assuming that this term will not contribute to photodissociation), and applying again the rotating wave approximation, one obtains the wavefunction \( |\Psi(t)\rangle \) for the entire molecule-field system. In particular, if initially \( |\Psi(0)\rangle = |E_0\rangle \otimes |\psi_{\text{photon}}\rangle \), we have

\[
\lim_{t \to +\infty} |\Psi(t)\rangle = \exp(-iH_0t/\hbar)[|\Psi(0)\rangle - \frac{1}{\hbar^2} \sum_{kk'} \sum_n \left\langle \sum_j \int dE |E, n, q^-\rangle \\
\otimes \frac{\sqrt{\hbar^2 \omega_k \omega_{k'}} d_{j0} \hat{a}_{kk'} \hat{a}_{kk'} / 2\varepsilon_0 V}{(\omega_{EE_0} - \omega_k - \omega_k + 2i\varepsilon)(\omega_{EE_j} - \omega_k + i\varepsilon)} |\psi_{\text{photon}}\rangle],
\]

(4.43)
where the intermediate states are assumed to be $|E_j\rangle$, and $d^{\alpha\gamma}_{E_j}$ and $d_{j0}$ are the corresponding transition dipole moments. As in the two-pulse control case, Eq. (4.43) implies that molecular states tend to be entangled with photon states. The resultant molecule-photon entanglement can, in general, decrease the indistinguishability of the multiple pathways via different intermediate states. Interestingly, this is not the case in the special situation cleverly used in the "$\omega_1 + \omega_2$" vs. "$\omega_2 + \omega_1$" control. In this scenario there are only two near-resonant and dominant intermediate bound states $|E_1\rangle$ and $|E_2\rangle$ of energy $E_1$ and $E_2$, and more importantly, for a particular energy $E$, $\omega_{EE_1} = \omega_{E_1} E_0$. Thus one gets

\[(\omega_{EE_1} - \omega_\nu + i\epsilon) = (\omega_{E_1} E_0 - \omega_\nu + i\epsilon)\]

\[= -(\omega_{EE_2} - \omega_\kappa + i\epsilon), \quad (4.44)\]

where in obtaining the second equality we used $(\omega_{EE_0} - \omega_\kappa - \omega_\nu + 2i\epsilon) \approx 0$ because the total energy is conserved. Using Eq. (4.44) and manipulating the order of the sum in Eq. (4.43), the $E, n, q$-component of the wavefunction is found to be

\[
\lim_{t \to \infty} |\Psi(t)\rangle_{E,n,q} = \frac{\exp(-iEt/\hbar)}{2\epsilon_0 \hbar V} \sum_{kk'} \left[ -d^{\alpha\gamma}_{E_1} d_{10} \sqrt{\omega_\kappa \omega_\nu} |E_1, n, q^-\rangle \otimes a_{k'} a_{k} |\psi_{\text{photon}}\rangle \right.
\]

\[+ d^{\alpha\gamma}_{E_2} d_{20} \sqrt{\omega_\kappa \omega_\nu} |E_2, n, q^-\rangle \otimes a_{k'} a_{k} |\psi_{\text{photon}}\rangle \left. \right] \frac{(\omega_{EE_0} - \omega_\kappa - \omega_\nu + 2i\epsilon)(\omega_{EE_1} - \omega_\nu + i\epsilon)}{(\omega_{EE_0} - \omega_\kappa - \omega_\nu + 2i\epsilon)(\omega_{EE_1} - \omega_\nu + i\epsilon)}. \quad (4.45)\]

Clearly, the first term on the right hand side of Eq. (4.45) represents the contribution from the first path through the intermediate state $|E_1\rangle$, and the second term represents the contribution from the second path through the intermediate state $|E_2\rangle$. Remarkably, without any restriction on the form of $|\psi_{\text{photon}}\rangle$, these two terms are seen
to be identical except some c-number coefficients, i.e., the degree of indistinguishability of these two components is one. Thus, in the particular control scenario \( \omega_1 + \omega_2 \) vs. \( \omega_2 + \omega_1 \) the final states arising from the two independent pathways happen to be absolutely indistinguishable, even after considering any possible molecule-photon entanglement. This is in sharp contrast to the two-pulse control case in which we show that only coherent states of light can guarantee the maximum degree of indistinguishability.

To conclude, incoherent interference control is markedly different from traditional coherent control, in that the former utilizes a special kind of quantum interference which results from the absolute indistinguishability of multiple excitation pathways to the same target state.

### 4.4 Discussion

The essence of our analyses in sections 4.3 and 4.4 is that, after molecule-molecule (laser-molecule) interaction, (a) if you can obtain enough information about the quantum state or the quantum process associated with the molecule of interest \( C \) by measuring the other molecule \( D \) (the light field), then not performing any measurement on \( D \) (the laser field) results in strong decoherence in the molecule \( C \), and (b) if there is still much uncertainty about the the quantum state or the quantum process associated with the molecule \( C \) even after you precisely measure the other molecule \( D \) (the light field), then by tracing over all other degrees of freedom of \( D \) (the light field) you not necessarily decohere the molecule \( C \).
In this section we would like to apply these insights to the relevant problem of quantum coherence creation in photodissociation processes. On one hand, this problem is similar to quantum coherence creation in bimolecular collisions since usually there are two or more products flying apart in photodissociation processes. On the other hand, it is related to the possibility of creating molecular coherence using light fields.

Suppose the photodissociation process is 

\[(AB) + \text{photon} \rightarrow (AB)^* \rightarrow C + D,\]

where \((AB)^*\) represents the excited complex before it breaks apart to form molecules \(C + D\). Conventional photodissociation experiments employ very long monochromatic laser pulses [24]. In this case \((AB)^*\) has both definite energy and momentum. Hence the process \((AB)^* \rightarrow C + D\) is exactly the same as the latter half part of a bimolecular collision discussed in section 4.2. It then follows that photodissociation fragments in this process can not have useful coherence between different translational states, or between nondegenerate ro-vibrational states. Fundamentally this is because one can, in principle, obtain which-state information about one fragment by measuring the other fragment, since the total momentum and the total energy are known. Indeed, while one can have final rovibrational state distribution of photodissociation fragments, no definite phase relationships between non-degenerate ro-vibrational states is available in traditional photodissociation processes (here we do not consider coincidence experiments). This even applies to the cases in which correlations in the final state distributions between two fragments seem very weak. For instance, in the photodissociation of \(H_2CO\) into \(H_2\) and \(CO\) [24], because the rotational excitations
of \( H_2 \) and \( CO \) are due to distinct mechanisms, the final rotational state distribution of \( CO \) is largely independent of that of \( H_2 \). Nonetheless, this weak correlation by no means indicates a weak quantum entanglement between \( H_2 \) and \( CO \). Which-state information contained in \( H_2 \) (\( CO \)), even though it is very difficult to demonstrate experimentally, forbids us to get coherence effects in \( CO \) (\( H_2 \)) as long as the light field is monochromatic.

As in bimolecular collisions, traditional photodissociation processes can also generate coherence between degenerate internal states of photodissociation fragments. To see this, let's suppose that the laser field is linearly polarized along the \( x \) direction while we consider various rotational states of \( C \) with different \( m_z \) (the quantum number associated with the projection of the angular momentum onto the \( z \)-axis). The corresponding selection rule is \( \Delta(m_z(C)+m_z(D)) = +1 \) or \( \Delta(m_z(C)+m_z(D)) = -1 \). Apparently, the knowledge of \( m_z(D) \) cannot tell us the exact value of \( m_z(C) \) since it still has two possibilities. Note also that further measuring the light state will not yield more information about \( C \) as long as the light field is close to the most classical state: coherent state. Thus, a superposition state of \( C \) made up of these two \( m_z(C) \) components may be created by a photodissociation process.

By contrast, today's femto-second laser technology opens tremendous new possibilities in photodissociation dynamics. Ultrafast laser pulses directly excite the molecule (\( AB \)) into a coherent superposition state of many ro-vibrational states embedded in the continuum, at a time scale much less than that of the ro-vibrational motions. These photodissociation processes are no longer analogous to the latter half
of bimolecular collisions, due to the large uncertainty in energy introduced by ultra-fast laser pulses. This suggests that quantum states of \( C \) and \( D \) can be largely free from entanglement in energy, i.e., by accurately measuring the energy of one fragment we are not necessarily able to specify the energy of the other fragment. Hence indistinguishability conditions can be satisfied, and ro-vibrational coherence effects of photodissociation fragments become possible. This possibility was first observed by Zewail et al. [25] in the reaction \( \text{HgI}_2 + \text{photon} \rightarrow \text{HgI} + I \). Later, other examples were found [26]. It can be concluded that in general femto-second photodissociation processes can be used as a coherence preparation step in coherent control of molecular processes. However, under the assumption that we can always neglect the momentum carried by photons, useful coherence in molecular translational motions still cannot be created due to the momentum entanglement between photodissociation fragments.

### 4.5 Summary

To summarize, in this chapter, in the context of coherent control, the subtle issue of indistinguishability and interference between independent pathways is examined. Interference occurs only when independent pathways are indistinguishable. Due to this indistinguishability requirement, creating a useful superposition state of nondegenerate molecular states for subsequent coherent control can not be achieved by multi-channel bimolecular collisions. Coherence can, however, be conveniently transferred from light fields to molecules. This coherence transfer, and the subsequent coherent control based on this coherence transfer, are best realized by the most clas-
sical states of light, i.e., coherent states of light. This is because quantum states of light may suppress the extent of phase-sensitive coherent control by leaking out some which-way information in molecular processes. By contrast, incoherent interference control scenarios are shown to have automatically ensured the maximum degree of indistinguishability of multiple pathways. The implication of the relationship between indistinguishability and interference for understanding coherence creation in photodissociation fragments is also discussed. It is shown that traditional photodissociation processes with very long monochromatic laser pulses can never create useful molecular coherence between non-degenerate ro-vibrational states due to quantum entanglement between photodissociation fragments. New possibilities brought about by femto-second photodissociation processes are understood in terms of disentanglement in energy between photodissociation fragments.
Bibliography


[13] Strictly speaking, the reason why we can neglect other channels not including C is that they provide no information whatsoever on the quantum states of C.

[14] Strictly speaking, from the quantum mechanical point of view, a moving particle can not be described by a momentum eigenstate. Rather, it should be cast as a Gaussian wavepacket. It is the coherence among various momentum components of Gaussian wavepackets that makes particles move. However, for two reasons it is most appropriate to use momentum eigenstates to describe the scattering processes. First, the wavepacket momentum width \( \delta p \) is often negligible compared with the average momentum \( \bar{p} \). Considering the sizes of particle sources and beam tubes, let's take the physical size of a wavepacket around the order \( 10^{-5} \) m. Then for one proton in a nuclear scattering experiment with 1 MeV translational energy, \( \delta p / \bar{p} = 10^{-9} \). The size of this wavepacket expands only by a factor of \( 10^{-10} \) after it travels the distance 1 m. Clearly within the corresponding energy spread in the translational wavepacket, the scattering matrix elements remain perfectly constant. In chemistry we have quite similar situations. For example, consider the hydrogen atoms having 1 eV translational energy in the \( H + H_2 \) scattering experiment, \( \delta p / \bar{p} = 10^{-6} \). The wavepacket will expand only by \( 10^{-3} \) times after atoms travel a distance 1 m. The corresponding energy spread in the translational wavepackets is given by \( 10^{-6} \) eV, which is
much smaller than the characteristic rotational and vibrational level spacings of the hydrogen molecule. Hence we can treat these wavepackets as momentum eigenstates. In this respect, all the translational eigenstates in this chapter can be understood as Gaussian wavepackets with very small momentum widths. Different translational states just mean different Gaussian wavepackets of this kind without any appreciable overlap. Second, it was shown (H.J. Bernstein and F.E. Low, Phys. Rev. Lett. 59, 951 (1987)) that experiments with directionally collimated beams incident on passive targets cannot distinguish between coherent wavepacket structure and the incoherent mixing of various momentum eigenstates.


[16] The most astonishing and counterintuitive aspect of quantum theory is the nonseparability of two distant and non-interacting quantum systems that had interacted in the past. This was first realized in the famous Einstein-Podolsky-Rosen paradox [see A. Einstein, B. Podolsky, and N. Rosen, Phys. Rev. 47, 777 (1935)].


Chapter 5

Coherent Control of Elastic and Inelastic Scattering of Identical Molecules
Chapter Summary:

In this chapter we study coherent control of elastic and inelastic scattering of identical molecules. An interesting role played by quantum entanglement of molecular rovibrational motions is identified as are two quantum effects due to entangled rovibrational states. These quantum effects are utilized to demonstrate phase control of both differential and total cross sections. Computational examples for the elastic and inelastic scattering of \textit{para} \(H_2\) and \textit{para} \(H_2\) are presented, with the collision energy ranging from 400 \(cm^{-1}\) to the ultracold region. The experimental realization of this scenario and possible extension to other systems are discussed.
5.1 Introduction

Recent years have witnessed an ever-increasing interest in coherent control (CC) of molecular and atomic processes [1]. By utilizing coherent laser fields, the CC approach suggests inducing constructive or destructive interference between multiple indistinguishable pathways to the same target state. The yield of desired or undesired product can thus been enhanced or suppressed, respectively. So far, most experimental and theoretical studies of CC of atomic and molecular processes (including our studies in Chaps. 2 and 3) have focused on unimolecular reactions or half collisions, such as photodissociation, photoionization and photoassociation.

By contrast, it remains a challenge to control full collision processes, such as atom-atom scattering, atom-molecule scattering, and molecule-molecule scattering. Existent studies along this direction have largely employed two scenarios [2, 3, 4, 5]. The first scenario [2, 3, 4] actively manipulates coherent light sources to alter the interaction potential of scattering particles. For example, in ultracold atom-atom collisions, the scattering cross sections can be extensively controlled by using laser fields in near resonance with one of the excited molecular electronic states [2, 3], or a d.c. field inducing an additional dipole-dipole interaction potential [4]. However, it is not straightforward to follow such an approach for atom-molecule or molecule-molecule scattering problems, since they involve a much larger number of degrees of freedom. The second approach [5] emphasizes quantum interference effects in scattering. A central issue there is to introduce quantum coherence into the scattering system, while keeping the interaction potential intact [5]. This approach has the
advantage that the actual realization of this scenario does not vary strongly from system to system, and that the resulting control is completely quantum in nature. There is also some interest in combining these two scenarios to achieve the CC of full collisions, such as the reaction \( H + H_2 \) [6].

Recently, a number of studies on the CC of full collisions using the second scenario were carried out. Specifically, a general theory for the control of bimolecular collisions has been developed [5], and various applications of this theory to several model systems have been successful [7]. However, it was also shown that [7, 8], for the scattering of non-identical molecules, extensive CC using the second scenario generally requires the preparation of quantum correlations between the translational and internal rovibrational states of the atoms and molecules. This presents a great experimental challenge, since the realization of translational coherence necessarily involves longitudinally coherent matter beams and establishing the required coherence with internal states requires extensions of current experimental skills.

Fortunately, for the scattering of identical molecules, it is not necessary to correlate the translational motion with internal rovibrational states in order to have phase control of cross sections [9]. Indeed, it was conjectured that just manipulating the coherence of initial rovibrational states may be enough to give extensive control [9]. That is, it was argued [9] that, if we prepare quantum superposition states of internal motions for both the projectile and the target molecules, both reactive and nonreactive cross sections should be controllable via manipulation of quantum phases embedded in the initial superposition states.
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The goal of this chapter is to continue the study of coherent control of scattering of identical molecules. We first address this issue, from a perspective that differs from Ref. [9]. In particular, we reveal and stress an interesting and utilizable molecular quantum entanglement in the scattering theory. We then present computational results for various cases of diatom-diatom elastic and inelastic scattering, in order to demonstrate extensive CC of both differential and total cross sections. Such results constitute the first CC study in diatom-diatom scattering. Both theoretical and computational results in this chapter confirm the idea of Ref. [9], and provide new insights into the CC of molecule-molecule scattering. Moreover, we extend our studies to the case of ultracold molecular scattering, thus opening up a new application of coherent control.

This chapter is organized as follows. In section 5.2, we consider the role of entangled molecular rovibrational states in the scattering of identical molecules. The rigorous theoretical formulation is presented for the collision between \textit{para} \textit{H}_2 and \textit{para} \textit{H}_2, without the loss of much generality. In section 5.3, we show how to utilize quantum entanglement of molecular rovibrational motions to alter both elastic and inelastic cross sections, by presenting detailed results of our calculations for the \textit{para} \textit{H}_2 + \textit{para} \textit{H}_2 system, with the collision energy ranging from 400 \textit{cm}^{-1} to the ultracold region. In section 5.4, we discuss possible experimental realization of our control scenario, in connection with the original proposal of Ref. [9]. In the same section we also consider several possible extensions of our results. Finally, a brief summary is given in section 5.5.
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5.2 The Role of Entangled Rovibrational States

Quantum entanglement is a striking feature of quantum physics. Once two particles are entangled, neither of them possesses a definite quantum state. Quantum entanglement has played a key role in various fascinating fields such as quantum teleportation [10], quantum computing [11] etc., and is a fundamental issue of great theoretical interest.

One interesting feature due to quantum entanglement of identical particles lies in the permutation symmetry of entangled states. Consider the system of two identical spin 1/2 particles, whose spin up and spin down states are represented by \( |\uparrow_1\rangle, |\downarrow_1\rangle, |\uparrow_2\rangle, |\downarrow_2\rangle \), respectively. If the total spin is zero, then the two spins are entangled and the resulting Einstein-Podolsky-Rosen state \(|EPR\rangle\) is given by

\[
|EPR\rangle = \frac{1}{\sqrt{2}} (|\uparrow_1\rangle \otimes |\downarrow_2\rangle - |\downarrow_1\rangle \otimes |\uparrow_2\rangle). \tag{5.1}
\]

Clearly, \(|EPR\rangle\) acquires a factor of \(-1\) upon permutation. Since the total permutation symmetry has to be \(-1\) for identical fermions, the permutation symmetry of the spatial degrees of freedom has to be \(+1\). Thus, in a simple bound system such as \(\text{para } H_2\), the rotational quantum number has to be even. Likewise, in unbound systems such as electron-electron or proton-proton scattering, the differential cross sections do depend strongly on how the two spins are entangled, even if the scattering potential is spin independent, e.g., a pure Coulomb potential [12].

In this section we consider quantum effects of entanglement of molecular rovibrational motions (rather than entanglement of nuclear or electronic spins) on the
scattering of identical molecules. In doing so we specifically study the scattering system of \textit{para} \textit{H}_2 and \textit{para} \textit{H}_2, the simplest case of diatomic-diatomic scattering. Although many of our arguments apply to both reactive and nonreactive scattering, here we confine ourselves to elastic and inelastic scattering only. As shown below, two different quantum effects arise if the incoming asymptotic state is an entangled molecular state. We believe that such quantum effects can not only have straightforward applications in coherent control of bimolecular scattering, but also provide intriguing physics of fundamental interest. To our knowledge, there has been no prior study of whether or not molecular entanglement can induce interesting quantum features in bimolecular scattering, either theoretically or experimentally.

We represent the vector pointing from the center of mass of the projectile to that of the target by \( R \), and the relative interatomic distance vectors of the two \textit{para} \textit{H}_2 molecules by \( r_1 \) and \( r_2 \), respectively. We further use \( j_i, m_i, v_i \) \((i = 1, 2)\) to denote the quantum numbers of angular momentum, the projection of angular momentum onto a space-fixed \( z \) axis, and vibrational motion, respectively, for each \textit{para} \textit{H}_2 molecule. The fact that both the nuclear spin and the electronic spin of \textit{para} \textit{H}_2 molecules are zero greatly simplifies the problem, while still keeping the essence of physics. To see this note that each \textit{para} \textit{H}_2 molecule can be treated as a boson, so that the permutation symmetry of the total wavefunction \(|\Psi(r_1, r_2, R)\rangle\) of the scattering problem is +1. That is,

\[
|\Psi(r_1, r_2, R)\rangle = |\Psi(r_2, r_1, -R)\rangle.
\]  

(5.2)

As we shall see more clearly below, this implies that the parity of \(|\Psi(r_1, r_2, R)\rangle\) with
regard to $\mathbf{R}$ depends on the permutation symmetry of the internal degrees of freedom $\mathbf{r}_1$ and $\mathbf{r}_2$.

In a traditional scattering case, the initial state of the scattering is characterized by $k, \hat{z}, j_1, m_1, v_1, j_2, m_2, v_2$, and the final state characterized by $k', \hat{R}, j_1', m_1', v_1', j_2', m_2', v_2'$, with the obvious meaning of each variable. Below we exclude the case of $(j_1, m_1, v_1) = (j_2, m_2, v_2)$ which does not provide new insights into entanglement. Since the scattering molecules are identical, both the incoming and the outgoing asymptotic states have to be appropriately symmetrized. However, for the scattering amplitude, it is sufficient to symmetrize only either the incoming or outgoing state [12]. If we choose to symmetrize the incoming state, the scattering amplitude is given by

$$f(k' \hat{R} j_1' m_1' v_1' j_2' m_2' v_2' \leftarrow k \hat{z} j_1 m_1 v_1 j_2 m_2 v_2)$$

$$= \tilde{f}(k' \hat{R} j_1' m_1' v_1' j_2' m_2' v_2' \leftarrow k \hat{z} j_1 m_1 v_1 j_2 m_2 v_2)$$

$$+ \tilde{f}(k' \hat{R} j_1' m_1' v_1' j_2' m_2' v_2' \leftarrow k (-\hat{z}) j_2 m_2 v_2 j_1 m_1 v_1), \quad (5.3)$$

where $\tilde{f}$ represents the unsymmetrized scattering amplitudes under the assumption that the two molecules are distinguishable. Specifically, in terms of the $T$-matrix elements, we have [13, 14]

$$\tilde{f}(k' \hat{R} j_1' m_1' v_1' j_2' m_2' v_2' \leftarrow k \hat{z} j_1 m_1 v_1 j_2 m_2 v_2)$$

$$= \frac{i \sqrt{\pi}}{\sqrt{k'k}} \sum_{J M m'} \sum_{l_1 m_1 l_2 m_2} \sum_{j_1' l_1' j_2' l_2'} \sqrt{2l + 1} i^{l-l'} Y_{l'}^{m'}(\hat{R}) C_{lm'}^{J M} C_{j_1' l_1' j_2' l_2'}^{J M}$$

$$\times C_{j_1 m_1 j_2 m_2}^{j_1' j_2'} T_{J M}^{J M}(j_1 v_1 j_2 v_2 j_1 v_1 j_2 v_2), \quad (5.4)$$
and

\[ f(k'\mathbf{R}, j' m_1' v_1' j_2' m_2' v_2) = k(-\mathbf{R})j m_2 v_2 j_1 m_1 v_1) \]

\[ = \frac{i\sqrt{\pi}}{\sqrt{k'k}} \sum_{JM'} \sum_{l j_1 m_1} \sum_{l' j_2 m_2} (-1)^l \sqrt{2l + 1} i^{l'-l'} Y_l^m(\mathbf{R}) C_{lm j_1 m_1}^{JM} C_{l'm' j_2 m_2}^{JM} \]

\[ \times C_{j_1 m_1 j_2 m_2}^{j_1 m_1 j_2 m_2} C_{j_2 m_2 j_1 m_1}^{j_2 m_2 j_1 m_1} T^{JM}(j_1 v_1 j_2 v_2 j_1 j_2 v_1 j_1 j_2 l), \]  

where \( Y_l^m \) is the spherical function and \( C_{j_1 m_1 j_2 m_2}^{j_1 m_1 j_2 m_2} \) is the Clebsch-Gordan coefficient.

Consider now scattering initiated in an entangled state of molecular rovibrational states:

\[ \langle r_1, r_2 | \psi(j_1 m_1 v_1 j_2 m_2 v_2) \rangle_{\alpha, \beta} = \sin(\alpha) \exp(i\beta) \langle r_1 | j_2, m_2, v_2 \rangle \langle r_2 | j_1, m_1, v_1 \rangle \]

\[ + \cos(\alpha) \langle r_1 | j_1, m_1, v_1 \rangle \langle r_2 | j_2, m_2, v_2 \rangle. \]  

(5.6)

It should be stressed that in Eq. (5.6) the two components of \( |\psi(j_1 m_1 v_1 j_2 m_2 v_2)\rangle_{\alpha, \beta} \) are degenerate in energy, allowing for interference effects to arise in scattering. Of particular interest are the two entangled states

\[ |\psi(j_1 m_1 v_1 j_2 m_2 v_2)\rangle \equiv \frac{1}{\sqrt{2}} \left( \langle r_1 | j_1, m_1, v_1 \rangle \langle r_2 | j_2, m_2, v_2 \rangle \right) \]

\[ \pm \left( \langle r_1 | j_2, m_2, v_2 \rangle \langle r_2 | j_1, m_1, v_1 \rangle \right). \]  

(5.7)

From Eq. (5.7), one sees that the only distinction between the two entangled states \( |\psi(j_1 m_1 v_1 j_2 m_2 v_2)\rangle \) is the relative phase \( \beta \) (0 or \( \pi \)) between the two participating states \( \langle r_1 | j_1 m_1 v_1 \rangle \langle r_2 | j_2 m_2 v_2 \rangle \) and \( \langle r_1 | j_2 m_2 v_2 \rangle \langle r_2 | j_1 m_1 v_1 \rangle \). These two states differ insofar as \( |\psi(j_1 m_1 v_1 j_2 m_2 v_2)\rangle_+ \) is invariant upon permutation of \( r_1 \) and \( r_2 \), whereas \( |\psi(j_1 m_1 v_1 j_2 m_2 v_2)\rangle_- \) acquires a factor of \(-1\) upon permutation of \( r_1 \) and \( r_2 \). Further,
these two entangled states also form a new set of basis states to describe a general entangled state, i.e.,

\[
|\psi(j_1m_1v_1j_2m_2v_2)\rangle_{a,o} = \frac{\cos(\alpha) + \sin(\alpha) \exp(i\beta)}{\sqrt{2}} |\psi(j_1m_1v_1j_2m_2v_2)\rangle_+ \\
+ \frac{\cos(\alpha) - \sin(\alpha) \exp(i\beta)}{\sqrt{2}} |\psi(j_1m_1v_1j_2m_2v_2)\rangle_-. \tag{5.8}
\]

The role of entangled states in the scattering problem can now be analyzed by focusing on \(|\psi(j_1m_1v_1j_2m_2v_2)\rangle_\pm\). Consideration of three special cases is in order. (a) \(j_1 = j_2, v_1 = v_2, m_1 \neq m_2\). Thus

\[
|\psi(j_1m_1v_1j_2m_2v_2)\rangle_\pm = \frac{1}{\sqrt{2}} (|m_1\rangle|m_2\rangle \pm |m_2\rangle|m_1\rangle) \otimes |j_1, v_1\rangle \otimes |j_2, v_2\rangle. \tag{5.9}
\]

Equation (5.9) shows that in this case only molecular rotational motions along a space fixed axis are entangled. This case is therefore totally analogous to two entangled spins [see Eq. (5.1)]. Indeed, quantum effects arising from such entanglement can also be understood in terms of polarization phenomena, according to a general polarization theory[15]. (b) \(m_1 = m_2, j_1 = j_2, v_1 \neq v_2\). Here we have

\[
|\psi(j_1m_1v_1j_2m_2v_2)\rangle_\pm = \frac{1}{\sqrt{2}} (|v_1\rangle|v_2\rangle \pm |v_2\rangle|v_1\rangle) \otimes |m_1, j_1\rangle \otimes |m_2, j_2\rangle. \tag{5.10}
\]

From Eq. (5.10), it is clear that only vibrational motions are entangled, whereas rotational motions are completely separable. Further, unlike case (a), the resulting quantum entanglement is entirely due to internal excitation. (c) \(m_1 = m_2, v_1 = v_2, j_1 \neq j_2\). Thus,

\[
|\psi(j_1m_1v_1j_2m_2v_2)\rangle_\pm = \frac{1}{\sqrt{2}} (|j_1\rangle|j_2\rangle \pm |j_2\rangle|j_1\rangle) \otimes |m_1, v_1\rangle \otimes |m_2, v_2\rangle. \tag{5.11}
\]
This is a complicated case. Eq. (5.11) shows that, while vibrational motions are not entangled, rotational degrees of freedom are partially entangled insofar as the motions along a space fixed axis are still separable. Note that quantum entanglement here is also due to internal excitation, and that it is intrinsically different from case (a) and beyond any description based on the general polarization theory.

Because case (a) is not of our interest and case (b) is very difficult to compute exactly, our calculational results in section 5.3 are exclusively about case (c). However, our theoretical considerations below do not distinguish between these three special cases. Using Eqs. (5.3) and (5.7), the scattering amplitude $f^\pm (\vec{R})$ from the initial entangled state $(k, \vec{z}, \psi(j_1, m_1, v_1, j_2, m_2, v_2))_\pm$ to the final state $k', \vec{R}, j'_1, m'_1, v'_1, j'_2, m'_2, v'_2$ is given by

$$f^\pm (\vec{R}) = \frac{1}{\sqrt{2}} \tilde{f}(k' \vec{R}, j'_1, m'_1, v'_1, j'_2, m'_2, v'_2 \leftarrow k \vec{z}, j_1, m_1, v_1, j_2, m_2, v_2)$$

$$+ \frac{1}{\sqrt{2}} \tilde{f}(k' \vec{R}, j'_1, m'_1, v'_1, j'_2, m'_2, v'_2 \leftarrow k(-\vec{z}), j_2, m_2, v_2, j_1, m_1, v_1)$$

$$\pm \frac{1}{\sqrt{2}} \tilde{f}(k' \vec{R}, j'_1, m'_1, v'_1, j'_2, m'_2, v'_2 \leftarrow k \vec{z}, j_2, m_2, v_2, j_1, m_1, v_1)$$

$$\pm \frac{1}{\sqrt{2}} \tilde{f}(k' \vec{R}, j'_1, m'_1, v'_1, j'_2, m'_2, v'_2 \leftarrow k(-\vec{z}), j_1, m_1, v_1, j_2, m_2, v_2).$$

(5.12)

Further, using Eqs. (5.4), (5.5) and (5.12), we obtain

$$f^\pm (\vec{R}) = \frac{1}{\sqrt{2}} \frac{i \sqrt{\pi}}{\sqrt{kk'}} \sum_{J'M'm'} \sum_{l_1 l_2 m_{12} l'_{12}} \sum_{v'_{12} v'_{12}} \sqrt{2l + 1} y_{l'}^{m'} (\vec{R}) C^{JM}_{l'l_1 l_2 m_{12}} C^{JM}_{l'2 l_1 m_{12}} C^{Jm_{12}}_{l'1 l_2 m'_{12}}$$

$$\times \{(1 \pm (-1)^{l'}) | C^{2a}_{j_1 m_1 j_2 m_2} T^{JM}(j_1 v'_1 j'_2 v'_2 j'_1 j'_2 j_1 v_1 j_2 v_2 j_1 l)$$

$$+ \{(-1)^{l'} \pm 1 | C^{12}_{j_2 m_2 j_1 m_1} T^{JM}(j_1 v'_1 j'_2 v'_2 j'_1 j'_2 j_1 v_1 j_1 v_2 j_2 v_2 j_1 l). \} \}$$

(5.13)

Equation (5.13) clearly shows that there are two important quantum effects caused by molecular entanglement. (1) Due to the factor $[1 \pm (-1)^{l'}]$ or $[(-1)^{l'} \pm 1]$, the
permutation symmetry induced by quantum molecular entanglement imposes a parity restriction on the incoming partial waves. That is, for the case of $|\psi(j_1m_1v_1j_2m_2v_2)\rangle_+$ ($|\psi(j_1m_1v_1j_2m_2v_2)\rangle_-$), contributions from odd (even) partial waves are completely suppressed whereas contributions from even (odd) partial waves are enhanced. For example, for the case of $|\psi(j_1m_1v_1j_2m_2v_2)\rangle_-$, although the two para $H_2$ molecules are spinless bosons, they avoid the $l = 0$ state due to quantum entanglement of rovibrational motions. (2) Further, Eq. (5.13) indicates that there is quantum interference between transitions $(j_1v_1j_2v_2j_1j_2l) \to (j'_1v'_1j'_2v'_2j'_1j'_2l')$ and $(j_2v_2j_1v_1j_1j_2l) \to (j'_1v'_1j'_2v'_2j'_1j'_2l')$. Clearly, whether this interference is constructive or destructive changes with the form of the entangled rovibrational state, and this interference is significant only when the magnitude of $T^{JM}(j'_1v'_1j'_2v'_2j'_1j'_2l'|j_1v_1j_2v_2j_1j_2l)$ is comparable to that of $T^{JM}(j'_1v'_1j'_2v'_2j'_1j'_2l'|j_2v_2j_1v_1j_1j_2l)$. Note that due to the fact that the total parity of the scattering system is conserved, one needs

$$(-1)^{j_1+j_2+l} = (-1)^{j'_1+j'_2+l'}$$

(5.14)

to ensure the $T$-matrix elements $T^{JM}(j'_1v'_1j'_2v'_2j'_1j'_2l'|j_1v_1j_2v_2j_1j_2l)$ to be nonzero. Note also that the scattering amplitude $f_{a,\beta}$ for an arbitrary incoming entangled state $(k, \hat{z}, |\psi(j_1m_1v_1j_2m_2v_2)\rangle_{a,\beta})$ can be expressed as

$$f_{a,\beta} = \frac{\cos(\alpha) + \sin(\alpha) \exp(i\beta)}{\sqrt{2}} f_+ + \frac{\cos(\alpha) - \sin(\alpha) \exp(i\beta)}{\sqrt{2}} f_-.$$  

(5.15)

As mentioned before, an alternative but equivalent way to symmetrize the scattering amplitude is to symmetrize the outgoing asymptotic state. That is,

$$f(k'\hat{R}j'_{1m'_1v'_1j'_2m'_2v'_2} \leftarrow k\hat{z}j_1m_1v_1j_2m_2v_2)$$
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\[ f(k') = \tilde{f}(k' \begin{array}{c} j1 \ v1 \ j2 \ v2 \ \to \ \pm j1 \ v1 \ j2 \ v2 \ \to \ \pm j1 \ v1 \ j2 \ v2 \ \to \ \pm j1 \ v1 \ j2 \ v2 \ \to \ \pm \end{array}) \]

Based on this procedure, we have

\[ f_\pm(\hat{k}) = \frac{1}{\sqrt{2}} \tilde{f}(k' \begin{array}{c} j1 \ v1 \ j2 \ v2 \ \to \ \pm j1 \ v1 \ j2 \ v2 \ \to \ \pm j1 \ v1 \ j2 \ v2 \ \to \ \pm j1 \ v1 \ j2 \ v2 \ \to \ \pm \end{array}) \]

In terms of the partial wave expansion, the scattering amplitude \( f_\pm(\hat{k}) \) in Eq. (5.17) can be further expressed as

\[ f_\pm(\hat{k}) = \frac{1}{\sqrt{2}} \tilde{f}(k' \begin{array}{c} j1 \ v1 \ j2 \ v2 \ \to \ \pm j1 \ v1 \ j2 \ v2 \ \to \ \pm j1 \ v1 \ j2 \ v2 \ \to \ \pm j1 \ v1 \ j2 \ v2 \ \to \ \pm \end{array}) \]

Interestingly, it is now far from obvious to see the equivalence of Eq. (5.17) with Eq. (5.13) (to prove their equivalence one needs to use Eq. (5.14)). As a result, we can no longer readily identify the parity restriction condition imposed on the incoming partial waves due to molecular entanglement. In this sense, in our theoretical considerations we prefer the expression (5.13) rather than (5.18). However, in our model
calculations, Eq. (5.18) is very useful to confirm the consistency of our results. For all computational examples presented below we have confirmed that Eqs. (5.13) and (5.18) give the same results.

### 5.3 Calculations and Results

#### 5.3.1 Method

Full dimensional calculations of diatom-diatom scattering are extremely difficult due to the large number of degrees of freedom. The exact numerical treatment of (non-reactive) rovibrational excitation of diatom-diatom scattering remains to be done, and exact computation of reactive diatom-diatom scattering is still restricted to only-one-reactive-bond cases for particular total angular momentum [16]. However, full dimensional rotor-rotor scattering was solved quite long ago, both theoretically and computationally [13, 14]. Thus, here we study the coherent control of rotational excitation in diatom-diatom scattering, with the vibrational motion frozen at the ground state. The rotor-rotor treatment should be satisfactory when the collision energy is not high enough to excite the vibrational motion.

MOLSCAT [17] is an ideal tool for our study. In particular, MOLSCAT can compute not only cross sections for the rotor-rotor scattering, but also all the corresponding $S$ matrix elements, a key feature for the study of phase control. MOLSCAT also provides a control parameter to account for whether or not the scattering particles are identical. Thus, we can first assume that the two scattering molecules are distin-
guishable and compute all the $S$ matrix elements $T^{JM}(j_1^i v_1^j j_2^i v_2^j j_1^{j''} j_2^{j''} | j_1 v_1 j_2 v_2)$ and $T^{JM}(j_1^i v_1^j j_2^i v_2^j j_1^{j''} j_2^{j''} | j_2 v_2 j_1 v_1)$, and then use Eq. (5.13) to calculate the cross sections.

In addition, MOLSCAT provides the Zarur-Rabitz interaction potential for $\text{para } H_2$ and $\text{para } H_2$. This model potential should be good enough for the demonstration of novel quantum effects in bimolecular scattering. However, we note that when it becomes possible to compare our theory with experiments in detail, the latest global potential for four $H$ atoms [18] may be a better choice.

### 5.3.2 Results for $E_k = 400, 40, 4 \text{ cm}^{-1}$

Here we present the results of our scattering calculations for different incoming entangled molecular states. The collision energy $E_k$ is chosen to be 400, 40, and 4 cm$^{-1}$. In particular, $E_k = 400 \text{ cm}^{-1}$ ($\approx 570$ K) represents a high collision energy case (but still much lower than the vibration excitation threshold), whereas $E_k = 4 \text{ cm}^{-1}$ ($\approx 5.7$ K) is very close to the lowest collision temperature currently achievable in a molecular crossed-beam experiment [19].

In our calculations, the entangled molecular state is chosen to be

$$|\psi_{j_1 j_2}^{\pm}\rangle = \frac{1}{\sqrt{2}}(|j_1| j_2) \pm |j_2| j_1\rangle \otimes |m_1 = 0, v_1 = 0\rangle \otimes |m_2 = 0, v_2 = 0\rangle. \quad (5.19)$$

That is, entanglement is due to molecular rotational excitation, belonging to the type (c) entanglement according to the previous section. Since we consider rotational excitation only, both the initial-state and final-state vibrational quantum numbers have been set to be zero, i.e., $v_1 = v_2 = v'_1 = v'_2 = 0$. As indicated by Eq. (5.19), we have also set $m_1$ and $m_2$ to be zero. Note that as long as $m_1 = m_2$ (so that we can...
not distinguish between the two scattering molecules by measuring the projection of their angular momentum), the results for nonzero $m_1$ and $m_2$ will be essentially the same.

Figure 5.1: The $\theta$ dependence of the elastic differential cross section summed over the final state quantum numbers $m'_1$ and $m'_2$ and integrated over $\phi$. The scattering system is $\text{para } H_2 + \text{para } H_2$, and the collision energy is (a) 400 cm$^{-1}$, (b) 40 cm$^{-1}$, and (c) 4 cm$^{-1}$. Dashed and solid lines are for the incoming free entangled states $|\psi^+_{j_1,j_2}\rangle$ and $|\psi^-_{j_1,j_2}\rangle$ [see Eq. (5.19)], respectively. $j_1 = 2, j_2 = 0$.

Figure 5.1 displays the $\theta$ dependence of the elastic differential cross section (DCS) summed over the final-state quantum numbers $m'_1$ and $m'_2$ and integrated over
the angle $\phi$ ($\hat{\mathbf{R}} \equiv (\theta, \phi)$), for the incoming entangled states $|\psi^\pm_{j_1j_2}\rangle$ with $j_1 = 2, j_2 = 0$. In particular, $E_k$ equals 400 cm$^{-1}$ in Fig. 5.1a, 40 cm$^{-1}$ in Fig. 5.1b, and 4 cm$^{-1}$ in Fig. 5.1c. For all three collision energy there is a clear difference in DCS between the cases of $|\psi^+_{j_1j_2}\rangle$ and $|\psi^-_{j_1j_2}\rangle$. For particular scattering angles, e.g., for $\theta$ close to $\pi/2$, molecular entanglement induces huge differences. It is also seen that the number of minima of DCS is always even (odd) for $|\psi^+_{j_1j_2}\rangle$ ($|\psi^-_{j_1j_2}\rangle$). This can be readily understood in terms of the parity restriction of incoming partial waves due to the permutation symmetry of entangled molecular states. Further, comparing Fig. 5.1c with Fig. 5.1a and Fig. 5.1b, it is seen that lower collision energy induces slower oscillations in DCS. This is expected due to the function $Y^{m'}_l(\hat{\mathbf{R}})$ in Eq. (5.13).

It is still unanswered whether or not the total cross section (TCS) of elastic scattering can be significantly altered as a result of different quantum entanglement in the incoming state. The answer is positive for the lowest collision energy case in Fig. 5.1c. In particular, TCS (in square angstrom) is 511 for $|\psi^+_{j_1j_2}\rangle$ (dashed curve in Fig. 5.1c) and 346 for $|\psi^-_{j_1j_2}\rangle$ (solid curve in Fig. 5.1c). For the other two cases (see Fig. 5.1a and Fig. 5.1b) with higher collision energy, we find that TCS is insensitive to the quantum entanglement in the incoming state.

Note also that the probability of the direct transition $j_1 = 2, j_2 = 0 \rightarrow j'_1 = 2, j'_2 = 0$ is much larger than that of the exchange transition $j_1 = 0, j_2 = 2 \rightarrow j'_1 = 2, j'_2 = 0$. Thus there is negligible effect from the quantum interference between the scattering amplitudes $T^{JM}(20002|20002)$ and $T^{JM}(20002|00202)$ [see Eq. (5.13)]. As a result, quantum features observed in Fig. 5.1 are due entirely to the first quantum
effect we identified in the previous section, i.e., the partial-wave parity selection effect.

Figure 5.2: The $\theta$ dependence of the inelastic differential cross section summed over the final state quantum numbers $m'_1$ and $m'_2$ and integrated over $\phi$. The scattering system is \textit{para} $H_2 + \text{para} H_2$, and the collision energy is (a) 400 cm$^{-1}$, (b) 40 cm$^{-1}$, and (c) 4 cm$^{-1}$. Dashed and solid lines are for the incoming free entangled states $|\psi_{j_1j_2}^+\rangle$ and $|\psi_{j_1j_2}^-\rangle$ [see Eq. (5.19)], respectively. $j_1 = 4$, $j_2 = 0$, $j'_1 = j'_2 = 2$.

In Fig. 5.2, we show inelastic DCS summed over $m'_1$ and $m'_2$ and integrated over the angle $\phi$, for the incoming entangled states $|\psi_{j_1j_2}^{\pm}\rangle$, with initial-state quantum numbers $j_1 = 4$, $j_2 = 0$, and final-state quantum numbers $j'_1 = j'_2 = 2$. The collision energy $E_k$ equals 400 cm$^{-1}$ in Fig. 5.2a, 40 cm$^{-1}$ in Fig. 5.2b, and 4 cm$^{-1}$ in Fig.
5.2c. First of all, for these initial-state and final-state channels, the $T$-matrix elements responsible for the cross sections are $T^{JM}(2020j''_{12}|40004l)$ and $T^{JM}(2020j''_{12}|00404l)$ [see Eq. (5.13)]. A careful examination of these $T$-matrix elements shows that

$$T^{JM}(2020j''_{12}|40004l) = (-1)^{j_1}T^{JM}(2020j''_{12}|00404l).$$ (5.20)

This suggests that the second quantum effect, described by Eq. (5.13), i.e., quantum interference between $T^{JM}(2020j''_{12}|40004l)$ and $T^{JM}(2020j''_{12}|00404l)$, becomes also important. Indeed, our choice of the final-state channel was motivated by the fact that for $j'_1 \neq j'_2$, the second quantum effect would be as insignificant as the elastic case. From Fig. 5.2, it is seen that, different incoming entangled states cause different oscillation patterns of DCS, leading to large differences in DCS for fixed scattering angle (e.g., for $\theta$ close to 0 or $\pi$ in Fig. 5.2b and Fig. 5.2c, and for $\theta$ around $\pi/2$ in Fig. 5.2b). Comparing Fig. 5.2a with Fig. 5.2b and Fig. 5.2c, one sees that in the highest collision energy case, quantum effects are least significant. This trend is similar to the elastic scattering case, and should also be understood via Eq. (5.13).

For the inelastic scattering case considered here, using Eqs. (5.14) and (5.20), Eq. (5.13) can be further reduced to

$$f_\pm(\hat{R}) = \frac{1}{\sqrt{2}\sqrt{k\kappa}} \sum_{j_{12}^m} \sqrt{2l+1}(-1)^n Y_{l+2n}(-m_{12}^m)(\hat{R}) C_{j_0}^{j_0} C_{0040}^{j_0} C_{2m_{12}^m}^{j_0}$$
$$\times C_{4000}^{j_0}[1 \pm (-1)^{j_1}T^{J0}(2020j_{12}(l+2n)|40004l)[1 + (-1)^{j'_1+j'_2}],$$ (5.21)

where $2n = l' - l$. Clearly, as the collision energy increases, the constructive or destructive interference between $T^{J0}(2020j_{12}|40004l)$ and $T^{J0}(2020j_{12}|00404l)$ tends to be washed out because in Eq. (5.21) the sum over a wide range of $n$ also includes
the oscillating factor \((-1)^n\). Further, Eq. (5.21) shows that, quantum interference between \(T^{\text{el}}(2020j'_{12}l'|000404l)\) and \(T^{\text{el}}(2020j'_{12}l'|0040404l)\) can also be interpreted as a selection rule imposed on the quantum number \(j'_{12}\): for the incoming entangled state \(|\psi_{\text{el}}^+\rangle\) [see Eq. (5.19)], only even incoming partial waves contribute and \(j'_{12}\) is further selected to be even; whereas for the incoming entangled state \(|\psi_{\text{el}}^-\rangle\) [see Eq. (5.19)], only odd incoming partial waves contribute and \(j'_{12}\) is further selected to be odd. This is consistent with the fact that the outgoing state is still made up of two indistinguishable molecules, with the same molecular state \((j'_1 = j'_2 = 2)\).

The case in Fig. 5.2c is worthy of further discussion. In this case one sees that DCS for \(|\psi_{j_{12},j'_{12}}^-\rangle\) (solid curve) is systematically smaller than that for \(|\psi_{j_{12},j'_{12}}^+\rangle\) (dashed curve), for almost the entire range of the scattering angle. This leads to significant difference in total inelastic cross section: TCS (in square angstrom) is 0.057 for \(|\psi_{j_{12},j'_{12}}^+\rangle\) and 0.032 for \(|\psi_{j_{12},j'_{12}}^-\rangle\). Thus, as in elastic scattering, inelastic scattering is also sensitive to the quantum phase embedded in the incoming entangled molecular state.

### 5.3.3 Ultracold molecular collisions

Encouraged by the results for \(E_k > 5\) K, we now investigate the role of entangled molecular states for ultracold collisions. Ultracold molecular scattering is a new and exciting area of molecular physics, where many interesting quantum effects occur [20, 21]. Understanding ultracold molecular collisions is also crucial to realize molecular Bose-Einstein condensates [22].

The advantage of considering ultracold collisions is that the scattering can
be dominated by very few partial waves. This feature should allow for tremendous new opportunities in manipulating molecular collisions [23]. Recalling that entangled molecular states as the incoming asymptotic states impose parity restrictions on the partial waves [see Eq. (5.13)], one naturally speculates that quantum entanglement could become even more important in ultracold collisions. For example, consider the zero collision energy limit. For usual long range potentials, only S-wave \((l = 0)\) partial wave) could contribute to cross sections [24]. Therefore, if S-wave scattering is selected by molecular entanglement, we have enhanced nonzero cross sections; and if it is not allowed due to molecular entanglement, there is complete suppression of molecular scattering. That is, in the completely suppressed elastic scattering case, all the scattering would be in the forward direction; and in the completely suppressed inelastic scattering case, there would be no scattering in all directions.

It is therefore important to confirm such theoretical considerations, and to determine how cold the collisions should be in order to experimentally observe such extreme quantum effects. Since MOLSCAT has no difficulty in computing \(S\) matrix elements for ultracold collisions, we employ it again to extend our calculations to the ultracold region, with \(E_k\) ranging from 0.4 cm\(^{-1}\) to 0.0004 cm\(^{-1}\). The computations are generally easier because at such ultracold collision energies the maximum angular momentum can be cut off at a small value [25].

In Fig. 5.3 we present the elastic DCS for two ultracold collision energy, with the incoming asymptotic states given by \(|\psi_{j_1j_2}^\pm\rangle\) \((j_1 = 2, j_2 = 0)\). Results in Fig. 5.3 are parallel to those in Fig. 5.1. The only difference is that here \(E_k\) equals 0.4
cm$^{-1}$ and 0.04 cm$^{-1}$ in Fig. 5.3a and Fig. 5.3b, respectively. It is seen that, in both cases the DCS for $|\psi_{j_1,j_2}^+\rangle$ (dashed line) displays fairly uniform behavior. This suggests that $S$-wave is already dominating the elastic scattering. Thus, preventing $S$-wave scattering via entanglement will lead to a dramatic decrease of cross sections. Indeed, in Fig. 5.3b, one sees that elastic scattering is almost totally suppressed for the case of $|\psi_{j_1,j_2}^-\rangle$.

Figure 5.3: Same as Fig. 5.1 except that elastic collision here is ultracold. The collision energy is (a) 0.4 cm$^{-1}$, and (b) 0.04 cm$^{-1}$.

In Fig. 5.4 we examine ultracold inelastic scattering. As in Fig. 5.2, we choose $|\psi_{j_1,j_2}^\pm\rangle$ $(j_1 = 4, j_2 = 0)$ as the incoming asymptotic state and examine the transitions to the channel of $j'_1 = 2, j'_2 = 2$. Results shown here mimic those in Fig. 5.2, but with $E_k$ equal to 0.04 cm$^{-1}$ and 0.0004 cm$^{-1}$ in Fig. 5.4a and Fig. 5.4b, respectively. In contrast to the elastic scattering case presented in Fig. 5.3b, Fig. 5.4a shows that $E_k = 0.04$ cm$^{-1}$ is not cold enough to guarantee the extreme quantum effects due to the partial wave parity restriction imposed by entanglement. That is,
the difference in the DCS between $|\psi_{j_1j_2}^+\rangle$ and $|\psi_{j_1j_2}^-\rangle$ in Fig. 5.4a is not much more significant than that in Fig. 5.2c (where the collision energy is 100 times larger). This is not totally unexpected since inelastic scattering is more complicated than elastic scattering, and quantum features observed here are still a combination of the two quantum effects discussed above. In Fig. 5.4b we present the results for a lowest $E_k$ equal to 0.0004 cm$^{-1}$. Clearly, in this case, inelastic scattering for $|\psi_{j_1j_2}^-\rangle$ is almost completely suppressed, whereas inelastic scattering for $|\psi_{j_1j_2}^+\rangle$ remains significant.

![Graphs](image)

Figure 5.4: Same as Fig. 5.2 except that inelastic collision here is ultracold. The collision energy is (a) 0.04 cm$^{-1}$, and (b) 0.0004 cm$^{-1}$.

Thus we have demonstrated that quantum entanglement in the incoming asymptotic state can drastically alter ultracold collisions. To our knowledge, this is the first study on the important role of molecular entanglement in ultracold collisions. As further discussed in the next section, quantum effects shown in Fig. 5.3 and Fig. 5.4 imply that ultracold molecular collisions can be dramatically controlled by introducing different coherence characteristics from laser fields into the scattering system.
5.4 Discussion

5.4.1 Experimental realization

In the previous section we have computationally shown that quantum molecular entanglement can play an important role in both low-energy and ultracold scattering problems. We now consider the possibility of experimentally realizing this result. First, note that the creation of quantum entanglement using atomic systems has been experimentally realized [26]. Further, mass production of entangled atomic beams seems to be within reach of today’s technology [27]. We thus expect that realizing the entangled molecular states $|\psi((j_1 m_1 v_1, j_2 m_2 v_2)) \rangle_\pm$ is not far from reality.

More significantly, below we show that, even without the preparation of such entangled molecular states, their effects can still be experimentally observed. This being the case, our results in the previous section essentially represent phase control results one can expect in the laboratory.

The idea is very simple. Suppose that prior to the scattering the projectile is prepared in a superposition state $\cos(\alpha_1) |j_1 m_1 v_1 \rangle + \sin(\alpha_1) \exp(i\beta_1) |j_2 m_2 v_2 \rangle$, and the target is prepared in a similar superposition state $\cos(\alpha_2) |j_1 m_1 v_1 \rangle + \sin(\alpha_2) \exp(i\beta_2) |j_2 m_2 v_2 \rangle$ [9]. Then the total internal wavefunction is a direct product state $|\psi^{dp} \rangle$ of these two superposition states rather than an entangled molecular state. Nevertheless, $|\psi^{dp} \rangle$ can be expressed in terms of an entangled state plus two additional components, i.e.,

$$
|\psi^{dp} \rangle = y \exp(i\beta_2) |\psi(j_1 m_1 v_1, j_2 m_2 v_2)\rangle_{\pm} + \cos(\alpha_1) \cos(\alpha_2) |j_1 m_1 v_1 \rangle \otimes |j_1 m_1 v_1 \rangle 
+ \sin(\alpha_1) \sin(\alpha_2) \exp[i(\beta_1 + \beta_2)] |j_2 m_2 v_2 \rangle \otimes |j_2 m_2 v_2 \rangle,
$$

(5.22)
where the entangled state component $|\psi(j_1m_1v_1j_2m_2v_2)\rangle_{\alpha\beta}$ is given by Eq. (5.8),

$$y = \sqrt{\cos^2(\alpha_1) \sin^2(\alpha_2) + \sin^2(\alpha_1) \cos^2(\alpha_2)},$$

$$\alpha = \cos^{-1}[\cos(\alpha_1) \sin(\alpha_2)/y],$$

$$\beta = \beta_1 - \beta_2,$$  

(5.23)

and the two additional components $|j_1m_1v_1\rangle \otimes |j_1m_1v_1\rangle$ and $|j_2m_2v_2\rangle \otimes |j_2m_2v_2\rangle$ can be called as “satellite” states.

Note that the energy of the “satellite” states in Eq. (5.22) is usually either lower or higher than that of $|\psi(j_1m_1v_1j_2m_2v_2)\rangle_\pm$. Thus, if we restrict our measurement to a particular total energy of the product, which is admittedly difficult, then contributions of the “satellite” states are guaranteed to be zero due to energy conservation, i.e., the scattering problem is essentially the same as that for an initially entangled molecular state.

Alternatively, by studying some special product-state channels without having to specify their respective total energy, we may also find that contributions from the entangled molecular state dominate over that of the “satellite” states. That is, for some channels characterized by $j_1', v_1', j_2', v_2'$, the scattering amplitude for the initial direct product state $|\psi^{\text{dir}}\rangle$ could be almost identical with that for the unnormalized entangled state $\gamma \exp(i\beta_2)|\psi(j_1m_1v_1j_2m_2v_2)\rangle_{\alpha\beta}$. For these cases supported by the examples below, we have

$$\frac{d\sigma}{d\Omega}|_{\psi^{\text{dir}}} \approx y^2 \frac{d\sigma}{d\Omega}|_{\psi(j_1m_1v_1j_2m_2v_2)_{\alpha\beta}},$$  

(5.24)

where $\frac{d\sigma}{d\Omega}|_{\psi}$ represents the differential cross section summed over $m_1'$ and $m_2'$ and
integrated over $\phi$ for the incoming state $|\psi\rangle$.

Indeed, Eq. (5.24) works very well for the computational examples shown in Figs. 5.1, 5.2, 5.3 and 5.4. Consider first the elastic scattering case ($j_1 = 2, j_2 = 0, v_1 = v_2 = 0, m_1 = m_2 = 0, v'_1 = v'_2 = 0, j'_1 = 2, j'_2 = 0$). For given translational energy, the scattering amplitude of the transition $j_1 = 2, j_2 = 2 \rightarrow j'_1 = 2, j'_2 = 0$ due to the first “satellite” state is orders of magnitude smaller than that for the transition $j_1 = 0, j_2 = 0 \rightarrow j'_1 = 2, j'_2 = 0$. Similarly, the probability for the transition $j_1 = 0, j_2 = 0 \rightarrow j'_1 = 2, j'_2 = 0$ due to the second “satellite” state is also negligible (indeed, it is exactly zero for $E_k < 364.8 \text{ cm}^{-1}$). For the inelastic scattering case ($j_1 = 4, j_2 = 0, v_1 = v_2 = 0, m_1 = m_2 = 0, v'_1 = v'_2 = 0, j'_1 = 2, j'_2 = 2$), the scattering amplitude due to the first “satellite” state corresponds to the deexcitation transition $j_1 = 4, j_2 = 4 \rightarrow j'_1 = 2, j'_2 = 2$. The probability of such deexcitation process is tiny due to the large rotational energy mismatch between the initial and final channels. The second “satellite” state has no contribution to the product channel $(j'_1 = 2, j'_2 = 2)$ for $E_k < 729.6 \text{ cm}^{-1}$.

More specifically, if $\alpha_1 = \alpha_2 = \pi/4$, Eq. (5.24) reduces into

$$\frac{d\sigma}{d\Omega}|_{\psi^{*}\sigma} \approx \frac{1}{2} \frac{d\sigma}{d\Omega}|_{\psi^{*}_{1,2}}, \quad \beta_1 - \beta_2 = 2n\pi;$$
$$\frac{d\sigma}{d\Omega}|_{\psi^{*}\sigma} \approx \frac{1}{2} \frac{d\sigma}{d\Omega}|_{\psi^{*}_{1,2}}, \quad \beta_1 - \beta_2 = (2n + 1)\pi. \quad (5.25)$$

The implication of Eq. (5.25) is worthy of further discussion in connection with the previous results. Let’s take ultracold collisions as an example. The elastic scattering results in Fig. 5.3b indicate that, $\beta_1 - \beta_2$ can enhance or completely suppress the yield of the channel $(j'_1 = 2, j'_2 = 0)$ in directions other than that of the incident momentum.
Likewise, the inelastic scattering results in Fig. 5.4b suggest that, manipulating the value of $\beta_1 - \beta_2$ can enhance or shut off the channel ($j'_1 = 2, j'_2 = 2$).

Finally, we note that STIRAP [28] may provide a natural choice for preparing the superposition states for both the projectile and the target molecules. A particularly promising version is the tripod-STIRAP scheme [29]. In that scheme, an additional laser couples the intermediate level (through which the initial and final state are radiatively connected via the pump and Stokes-laser) with another unpopulated state. Depending on the overlap in time of the interaction of the additional laser with that of the pump and Stokes-laser, any coherent superposition state of the initial and final state can be created. Thus, by introducing different coherence characteristics from laser fields into the scattering system, we can control $\beta_1 - \beta_2$ and thus select the form of the entangled state component of $|\psi_{dp}\rangle$, giving rise to phase control over differential and total cross sections.

### 5.4.2 Extension to vibration-vibration relaxation

Our theoretical formulation in this chapter does not distinguish between rotational and vibrational motions. This implies that we can also utilize the type (b) entanglement [see Eq. (5.10)] to realize phase control of vibrational energy transfer in the scattering of $\text{para } H_2 + \text{para } H_2$. Unfortunately, exact numerical treatment of such problems is still unavailable. A typical approximate method to deal with full dimensional diatom-diatom nonreactive scattering is the Sudden Approximation [30], which assumes that molecular rotational motions are slow compared with vibrational
and translational motions. This approximation will probably not be useful for light molecules such as $H_2$, particularly when the collision energy is quite low. A semiclassical treatment of rovibrational energy transfer is also available [31], with which the role of quantum phases in molecular scattering has not been explored. As such, it should be of theoretical interest to demonstrate phase control of vibration-vibration relaxation using some simplified model of diatom-diatom scattering.

To this end we carried out a study on quantum effects of entangled vibrational states using a three-dimensional model of vibration-vibration relaxation in the \textit{para} $H_2 + \text{para} H_2$ scattering. In particular, the three-dimensional model assumes that both the projectile and target \textit{para} $H_2$ molecules point at a fixed direction during the entire scattering process. Thus, molecular rotational motions here are frozen by construction. The scattering problem is then computationally solved by wavepacket propagation. In doing so we employ a time-dependent approach with real $L^2$ eigenfunctions with damping [32, 33].

Figure 5.5 displays the transition probability of the channel $(v'_1 = 1, v'_2 = 1)$ for three initial entangled vibrational states characterized by

$$\cos(\alpha)|v_1 = 0\rangle \otimes |v_2 = 2\rangle + \exp(i\beta) \sin(\alpha)|v_1 = 2\rangle \otimes |v_2 = 0\rangle \quad (5.26)$$

with $\alpha = \pi/4$, $\beta = 0$, $\pi/2$, and $\pi$, respectively. Note that here we do not have rotational quantum numbers since the rotational degrees of freedom are neglected. It is seen in Fig. 5.5 that the quantum phase $\beta$ embedded in the initial entangled vibrational states is also important in vibration-vibration relaxation. This result further stimulates full-dimensional studies of coherent control of nonreactive scattering.
of para $H_2$ and para $H_2$.

Figure 5.5: The inelastic transition probability of the channel ($v'_1 = 1, v'_2 = 1$) versus the collision energy in the para $H_2 +$ para $H_2$ scattering, for three incoming entangled vibrational states described by Eq. (5.26). $\alpha = \pi/4, \beta = 0$ (top curve), $\pi/2$ (middle curve) and $\pi$ (bottom curve). The internuclear axis of each para $H_2$ molecule is assumed to be parallel to the incident velocity during the scattering process.

5.4.3 Extension to other scattering systems

It is also important to extend our detailed studies to other molecular systems. Let's first recall that, our theoretical formulation [see Eq. (5.13)] assumes that both nuclear and electronic spins of the scattering molecules are zero. This assumption is essential to simplify our theoretical considerations, although in principle it is not essential to control. Clearly, it is of both theoretical and experimental interest to have several
alternatives to $\text{para } H_2$, which also have zero nuclear spin and zero electronic spin. For example, we note that both ground-state $C_2$ and $CO$ molecules are such candidates. Thus, instead of studying the scattering of $\text{para } H_2 + \text{para } H_2$, we can directly apply our theory to the scattering of $C_2 + C_2$ and $CO + CO$. In particular, vibrational energy transfer in $CO + CO$ is an important topic relevant to laser physics. Our results in this chapter suggest that quantum phases in low energy $CO + CO$ scattering can play an interesting role in vibration-vibration relaxation.

For molecules with nonzero nuclear spin or electronic spin, the extension is also straightforward. We give a qualitative picture here. For such molecules, one of the two quantum effects due to entangled molecular states, i.e., the parity selection of the incoming partial waves, may be substantially destroyed when either the nuclear or electronic spin is unpolarized. To see this note that the spin degree of freedom can introduce additional permutation symmetry into the system. Thus entangled rovibrational states such as $|\psi(j_1 v_1, l_1 m_1, j_2 m_2, v_2)\rangle_\pm$ are not sufficient to select the partial waves. For instance, for two unpolarized identical molecules with total integer nuclear spin $I_N$, the permutation symmetry of all other degrees of freedom has to be $+1$ with the probability $(I_N + 1)/(2I_N + 1)$ or $-1$ with the probability $(I_N)/(2I_N + 1)$ [14]. When $I_N$ is large, two permutation symmetries of all other degrees of freedom are equally allowed. As a result, the permutation symmetry induced by entanglement of molecular rovibrational motions can only have a negligible effect on differential or total cross sections. However, as is indicated in Ref. [9], one quantum effect still survives, i.e., quantum interference between transition amplitudes $T^{JM}(j'_1 v'_1 j'_2 v'_2 j'_2 l'_{12}|j_1 v_1 j_2 v_2 j_2 l_{12})$. 
and $T^{JM}(j_1'^{v_1'}j_2'^{v_2'}j_1^{j_1'}j_2^{j_2'}\mid j_2v_2j_1v_1J_{12})$. Establishing the magnitude of this effect will require a considerable extension of our computational approach.

5.5 Summary

In summary, we have studied coherent control of the elastic and inelastic scattering of identical molecules. Throughout this chapter we have stressed the important role played by quantum entanglement of rovibrational motions. We have revealed two quantum effects that can be induced by using entangled molecular states as the incoming asymptotic state. Such quantum effects are utilized to demonstrate the possibility of phase control of both differential and total cross sections. Our main computational results are for the scattering of $\text{para } H_2 + \text{para } H_2$ with frozen vibrational motions. The results can be readily extended to vibration-vibration relaxation phenomena and other molecular systems. We believe that this study could strongly stimulate both experimental and full-dimensional computational studies of phase control of diatom-diatom scattering.
Bibliography


[24] Even in the zero collision energy limit, it is still possible that many partial waves contribute to the cross section, e.g., when the interaction potential approaches zero as $1/R^3$ [4].

[25] In the close-coupling calculations, we find that, even though the total cross section has quickly converged, substantially increasing the cut-off value of the total angular momentum may cause some artificial oscillations in the differential cross sections for $\theta$ very close to 0 or $\pi$.


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[33] Direct wavepacket propagation is a powerful tool to extract scattering information. Wavepacket propagation would be formally and easily done if the scattering eigenfunction and eigenenergy in the continuum are known. The central idea of the approach in Ref. [32] is to replace the non-$L^2$ scattering eigenstates by real $L^2$ states which can be numerically treated. To do this the continuum is discretized in a box and real eigenstates are then obtained. The wavepacket evolution can then be carried out almost trivially. To avoid unphysical reflections at the grid edges, the wavepacket is damped at each time step. In obtaining eigenfunctions, potential-optimized discrete variable representation is employed, and the truncation/recoupling technique is essential for efficient calculations.
PART III

CORRESPONDENCE AND DECOHERENCE
IN CHAOTIC MOLECULAR DYNAMICS
Chapter 6

Chaos and Correspondence in
Distribution Functions
Chapter Summary:

Quantum classical correspondence in conservative and strongly chaotic Hamiltonian systems is examined using a structure measure for quantal and classical distribution functions. During the early stage of time evolution, quantum classical agreement is demonstrated by detailed numerical computations together with analytical results for zero time. With the increase of time, quantum classical correspondence is shown to break down rapidly. The corresponding break regime is understood, both analytically and numerically, by revealing the origin of quantum classical discrepancy in the development of phase space structure. Finally, the relevance of this break regime to correspondence in low order statistical moments is investigated. The results shed considerable light on quantum-classical correspondence.
6.1 Introduction

The study of quantum dynamics of classically chaotic systems has been a subject of considerable interest for nearly two decades. Chaos, usually defined as the exponential sensitivity of phase space trajectories to slight changes of the initial conditions, resists direct translation to the Hilbert space since there do not exist well-defined trajectories within the conventional interpretation of quantum mechanics. Hence, many studies on quantum chaos in the literature have been dedicated to the relatively modest study of quantum manifestations of classical chaos [1, 2]. Actual quantum-classical correspondence (QCC) in classical chaotic systems is still one of the outstanding issues in quantum theory.

Intuitively, QCC would not be an issue if quantum dynamics could also be formulated in terms of trajectories. This intuition has led to several new trajectory-based approaches to quantum chaos, e.g., the Bohm's dynamics approach [3, 4], the continuous wavefunction collapse approach [5, 6] (this approach will be discussed in detail in Chap. 7), etc. Although these methods usually involve unfamiliar interpretations of quantum mechanics, results available to date have offered novel perspectives into QCC in classically chaotic systems.

An alternative approach is to abandon the trajectory-based perspective of chaos, and focus on other essential characteristics of classical chaos which may have counterparts in quantum mechanics. As proposed recently, this seems possible if QCC is understood within the framework of the ensemble interpretation of quantum mechanics [7, 8]. More specifically, in this approach classical chaos is identified as
an exponential increase of the structure of classical distribution functions, and quantum chaos is naturally defined as an exponential increase of the structure of quantal distribution functions, e.g., of Wigner functions.

The distribution function strategy emphasizes that the classical counterpart of a quantum state is not a particular classical trajectory, but a classical ensemble instead. In addition to previous numerical studies [9, 10], a recent formal QCC theory [11] on the eigenfunctions and eigenvalues of the Liouville super-operator strongly supports the distribution function approach. As one of its advantages in the study of QCC, the distribution function strategy is also of considerable fundamental interest to the understanding of noise effects on quantum and classical ensembles. This is because the structure of classical distribution functions could determine the entropy production rate when the classical ensemble is subject to an environment, whereas the structure of quantal distribution functions is related to the decoherence rate when the quantum system is open [12, 13].

In this chapter, the distribution function approach to QCC in classically chaotic systems is carefully examined and substantially extended. The extension is from one-dimensional chaotic systems in previous work [7, 8] to two-dimensional conservative systems, from the special case of uniform dynamical instabilities to the general case of nonuniform stretching and folding rates fluctuating with time and phase space location. Indeed, armed with a measure of the structure of distribution functions, it becomes possible to quantitatively investigate the similarities and differences between quantal and classical distribution functions in a broad class of smooth, conservative
and strongly chaotic Hamiltonian systems. In particular, this chapter displays (1) the rich transient behavior of distribution functions shared by quantum and classical dynamics before a QCC break time scale $t_b$, a quantity which depends upon the logarithm of $\hbar$, (2) a simple but enlightening description of the break regime of QCC in the time development of phase space structure, and (3) interesting QCC in low order statistical moments during a complex relaxation process with a time scale much larger than $t_b$.

The model calculations in this chapter are based on a very strongly chaotic system: the quartic oscillator model [14]. The Hamiltonian is given by,

$$H(q_1, p_1, p_2) = \frac{p_1^2}{2} + \frac{p_2^2}{2} + \frac{\alpha}{2} q_1^2 q_2^2 + \frac{\beta}{4} (q_1^4 + q_2^4).$$  \hspace{1cm} (6.1)

When $\alpha = \beta$ or $3\beta$, this system is completely integrable. For very large values of $\alpha/\beta$ the system is strongly chaotic, with the characteristic Lyapunov exponent being an order of magnitude larger than that of other conservative chaotic systems, e.g., the Henon-Heiles system. All the variables in Eq. (6.1) are unitless scaled variables [15].

This chapter is organized as follows. Section 6.2 briefly reviews the distribution function approach to QCC in chaotic systems. Special emphasis is put on a structure measure of classical and quantal distribution functions, and on our definitions of classical and quantal finite-time Lyapunov exponents. In section 6.3, QCC during the early stage of time evolution is extensively studied for initially positive-definite Wigner functions in their most general form. In section 6.4, a simple analytical understanding of the break regime of QCC is presented, followed by supporting numerical results. In section 6.5, QCC in some low order statistical moments for much larger time scales
is considered. A brief summary is given in section 6.6.

6.2 Lyapunov Exponents in Distribution Function Dynamics

6.2.1 Classical distribution function dynamics

Classical chaos is usually defined as the extreme sensitivity to slight changes in initial conditions. Quantitatively, it is described by a positive maximum Lyapunov exponent or by the Kolomogorov entropy. Consider a conservative Hamiltonian system with two degrees of freedom with dimensionless canonical variables $q_1, q_2, p_1, p_2$. A phase space point is characterized by a 4-dimensional column vector $\gamma \equiv (q_1, q_2, p_1, p_2)^T$.

For brevity let us introduce the antisymmetric matrix $J = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$ where 0 and 1 are $2 \times 2$ zero and unit matrices, respectively. The canonical equations of motion (i.e., Hamilton's equations) now read as $\dot{\gamma} = J \frac{\partial H}{\partial \gamma}$. The sensitivity of a trajectory to its initial conditions is described by the stability matrix $M_{ij}(\gamma(0), t) \equiv \frac{\partial \gamma_i(0)}{\partial \gamma_j(0)}$. The maximal Lyapunov exponent $\lambda$ is given by

$$\lim_{t \to \infty} \frac{1}{t} \ln(|M(\gamma(0), t)\eta|) = \lambda(\gamma(0)), \tag{6.2}$$

where $\eta$ is a vector in the tangent space. The stability matrix $M$ is symplectic and its time evolution is governed by the differential equation

$$\dot{M} = J \frac{\partial^2 H}{\partial \gamma^2} M, \tag{6.3}$$
with

\[ M(0) = 1. \]  \hspace{1cm} (6.4)

A simple application of the Liouville theorem leads to an expression of Lyapunov exponents in terms of distribution function dynamics [7, 8]. Specifically, assume a well behaved probability distribution \( \rho_t \) and an arbitrary infinitesimal vector \( \xi \). From the incompressibility of the Liouville density function, one has

\[ \rho_t(\gamma(t)) + \nabla \rho_t(\gamma(t)) M \xi = \rho_0(\gamma(0)) + \nabla \rho_0(\gamma(0)) \xi. \]  \hspace{1cm} (6.5)

Further, using \( J^2 = -1 \), and \( JM^\dagger J = -M^{-1} \), one obtains

\[ MJ \nabla \rho_0(\gamma(0)) = J \nabla \rho_t(\gamma(t)). \]  \hspace{1cm} (6.6)

Substituting Eq. (6.6) into Eq. (6.2) yields

\[ \lambda(\gamma(0), t) = \lim_{t \to \infty} \frac{1}{t} \ln |J \nabla \rho_t(\gamma(t))| = \lim_{t \to \infty} \frac{1}{t} \ln |\nabla \rho_t(\gamma(t))|. \]  \hspace{1cm} (6.7)

In accord with Ref. [8], we define a particular ensemble average of the gradients of distribution functions as \( \chi_{2e} \), i.e.,

\[ \chi_{2e}(t) \equiv \left[ \frac{\int |\nabla \rho_t(\gamma)|^2 d\gamma}{\int \rho_t^2(\gamma) d\gamma} \right]^{1/2} = \left[ \frac{\int \rho_t(\gamma) \nabla^2 \rho_t(\gamma) d\gamma}{\int \rho_t^2(\gamma) d\gamma} \right]^{1/2}. \]  \hspace{1cm} (6.8)

The physical significance of \( \chi_{2e}(t) \) becomes apparent when one considers the Fourier space of the distribution function. That is, suppose \( \rho_t(\gamma) = \frac{1}{(2\pi)^2} \int dk \exp(2\pi i\mathbf{k} \cdot \gamma) \rho_t(\mathbf{k}) \), where \( \rho_t(\mathbf{k}) \) denotes the Fourier component evaluated at the 4-dimensional
wave vector \( k \). Then one has

\[
\chi_{2c}(t) = \frac{\int d\mathbf{k}^2 \rho_2(k)}{\int d\mathbf{k} \rho_1(k)^2}.
\]

(6.9)

Hence \( \chi_{2c} \) is the root-mean-square Fourier radius of the distribution function, thus serving as a measure of phase space structure. Combining Eqs. (6.6) and (6.8), one has

\[
\chi_{2c}(t) = \left[ \frac{1}{\int \rho_0(\gamma) d\gamma} \int |\mathbf{J}\mathbf{M}(\gamma, t)\mathbf{J} \nabla \rho_0(\gamma)|^2 d\gamma \right]^{1/2}.
\]

(6.10)

For completely integrable dynamics there exists a special set of generalized coordinates: action variables \( I_1, I_2 \) and angle variables \( \theta_1, \theta_2 \). In this representation, the Hamiltonian function depends only on the action variables which are constants of motion. For such cases, Eq. (6.3) has the simple solution

\[
\mathbf{M} = 1 + \mathbf{J} \frac{\partial^2 H}{\partial \gamma^2} t.
\]

(6.11)

Substituting this explicit time dependence of the stability matrix into Eq. (6.10), one obtains the limiting behavior of \( \chi_{2c} \) described by

\[
\lim_{t \to \infty} \frac{\chi_{2c}(t)}{t} = \left[ \frac{1}{\int \rho_0(\gamma) d\gamma} \int \left| \frac{\partial^2 H}{\partial \gamma^2} \mathbf{J} \nabla \rho_0(\gamma) \right|^2 d\gamma \right]^{1/2}.
\]

(6.12)

This says that for regular dynamics the structure of distribution functions, as measured by \( \chi_{2c} \), eventually shows a linear time dependence in the action-angle representation. In other canonical representations \( \chi_{2c}(t) \) may show a polynomial time dependence.

By contrast, for chaotic dynamics it was shown that \( [8] \)

\[
\lim_{t \to \infty} \frac{1}{t} \ln \chi_{2c}(t) = \lambda_2,
\]

(6.13)
where \( \lambda_2 \) is the so-called second order generalized maximal Lyapunov exponent. From Eq. (6.13) it is apparent that the root-mean-square Fourier radius of distribution functions increases, eventually, at an exponential rate of \( \lambda_2 \) for chaotic motions. Since a given resolution limit \( \delta \) corresponds to the inability to account for those Fourier modes larger than \( 1/\delta \), here a novel physical picture of chaos emerges: chaos is just a kind of exponential loss of accuracy or information encoded in the initial Fourier basis expansion of distribution functions.

By definition, the (generalized) Lyapunov exponent \( \lambda_2 \) is an asymptotic property. Thus, it can be referred to in the strict sense only when the time goes to infinity. By contrast, in bounded quantum systems, any quantum state will return to its initial state after a sufficiently long time, due to quantum recurrence. This characteristic of bounded quantum systems suggests that it is finite-time properties of classical chaotic dynamics that are of real interest to the study of QCC. Thus, it is important to analyze the transient dynamical behavior that is not addressed by classical Lyapunov exponents, such as the fluctuations of the degree of instability with time, the variations of the characteristic directions along which the system exhibits maximum or minimum finite-time sensitivity, etc. To this end it is necessary to introduce the concept of finite-time Lyapunov exponents. Equation (6.13) suggests that as a natural definition of finite-time Lyapunov exponents one could use the average exponential increase rate of \( \chi_{2e}(t) \) within a certain period. Specifically, classical finite-time Lyapunov exponents \( \lambda_{2e}(t) \) can be defined as

\[
\lambda_{2e}(t) = \frac{1}{t} \ln \frac{\chi_{2e}(t)}{\chi_{2e}(0)},
\]  
(6.14)
with its asymptotic value given by $\lambda_2$, i.e.,

$$\lim_{t \to +\infty} \lambda_{2c}(t) = \lambda_2.$$  \hspace{1cm} (6.15)

Further, using Eqs. (6.3), (6.4), and (6.10), one obtains

$$\lim_{t \to 0} \frac{d\chi_{2c}^2}{dt} = \frac{2}{\int \rho_0^2(\gamma) d\gamma} \int (\nabla \rho_0)^T \left( \frac{\partial^2 H}{\partial \gamma^2} \right) J(\nabla \rho_0) d\gamma.$$  \hspace{1cm} (6.16)

Substituting Eq. (6.16) into Eq. (6.14) gives the zero time limit of $\lambda_{2c}(t)$,

$$\lim_{t \to 0} \lambda_{2c}(t) = \frac{\int (\nabla \rho_0)^T \left( \frac{\partial^2 H}{\partial \gamma^2} \right) J(\nabla \rho_0) d\gamma}{\int |\nabla \rho_0|^2 d\gamma}.$$  \hspace{1cm} (6.17)

Clearly, $\lambda_{2c}(0)$ is seen to be the average of $\partial^2 H/\partial \gamma^2$ weighted by the gradients of the initial distribution function. It thus reflects the ensemble average of instantaneous instabilities, depending strongly on the shape and location of the initial distribution function. As will be seen in the next section, this further suggests very rich transient behavior in the time development of phase space structure.

### 6.2.2 Quantal analogue of classical Lyapunov exponents

From the ensemble point of view, QCC could be best understood by comparing the classical Liouville equation with the quantum von Neumann equation in the Wigner-Weyl representation. Consider a two-degree-of-freedom system $H = H(q_1, q_2, p_1, p_2)$. The quantum von Neumann equation in terms of the Wigner function $\rho^W$ is given by

$$\frac{\partial \rho^W}{\partial t} = \{H, \rho^W\} + \sum_{(l_1, l_2) > 1, \text{odd}} \frac{(\hbar)^{(l_1+l_2-1)}}{l_1! l_2!} \frac{\partial^{(l_1+l_2)} V(q_1, q_2)}{\partial q_1^{l_1} \partial q_2^{l_2}} \frac{\partial^{(l_1+l_2)} \rho^W}{\partial p_1^{l_1} \partial p_2^{l_2}},$$  \hspace{1cm} (6.18)

where the first term on the right hand side is the classical Poisson bracket, and the second term represents the sum over an infinite series of “quantum corrections”. 
CHAPTER 6. CHAOS AND CORRESPONDENCE...

Since the quantitative diagnostic for characterizing classical chaos using classical distribution functions has been introduced, it is straightforward to define the quantal analogue of classical Lyapunov exponents using quantal distribution functions.

Corresponding to Eq. (6.8) for defining $\chi_{2c}$, we define the measure $\chi_{2q}$ of quantal phase space structure as

$$\chi_{2q} = \left[ \frac{\int |\nabla \rho^w(\gamma)|^2 d\gamma}{\int (\rho^w)^2(\gamma) d\gamma} \right]^{1/2}. \quad (6.19)$$

Accordingly, in the Fourier space of quantal distribution function,

$$\chi_{2q}^2 = \frac{\int dk k^2 |\rho^w_2(k)|^2}{\int dk |\rho^w(k)|^2}. \quad (6.20)$$

Equation (6.20) indicates that, similar to $\chi_{2e}$, $\chi_{2q}$ is the root mean-square Fourier radius of the Wigner function. Moreover, finite-time Lyapunov exponents $\lambda_{2q}(t)$ for quantum distribution function dynamics can be defined by direct analogy to $\lambda_{2c}(t)$, i.e.,

$$\lambda_{2q}(t) = \frac{1}{t} \ln \frac{\chi_{2q}(t)}{\chi_{2q}(0)}. \quad (6.21)$$

Interestingly, $\chi_{2q}$ has an equivalent expression which is easier to handle. Suppose $\hat{\rho}$ is the density-matrix operator associated with the Wigner function $\rho^w$, and $\hat{\gamma}_i$ is the operator associated with the classical canonical variable $\gamma_i$. A simple calculation reveals that

$$\chi_{2q}^2 = 2 \sum_i \frac{Tr(\hat{\rho}^2 \dot{\hat{\gamma}}^2_i - \hat{\rho} \dot{\hat{\gamma}}_i \dot{\hat{\gamma}}_i)}{\hbar^2 Tr(\hat{\rho}^2)}. \quad (6.22)$$

Of particular interest is the pure state case. For pure states $\hat{\rho} = \hat{\rho}$, and consequently,

$$\chi_{2q}^2 = \frac{2}{\hbar^2} \sum_i (\langle \hat{\gamma}_i^2 \rangle - \langle \hat{\gamma}_i \rangle^2), \quad (6.23)$$
where \(\langle \cdot \rangle\) represents ensemble expectation values.

Consider now the quantum counterpart of Eq. (6.15). First note that Eq. (6.22) indicates that \(\chi_{2q}^2 \leq 2 \sum \text{Tr}(\rho^2 \tilde{\chi}^2) / \hbar^2 \text{Tr} \rho^2\). Thus, for any bounded Hamiltonian system, \(\chi_{2q}\) has an upper bound. As a result, for fixed \(\hbar\) and bounded systems,

\[
\lim_{t \to +\infty} \lambda_{2q}(t) = 0
\]

(6.24)

This reproduces the widely accepted result that bounded quantum systems cannot exhibit chaos in the strict sense.

Thus, as noted above, what is of interest to the study of QCC are the transient properties of \(\lambda_{2q}(t)\). In particular, one can easily obtain the quantum counterpart of Eq. (6.17) using Eqs. (6.18) and (6.19). That is,

\[
\lim_{t \to 0} \lambda_{2q}(t) = \frac{1}{\left| \nabla \rho_0^W \right|^2} \int \left( \nabla \rho_0^W \right)^T \left( \frac{\partial^2 H}{\partial \gamma^2} \right) \nabla \rho_0^W d\gamma + \int d\gamma \left( \nabla \rho_0^W \right)^T
\times \sum_{(i_1 + i_2) > 0, \text{odd}} \frac{A_{2i}}{i_1! i_2!} \left( \nabla \right)^{i_1 + i_2 + 1} V(q_{1}, q_{2}) \frac{\partial^{i_1 + i_2} \rho_0^W}{\partial q_{1}^i \partial q_{2}^j},
\]

(6.25)

where, obviously, the first term on the right hand side of Eq. (6.25) corresponds to the contribution from the classical Poisson bracket, and all other terms represent quantum "corrections".

Some aspects of the distribution function strategy have been applied to the Arnold-cat map model [7, 8], where the stretching and folding mechanism is uniform over the entire phase space. However, rich transient behavior of finite-time Lyapunov exponents, as implied in our derivation of the explicit state dependence of \(\lambda_{2q}(0)\) and \(\lambda_{2q}(0)\), has not been explored thus far. The next section is devoted to both analytical and numerical studies on this subject.
6.3 Short-time Correspondence

In this section we consider correspondence from the distribution function viewpoint at short times. To consider dynamics-induced quantum effects requires us to choose the initial quantal distribution function as classical as possible so that differences between classical and quantum dynamics are evidently from the dynamics. This suggests that initially the Wigner function should be chosen as positive definite, thus allowing the Wigner function to be interpreted as a function about classical probabilities. It is well known that for one-dimensional pure state dynamics the only positive-definite Wigner function is the Gaussian distribution function [16], which takes the following form,

$$\rho_{r, q, \tilde{q}, \tilde{p}}^{W} = \frac{1}{\pi \hbar} \exp\left[-\frac{2\eta^2}{\hbar^2} (p - \tilde{p})^2 - \frac{(q - \tilde{q})^2}{2\eta^2(1 - r^2)} + \frac{2r}{\hbar(1 - r^2)^{1/2}} (q - \tilde{q})(p - \tilde{p})\right], \quad (6.26)$$

where

$$\langle q \rangle = \tilde{q}, \quad \langle p \rangle = \tilde{p}, \quad \langle q^2 - \tilde{q}^2 \rangle = \eta^2,$$

$$\langle p^2 - \tilde{p}^2 \rangle = \frac{\hbar^2}{4\eta^2(1 - r^2)}, \quad \langle pq \rangle - \langle p \rangle \langle q \rangle = \frac{\hbar r}{2(1 - r^2)^{1/2}}. \quad (6.27)$$

This Wigner function in the Gaussian form corresponds to the so-called correlated coherent states in general [17], whose coordinate representation is given by

$$\Psi(q) = \frac{1}{(2\pi \eta^2)^{1/4}} \exp\left[-\frac{q^2}{4\eta^2} (1 - \frac{ir}{(1 - r^2)^{1/2}}) + \frac{\alpha x}{\eta} - \frac{1}{2} (\alpha^2 + |\alpha|^2)\right]. \quad (6.28)$$

In particular, for the case of $r = 0$, $\langle q^2 - \tilde{q}^2 \rangle \langle p^2 - \tilde{p}^2 \rangle = \hbar^2/4$, corresponding to the minimum-uncertainty-product state, which is also known as “Glauber coherent state” or simply “coherent state”. 
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For a two-degree-of-freedom system one would naturally extend one-dimensional correlated coherent states to two-dimensional ones. The initial quantal distribution function \( \rho_0^W \) and classical distribution function \( \rho_0 \) are thus chosen as the following,

\[
\rho_0^W = \rho_0 = \rho_{r_1, m_1, \vec{q}_1} \otimes \rho_{r_2, m_2, \vec{q}_2}.
\]

(6.29)

Substituting this initial state into Eq. (6.17) and approximating the average of the derivatives of \( V(q_1, q_2) \) as the derivative evaluated at the centroid of the Gaussian distribution, one gets

\[
\lim_{t \to 0} \lambda_{2c}(t) = \frac{1}{\sum_{i=1,2}[2\eta_i^2 + \frac{\lambda^2}{2(1-r_i^2)\eta_i^2}] \sum_{i=1,2} \left[ \frac{\eta_i}{(1-r_i^2)^{1/2}} \left( 1 - \frac{\partial^2 V(\vec{q}_1, \vec{q}_2)}{\partial q_i^2} \right) \right]}
\]

(6.30)

Clearly, \( \lambda_{2c}(0) \) depends strongly on both the shape parameters \( r_1, r_2 \) and the phase space locations of the initial distribution function. Equation (6.30) thus analytically demonstrates the spatial dependence and state-shape dependence of classical finite-time Lyapunov exponents \( \lambda_{2c}(t) \). Two special situations are worth more discussions. First, for the minimum-uncertainty-product state \( (r_1 = r_2 = 0) \), i.e., the 2-dimensional Glauber coherent state) which is commonly used as initial preparations in QCC studies, one obtains via Eq. (6.30) \( \lambda_{2c}(0) = 0 \). Second, when \( r_1 \cdot (1 - \partial^2 V(\vec{q}_1, \vec{q}_2)/\partial q_1^2) < 0 \), and/or \( r_2 \cdot (1 - \partial^2 V(\vec{q}_1, \vec{q}_2)/\partial q_2^2) < 0 \), it is possible that \( \lambda_{2c}(0) \) is negative. This indicates that, by choosing appropriate shape parameters \( r_1, r_2 \) and the central coordinates \( \vec{q}_1, \vec{q}_2 \) of the initial Gaussian ensemble, the folding mechanism associated with chaotic dynamics may initially dominate over the stretching mechanism, thus giving rise to a reduction in phase space structure.

The manifestations of the classical transient behavior of phase space structure
evolution in quantum dynamics can be examined by considering \( \chi_{2q}(t) \) in a similar manner. Specifically, substituting the initial positive-definite Wigner function (6.29) into Eq. (6.25), keeping the leading order term of quantum corrections in the quantum Liouville equation, one obtains the initial increase rate of \( \lambda_{2q}(0) \). Specifically,

\[
\lim_{t \to 0} \lambda_{2q}(t) = \lambda_{2c}(0) - \frac{1}{16\pi} \int \left[ \frac{\partial^4 V}{\partial q_1^2 \partial q_2^2} \right] \left[ \frac{r_2}{(1 - r_2^2)^{1/2}} \right]^2 dq_1 dq_2 \left[ \frac{r_1}{(1 - r_1^2)^{1/2}} \right]^2 dq_3 dq_4 \left[ \frac{r_2}{(1 - r_2^2)^{1/2}} \right]^2 \left[ \frac{r_1}{(1 - r_1^2)^{1/2}} \right]^2 \left[ \frac{\partial \rho_{2q}}{\partial r_1 \partial r_2} \right]^2.
\]

where for brevity some simple integrals have not been evaluated. Evidently, initial states with \((r_1 = r_2 = 0)\) gives \( \lambda_{2c}(0) = \lambda_{2q}(0) = 0 \). Thus, in this sense, the Glauber coherent state is identified as the most classical state of all correlated coherent states. For other kinds of initial states, the leading order quantum effect is seen to be proportional to \( \partial^4 V/\partial q_1^2 \partial q_2^2 \). After carrying out those integrals in Eq. (6.31), one further gets that \([\lambda_{2c}(0) - \lambda_{2q}(0)]\) is proportional to \( \hbar \). Therefore, for relatively large \( \hbar \), depending upon the sign of \( r_1 \) and \( r_2 \), \( \lambda_{2q}(t) \) can be significantly larger or smaller than \( \lambda_{2c}(t) \) at early times. In addition, if there is no quartic term in the potential \( \partial^4 V/\partial q_1^2 \partial q_2^2 = 0 \), e.g., in the Henon-Heiles model and similar systems, Eq. (6.31) suggests that \([\lambda_{2c}(0) - \lambda_{2q}(0)]\) will be given by even smaller terms that are proportional to higher power of \( \hbar \).

So far we have only correspondence between \( \lambda_{2c}(t) \) and \( \lambda_{2q}(t) \) at \( t = 0 \). For nonzero times, it is necessary to resort to high accuracy numerical methods to compare these quantities. We consider a coupled quartic oscillator system given by Eq. (6.1) with \( \alpha = 1.0 \) and \( \beta = 0.01 \) and examine three cases with \( \hbar = 0.5, 0.05, \) and 0.005. Classical calculations are done by Monte-Carlo methods, based on Eq. (6.10).
Quantum calculations are achieved using the FFT split operator technique [18]. For each case we examine three sets of initial distributions, i.e., (a) \( r_1 = r_2 = 0 \), (b) \( r_1 = r_2 = 0.6 \), and (c) \( r_1 = r_2 = -0.6 \). In addition, \( \eta_1 \) and \( \eta_2 \) are chosen to be \( \sqrt{\hbar}/2 \), and the centroid of the initial state is fixed at \( \bar{q}_1 = 0.40, \bar{q}_2 = 0.60, \bar{p}_1 = 0.50, \bar{p}_2 = 0.414 \). Note that this initial location of the Gaussian distribution gives that \( (1 - \partial^2 V / \partial q_1^2) > 0 \) and \( (1 - \partial^2 V / \partial q_2^2) > 0 \).

Figures 6.1, 6.2 and 6.3 display both \( \chi_{2c}(t) \) and \( \chi_{2q}(t) \) versus \( t \) for \( t \leq 4.0 \). The average slope (up to a certain time) of the curves in these logarithmic plots will give the finite-time Lyapunov exponents \( \lambda_{2c}(t) \) and \( \lambda_{2q}(t) \). Let's first examine Fig. 6.1 for the case of \( \hbar = 0.5 \). Since in the model Hamiltonian \( \partial^4 V / \partial q_1^2 \partial q_2^2 = 2.0 \), it is expected that \( \lambda_{2q}(0) \) can deviate considerably from \( \lambda_{2c}(0) \) for nonzero \( r_1 \) and \( r_2 \). Further, the prediction is that the initial quantum correction should be positive when \( r_1, r_2 \) are negative, and negative when \( r_1, r_2 \) are positive [see Eq. (6.31)]. All these predictions are confirmed very nicely. In particular, (1) in Fig. 6.1a \( (r_1 = r_2 = 0) \), both \( \chi_{2c}(t) \) and \( \chi_{2q}(t) \) assume a zero slope initially, characteristic of the initial Glauber coherent state, (2) in Fig. 6.1b \( (r_1 = r_2 = 0.6) \), the positive slope of \( \chi_{2q}(t) \) at \( t = 0 \) is appreciably lower than that of \( \chi_{2c}(t) \), and (3) in Fig. 6.1c \( (r_1 = r_2 = -0.6) \), it is indeed seen that at very short times \( \chi_{2q}(t) > \chi_{2c}(t) \), both of which have negative initial slopes. For all three situations, the quantum effects are so large that QCC is lost from the very beginning. With increasing time, the agreement between \( \chi_{2q}(t) \) and \( \chi_{2c}(t) \) worsens, i.e., while the classical phase space structure is seen to increase exponentially on the average, there is no sign of a similar exponential increase in quantum distribution.
Figure 6.1: Time dependence of $\chi_{2c}(t)$ (dashed line) and $\chi_{2q}(t)$ (solid line) for three initial Gaussian distributions ($\hbar = 0.5$). Both $\chi_{2c}(t)$ and $\chi_{2q}(t)$ are plotted in the logarithmic scale. The three panels correspond to (a) $r_1 = r_2 = 0$, (b) $r_1 = r_2 = 0.6$, (c) $r_1 = r_2 = -0.6$. Note that the initial slope of these solid and dashed lines are zero, positive, and negative in (a), (b) and (c), respectively. All variables are in dimensionless units [15].

Figure 6.2 shows the corresponding results with the value of $\hbar$ decreased by a factor of 10. This case is different from that in Fig. 6.1 insofar as perfect QCC for short times emerges for all three different correlated coherent states as initial
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Figure 6.2: Same as Fig. 6.1 except $\delta = 0.05$. The break regime of QCC is clearly between $t = 1.0$ and $t = 1.5$.

conditions. In particular, in Fig. 6.2b it is seen that the time dependence of both $\chi_{2c}(t)$ and $\chi_{2q}(t)$ is very close to an exponential law for $t \leq 1.5$. However, this is partially because $\lambda_{2q}(0)$ and $\lambda_{2c}(0)$ happen to be close to the long time behavior of classical finite-time Lyapunov exponents. Indeed, in Fig. 6.2c, the transient behavior of finite-time Lyapunov exponents assumes a completely different nature, i.e., the increase of both $\chi_{2c}(t)$ and $\chi_{2q}(t)$ is significantly suppressed for time up to $t = 0.5$. Fluctuations of finite-time Lyapunov exponents can be further appreciated by comparing the magnitudes of $\chi_{2c}(t = 4.0)$ and $\chi_{2q}(t = 4.0)$ in Fig. 6.2b with those in Fig. 6.2a and Fig. 6.2c. It is seen that they can be differed by a factor as large as 1.5.
Since the structure of quantal distribution functions determines the decoherence rate if the quantum system is open [12], these fluctuations imply that even in classically strongly chaotic systems it is still possible to pick out some initial states which are relatively robust to decoherence effects. Note also that Fig. 6.2 shows that the break regime of QCC is between \( t = 1.0 \) and \( t = 1.5 \), i.e., on the order of one average period of motion [15].

![Graphs showing phase space structure](image)

Figure 6.3: Same as Fig. 6.1 except \( \hbar = 0.005 \). The break regime of QCC is clearly between \( t = 2.0 \) and \( t = 2.5 \). From \( t = 0.5 \) to \( t = 2.5 \), for all three initial conditions (a), (b), and (c), there is an exponential increase of phase space structure for both classical and quantum dynamics.
As shown in Fig. 6.3, with a further large decrease of \( \hbar \), the break regime of QCC is considerably shifted to \( t = 2.0 - 3.0 \). The transient behavior caused by different initial states still persist for \( t \leq 0.5 \). After the transient period and before the break time, all quantal distribution functions in Figs. 6.3a-c emanating from the three different initial conditions are seen to undergo an exponential increase of structure on the average. This is also seen to be in good agreement with the behavior of classical distribution functions. Thus, quantum sensitivity in classically chaotic systems is clearly demonstrated. The results here for smooth, conservative, and strongly chaotic systems thus give further support to the distribution function approach to the study of quantum chaotic dynamics.

6.4 The Break Regime of Correspondence

Understanding the break regime of QCC is a central problem in the study of correspondence versus chaos. According to the previous results using the distribution function strategy, the break regime is where the classical distribution function begins to significantly develop different structure from the quantal distribution function, i.e., \( \chi_{2c}(t) \) begins to appreciably deviate from \( \chi_{2q}(t) \). Further, since \( \chi_{2c}^2(t) \) gives the initial entropy production rate when the classical system is subject to a certain noise, and \( \chi_{2q}^2(t) \) determines the initial decoherence rate when the quantum system is open [12, 13], an understanding of the QCC break regime will also shed considerable light on the extent to which the decoherence rate of quantum states at early times can be seen as the entropy production rate of classical ensembles.
It is tempting to further use the quantum Liouville equation [Eq. (6.18)] to describe how QCC breaks down with time. However, this is not an easy task, since, for nonzero times, it is extraordinarily difficult to analytically deal with distribution function dynamics. Rather, we shall present a simple description of the break regime of QCC by first re-interpreting $\chi_{2q}^2(t)$ and then comparing it with $\chi_{2q}^2(t)$. As will be quite clear, our description relates the distribution function strategy to the trajectory viewpoint of chaos.

It is desirable to restrict the discussions to the minimum-uncertainty-product state case, although the following considerations can be readily extended to the most general cases. Further, let's focus on the pure state dynamics because mixed state dynamics will simply make the study of QCC more complicated without adding new physical content.

To begin let us first obtain the Taylor series expansion of the stability matrix $M(\gamma(0), t)$ around $\bar{\gamma}(0)$ where $\delta \gamma(0) \equiv (\gamma(0) - \bar{\gamma}(0))$, we have

$$M_{kl}(\gamma(0), t) = M_{kl}(\bar{\gamma}(0), t) + \sum_m \delta \gamma_m(0) \frac{\partial M_{kl}(\bar{\gamma}(0), t)}{\partial \gamma_m(0)}$$

$$+ \frac{1}{2} \sum_{mn} \delta \gamma_m(0) \delta \gamma_n(0) \frac{\partial^2 M_{kl}(\bar{\gamma}(0), t)}{\partial \gamma_m(0) \partial \gamma_n(0)} + O((\delta \gamma(0))^3)$$

$$\equiv A_{kl} + \sum_m \delta \gamma_m(0) B_{klm} + \sum_{mn} \frac{1}{2} \delta \gamma_m(0) \delta \gamma_n(0) C_{klmn}$$

$$+ O((\delta \gamma(0))^3), \quad (6.32)$$

where we have defined $A_{kl}$, $B_{klm}$, and $C_{klmn}$, as the zeroth, first, and second order derivatives of the stability matrix at $\bar{\gamma}(0)$, respectively, and the summation indices $m, n, etc.$ run from 1 to 4 for a two-degree-of-freedom system. The time dependence
of $A_{kl}$, $B_{kln}$, and $C_{kln}$ is governed by the following set of first order differential equations together with the canonical equations for classical trajectories,

$$\frac{dA_{kl}}{dt} = \sum_{k' l'} J_{k'l'} \frac{\partial^2 H}{\partial \gamma_{k'} \partial \gamma_{k'}} A_{k' l'},$$

$$\frac{dB_{kln}}{dt} = \sum_{k' l'n'} J_{k'l'n'} \left( \sum_{n'} \frac{\partial^3 H}{\partial \gamma_{k'} \partial \gamma_{k'} \partial \gamma_{n'}} A_{n'm} A_{k' l'} + \frac{\partial^2 H}{\partial \gamma_{k'} \partial \gamma_{k'}} B_{k'ln} \right),$$

$$\frac{dC_{kln}}{dt} = \sum_{k' l'n'n'} J_{k'l'n'n'} \left( \sum_{m} \frac{\partial^3 H}{\partial \gamma_{k'} \partial \gamma_{k'} \partial \gamma_{m'}} A_{m'n} B_{k'ln} + \frac{\partial^2 H}{\partial \gamma_{k'} \partial \gamma_{k'}} C_{k'ln} \right) + \sum_{k' l'n'n'} J_{k'l'n'n'} \frac{\partial^3 H}{\partial \gamma_{k'} \partial \gamma_{k'} \partial \gamma_{n'}} (B_{k'ln} A_{n'm} + B_{n'mn} A_{k' l'}) + \sum_{k' l'n'n'} J_{k'l'n'n'} \frac{\partial^4 H}{\partial \gamma_{k'} \partial \gamma_{k'} \partial \gamma_{m'} \partial \gamma_{n'}} A_{k' l'} A_{n'm} A_{m'n}. \tag{6.33}$$

Imagine two initial points in the phase space, $\gamma(0)$ and $\varphi(0)$. They will give two trajectories, denoted by $\gamma(t)$ and $\varphi(t)$, respectively. From the trajectory point of view, of most interest is the difference $\delta \gamma_j(t) \equiv (\gamma_j(t) - \varphi_j(t))$, which is a differentiable function of $\gamma(0)$, $\delta \gamma(0)$, and $t$. Fixing $\varphi(0)$ and thus $\gamma(t)$ gives a reference trajectory. Consider now the Taylor series expansion of $\delta \gamma_j(t)$ in terms of $\delta \gamma(0)$. Obviously $\delta \gamma_j(t) = 0$ if $\delta \gamma(0) = 0$, $\partial \delta \gamma_j(t)/\partial \delta \gamma_n(0)|_{\gamma(0)=0} = A_{jln}$, $\partial^2 \delta \gamma_j(t)/\partial \delta \gamma_k(0) \partial \delta \gamma_n(0)|_{\gamma(0)=0} = B_{ijkl}$, and so on. In fact, the $n$th order derivative of $\delta \gamma_j(t)$ with respect to $\delta \gamma(0)$ is simply given by the $(n-1)$th order derivative of the stability matrix $M(\gamma(0), t)$ with respect to $\gamma(0)$. Based on this observation, one obtains the following relation,

$$\sum_{l} A_{jln} \delta \gamma_l(0) = \delta \gamma_j(t) - \frac{1}{2} \sum_{lk} \delta \gamma_k(0) \delta \gamma_l(0) B_{ijkl} - \frac{1}{6} \sum_{jklm} \delta \gamma_k(0) \delta \gamma_l(0) \delta \gamma_m(0) C_{ijklm} - O((\delta \gamma(0))^4). \tag{6.34}$$

The initial classical distribution function corresponding to the Glauber coher-
ent state is generally given by

\[ \rho_0(\gamma(0), \bar{\gamma}(0)) = \frac{1}{4\pi^2 \sigma_{\gamma_1} \sigma_{\gamma_2} \sigma_{\gamma_3} \sigma_{\gamma_4}} \exp\left[\frac{-(q_1 - \bar{q}_1)^2}{2\sigma_{\gamma_1}^2} - \frac{(q_2 - \bar{q}_2)^2}{2\sigma_{\gamma_2}^2} - \frac{(p_1 - \bar{p}_1)^2}{2\sigma_{p_1}^2} - \frac{(p_2 - \bar{p}_2)^2}{2\sigma_{p_2}^2}\right]. \]  

(6.35)

Substituting Eq. (6.32) and the initial distribution function \( \rho_0(\gamma(0), \bar{\gamma}(0)) \) [Eq. (6.35)] into Eq. (6.10), evaluating the first derivatives of \( \rho_0(\gamma(0), \bar{\gamma}(0)) \), and finally rescaling all integration variables by a factor of \( 1/\sqrt{2} \), one obtains

\[ \chi_{2e}^2(t) = \frac{1}{2} \int d\gamma(0) \rho_0(\gamma(0), \bar{\gamma}(0)) \]

\[ \times \sum_j \sum_k \alpha_k (A_{jk} + \sum_m \frac{1}{\sqrt{2}} B_{jkm} \delta \gamma_m(0)) \]

\[ + \sum_{mn} \frac{1}{4} C_{jkmn} \delta \gamma_m(0) \delta \gamma_n(0) + O((\delta \gamma(0))^4)) \]

(6.36)

where

\[ \alpha_1 = \left( -\frac{p_1(0) - \bar{p}_1(0)}{\sigma_{p_1}^2} \right), \]

\[ \alpha_2 = \left( -\frac{p_2(0) - \bar{p}_2(0)}{\sigma_{p_2}^2} \right), \]

\[ \alpha_3 = \left( \frac{q_1(0) - \bar{q}_1(0)}{\sigma_{\gamma_1}^2} \right), \]

\[ \alpha_4 = \left( \frac{q_2(0) - \bar{q}_2(0)}{\sigma_{\gamma_2}^2} \right). \]  

(6.37)

Noticing that \( A_{jk}, B_{jkm}, \) and \( C_{jkmn} \) do not depend upon \( \gamma(0) \), and only the even functions of \( \delta \gamma(0) \) will contribute when integrated over \( \rho_0(\gamma(0), \bar{\gamma}(0)) \), Eq. (6.36) can be further reduced to

\[ \chi_{2e}^2(t) = \sum_{jkk'mm'} \left( \frac{1}{4} A_{jkk'} \frac{1}{4} B_{jkm} B_{jkm'} \langle \alpha_k \alpha_{k'} \delta \gamma_m(0) \delta \gamma_{m'}(0) \rangle \right) \]

\[ + \frac{1}{2} \int d\gamma \rho_0(\gamma(0), \bar{\gamma}(0)) \left( \sum_j \sum_k \left| A_{jk} \alpha_k \right|^2 \right) + O(\alpha^2(\delta \gamma(0))^4). \]  

(6.38)
where \( \langle \cdot \rangle_0 \) means the ensemble average over the initial Gaussian distribution.

To further simplify the expression for \( \chi^2_{2c}(t) \), we make a change of the integration variables in the second term on the right side of Eq. (6.38), i.e.,

\[
-(p_1 - \bar{p}_1) \rightarrow \frac{\sigma_{p_1}}{\sigma_{q_1}} (q - \bar{q}_1), \quad -(p_2 - \bar{p}_2) \rightarrow \frac{\sigma_{p_2}}{\sigma_{q_2}} (q_2 - \bar{q}_2),
\]

\[
(q_1 - \bar{q}_1) \rightarrow \frac{\sigma_{q_1}}{\sigma_{p_1}} (p_1 - \bar{p}_1), \quad (q_2 - \bar{q}_2) \rightarrow \frac{\sigma_{q_2}}{\sigma_{p_2}} (p_2 - \bar{p}_2).
\]

(6.39)

Note that the Jacobi matrix of this transformation is a unity matrix and it has no effect on the form of \( \rho_0(\gamma(0), \bar{\gamma}(0)) \). As a result of this coordinate transformation we have \( \alpha_k \rightarrow \delta \gamma_k(0)/(\sigma_{q_1} \sigma_{p_1}) = \delta \gamma_k(0)/(\sigma_{q_2} \sigma_{p_2}) \). This makes it possible to reexpress the second term on the right side of Eq. (6.38) with the help of Eq. (6.34). Specifically,

\[
\frac{1}{2} \int d\gamma(0) \rho_0(\gamma(0), \bar{\gamma}(0)) \left( \sum_j \sum_k A_{jk} \alpha_k \right)^2
\]

\[
= \frac{1}{2(\sigma_{q_1} \sigma_{p_1})^2} \int d\gamma(0) \rho_0(\gamma(0), \bar{\gamma}(0)) \left( \sum_j \sum_k A_{jk} \delta \gamma_k(0) \right)^2
\]

\[
= \frac{1}{2(\sigma_{q_1} \sigma_{p_1})^2} \left[ \sum_j (\langle \gamma_j(t) \rangle^2_0 - \langle \gamma_j(t) \rangle^2) \right] - \sum_{jkl} B_{jkl} \langle \delta \gamma_j(t) \delta \gamma_k(0) \delta \gamma_l(0) \delta \gamma_m(0) \rangle_0
\]

\[
+ \frac{1}{4} \sum_{jklm} B_{jkl} B_{jlm} \langle \delta \gamma_k(0) \delta \gamma_l(0) \delta \gamma_m(0) \delta \gamma_m(0) \rangle_0
\]

\[
- \frac{1}{3} \sum_{jklm} C_{jklm} \langle \delta \gamma_j(t) \delta \gamma_k(0) \delta \gamma_l(0) \delta \gamma_m(0) \rangle_0 + O((\delta \gamma(0))^6). \tag{6.40}
\]

The second and the fourth terms in the above expression are a linear function of \( \delta \gamma(t) \) and they can be further transformed into some functions of \( \delta \gamma(0) \) by using Eq. (6.34) a second time. We then get

\[
\frac{1}{2} \int d\gamma(0) \rho_0(\gamma(0), \bar{\gamma}(0)) \left( \sum_j \sum_k A_{jk} \alpha_k \right)^2
\]

\[
= \frac{1}{2(\sigma_{q_1} \sigma_{p_1})^2} \sum_j (\langle \gamma_j(t) \rangle^2_0 - \langle \gamma_j(t) \rangle^2) \]
Now inserting Eq. (6.41) into Eq. (6.38) yields a compact form of $\chi^2_{2c}(t)$, which reads

$$
\chi^2_{2c}(t) = \frac{2}{\hbar^2} \sum_j \left( \langle (\gamma_j(t))^2 \rangle_0 - \langle \gamma_j(t) \rangle_0^2 \right) + \frac{2}{\hbar^2} \sum_{jkk'\ell'} \left( \frac{1}{4} B_{jk\ell} B_{j\ell'k'} + \frac{1}{3} A_{jkC_{j\ell'k'}} \right) \langle \delta \gamma_k(0) \delta \gamma_{k'}(0) \delta \gamma_l(0) \delta \gamma_{l'}(0) \rangle_0 \\
+ \sum_{jkk'\ell'} \left( \frac{1}{4} B_{jk\ell} B_{j\ell'k'} + \frac{1}{3} A_{jkC_{j\ell'k'}} \right) \langle \alpha_k \alpha_{kl} \delta \gamma_l(0) \delta \gamma_{l'}(0) \rangle_0 \\
+ \frac{1}{\hbar^2} O((\delta \gamma(0))^6).
$$

(6.42)

Note that the factor $\hbar^2$ in the above equation is simply due to the fact $\sigma_{q1} \sigma_{p2} = \sigma_{q2} \sigma_{p2} = \hbar/2$ for any classical distribution function corresponding to a minimum-uncertainty-product state.

For simplicity consider now a special case in which the initial coordinate variances are identical with the initial momentum variances, i.e., $\sigma_{q1} = \sigma_{p1} = \sigma_{q2} = \sigma_{p2}$. One then obtains

$$
\chi^2_{2c}(t) = \frac{2}{\hbar^2} \sum_j \left( \langle (\gamma_j(t))^2 \rangle_0 - \langle \gamma_j(t) \rangle_0^2 \right) + f(t) + O(\hbar),
$$

(6.43)

where $f(t)$ is given by

$$
f(t) = - \sum_{jkk'\ell'} \left( \frac{1}{2} B_{jk\ell} B_{j\ell'k'} + \frac{2}{3} A_{jkC_{j\ell'k'}} \right) \\
\times \left[ \frac{3}{4} \delta_{kk'} \delta_{ll'} + \frac{1}{4} \left( \delta_{kk'} \delta_{ll'} + \delta_{kk'} \delta_{ll'} - \delta_{ll'} \delta_{kk'} \right) \right] \\
+ \sum_{jkk'\ell'mm'} J_{km} J_{k'm'} (B_{jk\ell} B_{j\ell'k'} + A_{jkC_{j\ell'k'}}) \\
$$
This new expression for the measure $\chi_{2q}^2(t)$ of classical phase space structure affords new perspectives into QCC. Our previous discussion shows [see Eq. (6.23)] that, for pure state dynamics the quantal measure $\chi_{2q}^2(t)$ of phase space structure can be expressed in terms of the sum of second order moments. This is more or less a consequence of quantization: the smallest scale in coordinates is related to the largest momentum component of the wavefunction, and vice versa. Clearly, this is not the case for classical distribution functions. Nevertheless, from Eqs. (6.42) and (6.43) it is clearly seen that, to some extent, $\chi_{2q}^2(t)$ can also be related to the sum of second order statistical moments. As shown in Eq. (6.43) for an initially symmetric coherent state, the first term contributing to $\chi_{2q}^2(t)$ is given by the sum of some second order moments divided by $\hbar^2/2$. Interestingly, this term is exactly the same as the right hand side of Eq. (6.23) for $\chi_{2q}^2(t)$. In addition, $\chi_{2q}^2(t)$ contains contributions from other terms absent in the quantum dynamics. Among such terms, the leading order correction term $f(t)$ is independent of $\hbar$. As shown by Eq. (6.44), it is simply determined by the stability characteristics $A_{jk}$, $B_{jkm}$, and $C_{jkmn}$ associated with the trajectory starting from the centroid of the initial Gaussian distribution. Evidently, Eqs. (6.42), (6.43) and (6.44) not only reveal a remarkable similarity between $\chi_{2c}(t)$ and $\chi_{2q}(t)$, but also allow for a closer examination of when and how classical distribution functions begin to develop different structure from quantal distribution functions. In addition, through the derivations in this section it is seen that there is a close relationship
between the development of phase space structure and the instability characteristics of classical trajectories.

A simple application of Eq. (6.43) relates to quadratic Hamiltonian systems such as the harmonic oscillator or inverted harmonic oscillator systems. In such systems, the time evolution is linear canonical transformation in phase space. Hence the stability matrix elements $M_{jk}(\gamma(0), t)$ do not depend on $\gamma(0)$. Consequently, $B_{jkl}, C_{jklm}$ and all other higher order derivatives of the stability matrix with respect to $\gamma(0)$ are exactly zero. Thus, in linear systems, $\chi_{2\alpha}^{2}(t)$ will be precisely given by the sum of some second order moments divided by $\hbar^2/2$, in perfect correspondence with $\chi_{2\alpha}^{2}(t)$ [see Eq. (6.23)].

Returning to chaotic systems, one can qualitatively estimate that the stability matrix increases exponentially, i.e., $A_{kl} \propto \exp(\lambda t)$, with $\lambda$ being the average exponential increase rate up to time $t$. Likewise, one expects $B_{klm} \propto \exp(\lambda t), C_{klmn} \propto \exp(\lambda t)$, etc. Due to Eq. (6.44) this further suggests that $f(t) \propto f_0 \exp(2\lambda t)$. By contrast, the first term on the right hand side of Eq. (6.43) is determined by second-order moments and cannot increase for all time for bounded systems. Indeed, assuming that the characteristic magnitude of the second order moments $(\langle \gamma_j(t) \rangle_0^2 - \langle \gamma_j(t) \rangle_0^2)$ ($j = 1, 2, 3, 4$) is given by $\Omega^2$, then the first term on the right hand side of Eq. (6.43) would be bounded by $8\Omega^2/\hbar^2$. Thus, in Eq. (6.43) the $f(t)$ term will be comparable to the preceding term after a time scale $t_b$, which is approximately given by

$$t_b = \frac{1}{2\lambda} \ln \left[ \frac{8\Omega^2}{\hbar^2 f_0} \right].$$

(6.45)

Since $t_b$ scales with the logarithm of $\hbar$, it could be extremely short even for very
small $\hbar$. More significantly, a comparison between Eqs. (6.23) and (6.43) shows that $t_0$ corresponds to the time scale after which classical descriptions of phase space structure no longer have clear quantum counterparts. That is, the structure is smaller than the scale set by $\hbar$. Thus, $t_0$ is identified as the logarithmic break time of QCC. Further, since Eq. (6.45) involves classical variables only, one can easily calculate $t_0$ without any quantum calculations.

The fact that the QCC break time should depend on $\hbar$ logarithmically was pointed out more than two decades ago [19]. However, most often the logarithmic break time of QCC is understood from a perspective afforded by Ehrenfest's theorem. That is, only before the logarithmic break time scale, can the centroid of a wavepacket closely follow a classical trajectory. Unfortunately, such understanding of the break time makes little sense from the ensemble point of view, since even in classical distribution function dynamics, the centroid of an ensemble may not follow any trajectory, either. It is thus clear that this work further improves the understanding of the logarithmic break time of QCC, providing a proper distribution function perspective.

The fundamental reason why $f(t)$ does not have the quantal analogue is that it reflects classical phase space structure which is beyond the resolution limit of quantal distribution functions. It is thus very interesting to actually compare $[\chi_{2q}^2(t) - \chi_{2q}^3(t)]$ from the direct calculations of the previous section with $f(t)$ given by Eq. (6.44). However, to obtain $f(t)$ according to Eq. (6.44), one has to compute numerically the instability characteristics $A_{jk}$, $B_{jkl}$ and $C_{jklm}$. Fortunately, this can be done by
integrating the entire set of differential equations in Eq. (6.33). Interesting numerical

Figure 6.4: Time dependence of \( (\chi^2_{2e} - \chi^2_{2q}) \) compared with \( f(t) \) in our analytical considerations [see Eqs. (6.43) and (6.44) in the text]. All variables are in dimensionless units [15]. The initial condition is the minimum-uncertainty-product state considered in the previous section. Dashed lines denote \( (\chi^2_{2e} - \chi^2_{2q}) \) based on direct calculations in the previous section, and solid lines denote \( f(t) \) given by Eq. (6.44). (a) \( \hbar = 0.05 \), (b) \( \hbar = 0.005 \). Note that Figs. 6.2 and 6.3 have shown that the QCC break time is around \( t = 1.5 \) for \( \hbar = 0.05 \), and around \( t = 2.5 \) for \( \hbar = 0.005 \). Good agreement between \( (\chi^2_{2e} - \chi^2_{2q}) \) and \( f(t) \) for the QCC break regime is evident.

results have been obtained for the break regime of QCC. In particular, two cases with the value of \( \hbar \) differing by a factor of ten are examined. As implied by Eq. (6.44), the two cases can be examined by calculating \( f(t) \) only once since \( f(t) \) is \( \hbar \)-independent. Figures 6.4a and 6.4b show the comparison between \( [\chi^2_{2e}(t) - \chi^2_{2q}(t)] \) and \( f(t) \) for both cases. The agreement between direct numerical calculations and
analytical considerations is remarkable. It can be safely concluded that \( f(t) \) catches the essence of the break regime of QCC.

In Fig. 6.4 one can also see some small discrepancies between \( \left[ \chi_{2c}(t) - \chi_{2q}(t) \right] \) and \( f(t) \), especially at later times. This indicates that gradually other higher order terms in Eq. (6.43) become also responsible for quantum classical differences. Admittedly, little is known about the nature of these higher order terms. As a matter of fact, we find that if \( f(t) \) tends to be drastically oscillating, these higher order terms may be indeed non-negligible at relatively earlier times. Nevertheless, the physics is still the same. That is, the sum of \( f(t) \) and these higher order terms measures very fine phase space structure which is unresolvable by quantum distribution functions.

### 6.5 Long After the Break Regime

The logarithmic break time \( t_b \) of QCC challenges many understandings of the relationship between quantum dynamics and classical mechanics. For instance, Zurek et al. [20] pointed out that a logarithmic break time (somewhat different from that obtained above) is actually counter-intuitively short even for macroscopic objects (more discussions on this can be found in Chap. 7). This being the case, our everyday experience in a macroscopic classical world full of chaotic events seems incompatible with the notion that classical physics is a large-quantum-number limit of fundamental quantum principles. Likewise, the smallness of the QCC break time seems to imply that there is no room for classical physics to play a role in nonlinear molecular dynamics, contradicting the fact that classical physics can work very well in many
dynamics simulations. To at least partially resolve these puzzles, this section is motivated to understand the implications of the quantum classical discrepancy in phase space structure for ensemble statistics.

As already implied by a comparison between Eqs. (6.23) and (6.43), what is directly responsible for the logarithmic break time is not quantum classical difference in expectation values, but simply the exponential increase of \( f(t) \) which reflects the richness of fragmentation of classical distribution functions. This point has been confirmed by our numerical results, for times not far away from the break regime.

It is thus very interesting to examine correspondence in some low order statistical moments long after the break regime of QCC. In particular, Fig. 6.5 displays the time dependence of four variances, i.e., \( \langle q_1^2 \rangle - \langle q_1 \rangle^2 \), \( \langle q_2^2 \rangle - \langle q_2 \rangle^2 \), \( \langle p_1^2 \rangle - \langle p_1 \rangle^2 \), and \( \langle p_2^2 \rangle - \langle p_2 \rangle^2 \), for both classical and quantum dynamics. The initial state corresponds to that used in Fig. 6.3a and Fig. 6.4b. \( h \) is chosen to be 0.005, for the sake of a direct comparison with the previous results.

Remarkably, results in Fig. 6.5 show that QCC in these second order moments is perfect, for times up to \( t \approx 12 \), which is much longer than the break time \( t_b < 3.0 \) identified in Fig. 6.3 and on the order of 12 system periods. In particular, for times less than \( t = 2.5 \), both quantal and classical variances are seen to increase very rapidly, in exactly the same manner. In fact, this rapid increase is exponential in nature because, in this regime, the sum of these variances (divided by \( h^2/2 \)) give \( \chi_{2c}^2 \) (or \( \chi_{2q}^2 \)), which indeed increases exponentially on the average (see Fig. 6.3a). This confirms a recent suggestion that the initial rapid increase of both quantal and
classical variances could be used to identify classical chaos from quantum dynamics [9].

Figure 6.5: Quantum classical comparison of the time dependence of four second-order statistical moments, for the time scale much larger than the logarithmic break time $t_b$. $\hbar = 0.005$, and the initial distribution function corresponds to that in Figs. 6.3a and 6.4b. Note that Fig. 6.3a shows that $t_b < 3.0$. Dashed lines denote classical results, solid lines are quantum results. The four second-order statistical moments are (a) $\langle q_1^2 \rangle - \langle q_1 \rangle^2$, (b) $\langle q_2^2 \rangle - \langle q_2 \rangle^2$, (c) $\langle p_1^2 \rangle - \langle p_1 \rangle^2$, and (d) $\langle p_2^2 \rangle - \langle p_2 \rangle^2$. All variables are in dimensionless units [15]. QCC during the complex relaxation process ($0 < t < 12$) is remarkable.

For times $2.5 < t < 12$ during which perfect QCC persists, the second order moments are seen to be experiencing a very complex evolution. For example, there is clearly a diffusive regime between $t = 5.0$ and $t = 7.0$ with very large diffusive constants. After
that, several very strong oscillations (particularly in Figs. 6.5b-d) can be observed, suggesting that both the quantal and classical distribution functions are alternating between a high degree of delocalization and a certain degree of localization over the entire accessible phase space. The perfect QCC in this complex relaxation pattern is in sharp contrast to the results in Fig. 6.4b, where quantum classical differences, as quantitatively described by \( \chi_{2q}^2(t) - \chi_{2q}^2(t) \) and predicted by \( f(t) \), are already very large before \( t = 4.0 \). Further, due to this oscillation behavior with time, one expects that the corresponding time window scales with \( 1/\hbar \), rather than \( \ln \hbar \). For even later times (\( t > 12 \)), Fig. 6.5 shows that quantum classical discrepancies begin to show up, but still with very similar trends of the oscillations.

The results demonstrate that the logarithmic break time is irrelevant to QCC viewed from the perspective of some low order statistical moments. This is the case since considering only low order statistical moments is equivalent to projecting the quantal and classical distribution functions onto some much smaller subspace. In this projection or coarse-graining procedure, all the information encoded in an infinite number of higher order statistical moments is lost. An amazingly accurate QCC is thus restored due to the loss of detailed information.

The results here also give further support to the idea of applying classical propagation methods to quantum distribution functions, as an approximation to the true quantum mechanics [21]. The results also suggest that chaos may not cause a rapid failure of classical dynamics simulations if only expectation values of some observables are of interest. More importantly, the results in this chapter and Chap.
7 provide more insights into a fundamental issue regarding the role of decoherence in understanding correspondence [22, 23]. On one hand, our results here show that during the relaxation process whose time scale is much larger than the logarithmic break time, decoherence is still not necessary to ensure perfect QCC in low order statistical moments. Thus, decoherence effects on correspondence in expectation values, if any, should be considered after the relaxation process is essentially completed, e.g., after \( t = 12 \) in Fig. 6.5. This point supports the argument of Casati et al. [23] and generalizes their considerations from one dimensional kicked systems to conservative systems. On the other hand, as shown in Chap. 7, QCC for much larger time scales can be much improved with the introduction of decoherence [24].

### 6.6 Summary

In summary, in this chapter the problem of QCC in conservative chaotic systems has been extensively studied by a distribution function strategy. The nature of QCC in three different regimes is exposed. In particular, (1) the short time increase rate of phase space structure is studied in connection with finite-time Lyapunov exponents; (2) a simple and enlightening description of the break regime of QCC is obtained, by successfully accounting for the classical phase space structure which is beyond the quantum description; and (3) perfect QCC in low order statistical moments is demonstrated during a complex relaxation process, where the time scale is much larger than the logarithmic break time.
Bibliography


[15] Note that we begin with a dimensionless scaled Hamiltonian [Eq. (6.1)]. As a result, all relevant variables are understood to be dimensionless and scaled. The relation between the scaled variables and unscaled variables is, however, crucial for retrieving specific units when necessary. For a general Hamiltonian $\tilde{H} = \frac{\tilde{s}^2}{2m_1} + \frac{\tilde{s}^2}{2m_2} + \tilde{V}(\tilde{q}_1, \tilde{q}_2)$ with all variables with tildes denoting ordinary unscaled variables, we can define the dimensionless scaled variables $q_1 \equiv \sqrt{\frac{m_1 \omega}{\ell}} \tilde{q}_1$, $p_1 \equiv \sqrt{\frac{1}{m_1 m_2 \omega}} \tilde{p}_1$, $q_2 = \sqrt{\frac{m_2 \omega}{\ell}} \tilde{q}_2$, and $p_2 \equiv \sqrt{\frac{1}{m_1 m_2 \omega}} \tilde{p}_2$. Here $\ell$ has units of action, and $m_i$ and $\omega$ are ordinary constants with units of mass and frequency. Typically, $\omega$ is taken as the average frequency of this system and $\ell$ is taken to scale the true Planck's constant; that is $\hbar = \tilde{\hbar} / \ell$, where $\tilde{\hbar}$ is the ordinary Planck's constant and $\hbar$ is the dimensionless scaled Planck's constant. The scaled variables satisfy the canonical equations of motion for the scaled time $t = \omega \tilde{t}$ and the scaled Hamiltonian $H = \tilde{H} / \ell \omega$. For quantum descriptions one can verify that $[q_1, p_1] = i\hbar$, $[q_2, p_2] = i\hbar$.


Chapter 7

Decoherence and Correspondence in Conservative Chaotic Dynamics
Chapter Summary:

Based on a novel and generally useful numerical approach, we compare the quantum and classical dynamics of a conservative nonlinear Hamiltonian system in the chaotic regime in the absence and presence of decoherence effects. Expectation values of various observables display marked improvement in quantum-classical correspondence upon the introduction of decoherence, with the initial quantum dynamics being far from the semiclassical limit. The issue of the emergence of chaotic trajectories from quantum mechanics is also discussed.
7.1 Introduction

The means by which quantum mechanics approximates classical mechanics for macroscopic systems remains a subject of considerable theoretical interest. Traditional, often heuristic, approaches argue that the equations of classical mechanics emerge naturally as the DeBroglie wavelength becomes small. By contrast, others argue that classical mechanics is not a limiting case of quantum mechanics, but rather that decoherence, i.e. loss of coherence due to coupling to other degrees of freedom, is necessary to ensure the validity of the correspondence principle [1, 2, 3]. This proposal, however, is the topic of considerable controversy, with many arguing that the relationship between decoherence and correspondence is tenuous [4].

To study the role of decoherence in classically chaotic systems is even more challenging. A widely accepted approach, mainly due to Zurek and his collaborators, is based on the distribution function strategy. In Chap. 6, we have seen that, since quantum distribution functions can not assume very fine structure due to interference effects, QCC in the time development of phase space structure breaks down at an unusually short time which scales with \( \ln \hbar \). This time scale can be much shorter than the ages of some celestial bodies which indeed display chaotic motions\(^1\). Zurek et al. [1, 2] argued that, upon introducing environment-induced decoherence, chaos-induced fragmentation of both quantum and classical distribution functions would be dramatically suppressed due to coarse-graining effects of the environment. Thus,

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\(^1\)Strong evidence has been established that the tumbling of Hyperion, one of the moons of Saturn, the orbital motion of Chiron in the asteroid belt, and the dynamics of the solar system as a whole are chaotic.
quantum classical correspondence (QCC) in chaotic systems could be substantially restored upon introducing decoherence.

Decoherence effects on classically chaotic quantum dynamics are more than just a conceptual problem on QCC. The interplay of decoherence and quantum chaos is also of direct relevance to theoretical chemical physics problems, e.g., the understanding and description of intramolecular statistical behaviors [5, 6, 7]. This is because (1) rovibrational motions in polyatomic molecular systems lie closely to the border between quantum and classical descriptions, (2) as the anharmonic coupling strength between different normal degrees of freedom becomes large, molecular motions begin to display irregular dynamical behavior, and (3) rovibrational degrees of freedom are inevitably coupled with much faster electronic processes, and each molecule is subject to an environment consisting of other molecules.

Consider now the model of Caldeira and Leggett and of Zurek [8] in which the system interacts with a harmonic bath in the weak coupling and high temperature limit. Extending this model to a system with two degrees of freedom gives the time evolution of the density matrix \( \hat{\rho} \) in the Wigner representation [8]:

\[
\frac{\partial \rho^W}{\partial t} = \{H, \rho^W\} + \sum_{(l_1+l_2>1)}^{\text{odd}} \frac{\mathcal{A}}{l_1!l_2!} \frac{\partial^{(l_1+l_2-1)} V(q_1, q_2)}{\partial q_1^{l_1} \partial q_2^{l_2}} \frac{\partial^{(l_1+l_2)} \rho^W}{\partial p_1^{l_1} \partial p_2^{l_2}} + D \left( \frac{\partial^2 \rho^W}{\partial p_1^2} + \frac{\partial^2 \rho^W}{\partial p_2^2} \right)
\]

Here \((p_1, p_2, q_1, q_2)\) are the system momenta and coordinates, \(V(q_1, q_2)\) is the potential contribution to the Hamiltonian \(H\) and \(\rho^W = \rho^W(p_1, p_2, q_1, q_2; t)\) is the Wigner function for the density matrix \(\hat{\rho}\). The first term on the right hand side of Eq. (7.1)
is the classical Poisson bracket which generates classical dynamics, the second Moyal term is responsible for quantum/classical differences, and the third term induces decoherence. Let us first recall the closed system case ($D = 0$). Due to the underlying classical chaos, the Poisson bracket term generates exponential stretching and folding of the distribution function (this has been described in detail in Chap. 6 via a measure of phase space structure $\chi_{2e}$). Roughly speaking, the finest scale in momentum ($p_1$ or $p_2$) denoted by $\delta p(t)$ will then decrease as

$$\delta p(t) = \delta p_0 \exp(-\lambda t), \quad (7.2)$$

where $\lambda$ is the Lyapunov exponent of the classical dynamics. This leads to an exponential increase of the derivatives of $\rho^W(p_1, p_2, q_1, q_2; t)$ with respect to momentum, such that the magnitude of the second Moyal term shortly becomes comparable to that of the classical Poisson term after a time scale proportional to $\ln \hbar$. However, if $D$ is nonzero, then the last term responsible for decoherence causes diffusion in the momentum space, i.e., the fragmentation in momentum can not proceed indefinitely. This decoherence-induced diffusion could be described by the increase of the finest scale in momentum represented by $\delta p_d$, i.e.,

$$\delta p_d(t) = \sqrt{2Dt}. \quad (7.3)$$

As a compromise between the two processes described by Eqs. (7.2) and (7.3), the increase of phase space structure in momentum should stop at a critical time $t_c$, at which we have

$$\delta p_0 \exp(-\lambda t_c) = \sqrt{2Dt_c}. \quad (7.4)$$
Further requiring that the second Moyal term should be negligible compared with the first term at \( t_c \) (to ensure QCC), Zurek et al. [1] (and independently, Kolovsky [9]) derived the following condition for the quantum-classical transition in chaotic systems:

\[
\sqrt{\frac{2D}{\lambda}} \chi > \hbar
\]  

(7.5)

where \( \chi \) is a characteristic potential length. For one-degree-of-freedom systems they examined, \( \chi \) is defined as the average value of \( \sqrt{|\partial_{q_1} V / \partial_{q_1}^3 V|} \). For a two-degree-of-freedom conservative chaotic system, there of course exist various characteristic lengths, which could be defined as the average values of \( \sqrt{|\partial_{q_1} V / \partial_{q_1}^3 V|} \), \( \sqrt{|\partial_{q_1} V / \partial_{q_1} \partial_{q_2} V|} \), \( \sqrt{|\partial_{q_1} V / \partial_{q_1} \partial_{q_2} V|} \), and \( \sqrt{|\partial_{q_2} V / \partial_{q_2}^3 V|} \).

Despite its success, this physical picture of decoherence in chaotic systems should be viewed with caution. Note first that in most circumstances the details of the distribution functions are not of direct theoretical or experimental interest. Rather, a modest and common view of QCC is usually taken in terms of ensemble expectation values of some observables. That is, if, for some range of time and some observables, quantum classical ensembles give very similar expectation values, the system of interest could be regarded as classical. In this sense, Zurek's condition (7.5) for QCC could have over-estimated quantum classical disagreement. Indeed, as revealed in Chap. 6, even with large discrepancies in phase space structure between quantum and classical distribution functions, expectation values given by quantum and classical dynamics usually agree extremely well long after the logarithmic correspondence time (see also [10, 11]). Thus, to clearly observe the interplay of decoherence effects
and the underlying classical chaos manifested in expectation values of observables, quantum effects in the closed system should be chosen to be large enough and a right choice of the time scale under investigation is needed.

Zurek's decoherence program has also left open a fundamental problem. In his scenario, the environmental coarse-graining effects are to destroy the quantum coherence over a coordinate scale which is larger than $l_c \equiv \hbar/\delta p(t_c)$. This is essentially a practical solution to the Schrödinger cat paradox. This practical solution can not explain the definiteness of the classical world. Thus, the emergence of extremely localized and chaotic classical trajectories from quantum physics remains a puzzle. To see this more clearly let us consider the chaotic motions of some celestial bodies. What is achieved in Zurek's scenario is that, due to environmental decoherence, the quantum distribution function will evolve very much like the classical distribution function, thus preventing the rapid occurrence of coherent superposition of macroscopically distinct quantum states. Yet the resultant classical-like ensemble (subject to a coarse-graining) still spreads over the available phase space exponentially fast, and the corresponding incoherent statistical mixture of macroscopically distinguishable states of these celestial bodies are not what we actually observe. Clearly, Zurek's scenario ignored the serious gap between the statistical description of chaotic motions and the definite physical reality, which is chaotic trajectories satisfying Newton's equation. It therefore appears that some localization mechanism is needed to completely resolve the issue of QCC in classically chaotic systems.

The first goal of this chapter is to examine decoherence effects in a typical con-
servative chaotic system and show that decoherence does indeed lead to substantially improved agreement in expectation values between classical and quantum ensembles. This constitutes a major extension of previous work on the effect of decoherence, which were limited to one dimensional driven chaotic systems [13, 14]. In particular, our extension is to the broad class of conservative nonlinear Hamiltonian systems, and into the domain where the system is far from the semiclassical regime. In doing so, we develop a quantum state diffusion-split operator method that provides a generally useful and efficient method for studying decoherence described by Eq. (7.1).

As further discussed in the following sections, the quantum state diffusion perspective is essentially equivalent to other spontaneous wavefunction collapse models which aim directly to explain the definiteness of the classical world. Thus, the decoherence term in Eq. (7.1) could be of a non-environmental origin. This fact affords new insights into QCC in classically chaotic systems. As the second goal of this chapter, we examine the wavepacket dynamics in QSD for a two-degree-of-freedom conservative chaotic system. We shall discuss the condition for the emergence of localized wavepackets as the system gets closer to the classical limit. In particular, we provide interesting numerical evidence that Zurek's condition (7.5) is not sufficient to guarantee correspondence from the trajectory point of view. In this sense, Zurek's condition (7.5) could have under-estimated quantum effects.
Chapter 7. DECOHERENCE AND CORRESPONDENCE...

7.2 Quantum State Diffusion-Split Operator Approach

For a two-degree-of-freedom open quantum system, if the number of basis states required is \( N \) for each degree of freedom, then a matrix of the size \( N^2 \times N^2 \) is needed to describe the density operator. This indicates that directly propagating the corresponding density matrix for a two-degree-of-freedom open system would be prohibitively memory intensive. Fortunately, there do exist indirect quantum mechanical methods to solve such problems. In this section we introduce the so-called quantum state diffusion (QSD) approach and adapt it to a useful scheme for coupled nonlinear oscillator systems.

In QSD the time evolution of a pure state vector, rather than the density operator, is computed directly by a stochastic Schrödinger equation [15],

\[
|d\psi\rangle = \frac{-i}{\hbar} H|\psi\rangle dt + \sum_m (2\langle L^\dagger_m |\psi\rangle L_m - L^\dagger_m L_m - \langle L^\dagger_m |\psi\rangle \langle L_m |\psi\rangle)|\psi\rangle dt
+ \sum_m (L_m - \langle L_m |\psi\rangle)|\psi\rangle d\xi_m,
\]

where operators \( L_m \) represent the coupling between the system of interest and the environment, \( \langle L_m |\psi\rangle = \langle \langle \psi |L_m |\psi\rangle \rangle / \langle \langle \psi |\psi\rangle \rangle \) is the expectation value of \( L_m \) for the pure state \( |\psi\rangle \), and \( d\xi_m \) are independent complex differential random variables of a complex normalized Wiener process, of which the mean properties are as follows:

\[
M[\Re(d\xi_n)\Re(d\xi_m)] = M[\Im(d\xi_n)\Im(d\xi_m)] = \delta_{nm} dt,
M[\Im(d\xi_n)\Re(d\xi_m)] = 0.
\]
Using the Itô calculus for differential stochastic variables [16], it can be shown that averaging Eq. (7.6) over the stochastic Wiener process yields the following time evolution equation for the density operator $\bar{\rho}$,

$$\dot{\bar{\rho}} = \frac{-i}{\hbar} [H, \bar{\rho}] + \sum_m \left( 2L_m \bar{\rho} L_m^\dagger - L_m^\dagger L_m \bar{\rho} - \bar{\rho} L_m^\dagger L_m \right)$$

(7.8)

where

$$\bar{\rho}(t) = \frac{1}{S} \sum_{\xi_m} \ket{\psi(\xi_m(t), t)} \bra{\psi(\xi_m(t), t)},$$

(7.9)

and $S$ is the total realization number of the time dependent stochastic variables $\xi_m$.

According to Lindblad's semigroup theory [17], Eq. (7.8) is the most general form of the quantum master equation which (1) preserves the norm of the density operator, (2) preserves the positivity of the density matrix, and (3) assumes the Markovian limit. Thus, QSD has very wide applicability. For instance, a non-Hermitian coupling operator $\hat{L}_m$ immediately introduces some dissipation into the system of interest, while all computations in the framework of QSD remain essentially the same.

The most attractive feature of QSD lies in that the final expression for the density operator $\bar{\rho}$ contains only a sum of projection operators computed from individual realizations and does not include any nondiagonal terms like $|\psi(\xi(t), t)\rangle \langle \psi(\xi'(t), t)|$. This suggests that $\bar{\rho}$ is an incoherent mixture of all possible individual realizations characterized by $|\psi(\xi(t), t)\rangle \langle \psi(\xi(t), t)|$. Thus, one comes up with a natural interpretation of $|\psi(\xi(t), t)\rangle \langle \psi(\xi(t), t)|$: it represents an individual experiment on an open system. Indeed, QSD is much more than a numerical method. It overlaps strongly with spontaneous wavefunction collapse models, such as the Ghirardi-Rimini-Weber
(GRW) model [18], the Ghirardi-Pearle-Rimini (GPR) model [19], and the GhirardiGrassi-Rimini (GGR) gravity-induced collapse model [20]. In these models, the non-linear and stochastic terms in Eq. (7.6) are regarded as fundamental modifications to the Schrödinger equation, rather than a computational unraveling of the master equation (7.8). As such, the QSD approach to decoherence effects on quantum chaotic dynamics is both computationally economical and conceptually intriguing.

To solve Eq. (7.1) numerically via QSD, we can choose two Hermitian coupling operators $L_1 = (\sqrt{D}/\hbar)\hat{q}_1$ and $L_2 = (\sqrt{D}/\hbar)\hat{q}_2$. The master equation corresponding to Eq. (7.6) with this choice of $L_1$ and $L_2$ takes exactly the form of Eq. (7.1) in the Wigner representation. Further, we discretize the time variable by a time step $\delta t$, such that

$$|\psi(t + \delta t)\rangle = \exp(-\frac{i\mathcal{H}\delta t}{\hbar})|\psi(t)\rangle$$

$$+ \frac{D}{\hbar^2}(2\langle q_1 \rangle q_1 - q_1^2 - \langle q_1 \rangle^2)|\psi(t)\rangle \times \delta t$$

$$+ \frac{\sqrt{D}}{\hbar}(q_1 - \langle q_1 \rangle)|\psi(t)\rangle W_1$$

$$+ \frac{D}{\hbar^2}(2\langle q_2 \rangle q_2 - q_2^2 - \langle q_2 \rangle^2)|\psi(t)\rangle \times \delta t$$

$$+ \frac{\sqrt{D}}{\hbar}(q_2 - \langle q_2 \rangle)|\psi(t)\rangle W_2,$$

(7.10)

where $W_1$ and $W_2$ are two ordinary independent complex random variables satisfying these mean properties:

$$M[\Re(W_1)\Re(W_1)] = M[\Im(W_1)\Im(W_1)] = \delta t$$

$$M[\Re(W_2)\Re(W_2)] = M[\Im(W_2)\Im(W_2)] = \delta t$$

$$M[\Re(W_1)\Re(W_2)] = M[\Im(W_1)\Im(W_2)] = 0$$
\[ M[W_1] = M[W_2] = 0. \] (7.11)

Due to a weak order accuracy theory [21] for stochastic equations, the lowest order integration scheme, i.e., the Euler method, is believed to suffice many purposes. In our numerical implementation we employ this integration scheme for stochastic terms and the fourth order Runge-Kutta scheme to incorporate the nonlinear terms such as 
\[
\frac{D}{h^2}(2\langle q_1 \rangle q_1 - q_1^2 - \langle q_1 \rangle^2)\psi(t) \text{ and } \frac{D}{h^2}(2\langle q_2 \rangle q_2 - q_2^2 - \langle q_2 \rangle^2)\psi(t).
\]
As to the contribution of the first Hamiltonian term, we employ the split operator technique [22] in order to correctly account for the Hamiltonian (unitary) term with considerably large time steps. This is justified since the Hamiltonian term just represents the time evolution from time \( t \) to \( t + \delta t \) for a closed system. So for each time step, (1) the wavefunction from the previous step is first propagated as if there were no decoherence, using the split operator technique; (2) then contributions from the second and third terms on the right hand side of Eq. (7.10) are evaluated using a fourth-order Runge-Kutta scheme; (3) finally, the stochastic contributions are directly computed to obtain the fully updated new wavefunction. Although there should be many opportunities for improving this integration scheme, we trust that this quantum state diffusion-split operator approach is a systematic approach to the study of decoherence effects in many problems. Currently this approach is being applied to a scattering problem as well [23]. Note also that very recently another group proposed a similar approach (independently) to examine decoherence in a photodissociation process [24].
7.3 The Model and Calculation Details

The particular model system we examine is the same as that in Chap. 6. Its Hamiltonian is given by

\[ H = \frac{1}{2}(p_1^2 + p_2^2) + \frac{\alpha}{2}q_1^2q_2^2 + \frac{\beta}{4}(q_1^4 + q_2^4). \]  

(7.12)

As well as an integrable case with \( \alpha = \beta = 0.01 \), we still choose \( \alpha = 1.0, \beta = 0.01 \) to represent a chaotic case. This system is particularly useful for decoherence studies because (1) it has the simple energy scaling property that all trajectories can be scaled onto one energy surface, ensuring that the dynamics is essentially the same even if the system energy changes due to system-environment interaction; (2) as mentioned in Chap. 2, the dynamics of this system at \( \alpha = 1.0, \beta = 0.01 \) is strongly chaotic, enhancing the classical quantum discrepancy for the closed system and allowing for a study in the quantum regime; (3) the potential has no simple harmonic terms. Thus, any observed agreement between classical and quantum behavior can not be attributed to the similarity of classical and quantum harmonic oscillator dynamics.

Our initial preparation \( \psi(q_1, q_2, 0) \) is a two-dimensional coherent state,

\[ \psi(q_1, q_2, 0) = \frac{1}{\pi \hbar} \exp\left[-\frac{(q_1 - \bar{q}_1)^2}{2\hbar} + i\frac{\bar{p}_1 q_1}{\hbar} - \frac{(q_2 - \bar{q}_2)^2}{2\hbar} + i\frac{\bar{p}_2 q_2}{\hbar}\right] \]  

(7.13)

where \( \bar{q}_1, \bar{q}_2, \bar{p}_1, \) and \( \bar{p}_2 \) are mean positions and momenta, respectively. As discussed in Chap. 6, this choice is motivated by the desire to satisfy both the requirement that the initial state be pure and that the associated Wigner distribution be everywhere positive. The corresponding Gaussian distribution function

\[ \rho_0(q_1, q_2, p_1, p_2) = \left(\frac{1}{\pi^2 \hbar^2}\right) \exp\left[-\frac{(q_1 - \bar{q}_1)^2}{\hbar} - \frac{(q_2 - \bar{q}_2)^2}{\hbar}\right] \]
is thus also allowed in classical dynamics, i.e., quantum and classical distribution functions are identical at \( t = 0 \). Consequently, results described below are solely about decoherence effects on dynamics-induced quantum classical disagreement. The initial average positions of this distribution are the same as in Chap. 6, i.e., \( \bar{q}_1 = 0.40, \bar{q}_2 = 0.60, \bar{p}_1 = 0.50, \bar{p}_2 = 0.414 \). In addition, corresponding to the energy region of this initial preparation, the characteristic lengths of the potential estimated from

\[
\sqrt{\frac{\partial q \cdot V}{\partial q_1 \cdot V}}, \sqrt{\frac{\partial q \cdot V}{\partial q_2 \cdot V}}, \sqrt{\frac{\partial q \cdot V}{\partial q_1 \cdot q_2 \cdot V}}, \text{ and } \sqrt{\frac{\partial q \cdot V}{\partial q_2 \cdot q_2 \cdot V}}, \text{ are approximately given by } 8.0, 1.5, 1.0 \text{ and } 1.0.
\]

In the quantum computations we choose \( \hbar = 0.1, \delta t = 0.001, D = 6.0 \times 10^{-4} \). The spatial grid spacing \( \delta q_1 \) (and \( \delta q_2 \)) in FFT calculations in the split-operator technique is chosen to be 0.125. The corresponding grid size is \( 64 \times 64 \). Typically several thousands of realizations of the time dependent stochastic variables \( W_1 \) and \( W_2 \) [see Eq. (7.10)] are required. The results presented in this chapter have used 3500 stochastic realizations. The convergence can be conveniently checked by varying the time step, the grid spacing of both coordinates and the total number of stochastic realizations. \(^2\)

It is worth noting that our choice of the decoherence strength \( D \) lies close to the quantum classical transition condition predicted by the inequality (7.5). Further, due to the diffusion in the momentum space described by Eq. (7.3), the energy absorption

\(^2\)The values of the time step, the grid spacing of both coordinates, and the total number of stochastic realizations chosen here are different from those in our published work: J. Gong and P. Brumer, Phys. Rev. E. 60, 1643 (1999). This is to further demonstrate that good convergence is indeed obtained.
rate of the system is given by $D$ for each degree of freedom. This energy absorption is necessarily non-negligible for quite large $\hbar$ since $D$ scales with $\hbar^2$ according to Zurek's condition (7.5). For the case of $D = 6.0 \times 10^{-4}$, the theory predicts a 19% increase in energy at $t = 48.0$, whereas our quantum state diffusion-split operator treatment gives a 21% increase. The small discrepancy between the rigorous result and our numerical result is within our expectation since we have employed the lowest-order integration scheme for the stochastic terms.

As to classical calculations, there are also two cases, i.e., with and without the system-environment interaction. In the absence of system-environment coupling, the propagation of the classical distribution function is realized using the Monte-Carlo simulation, which consists of three steps: (1) sampling the initial Gaussian distribution by the Box-Muller technique, (2) integrating each sample trajectory according to the classical canonical equations of motion, and (3) recovering the distribution function by averaging all sample trajectories. It is found that only $5 \times 10^4$ sample trajectories are needed to obtain very accurate results. In the presence of system-environment coupling, the time evolution of the classical distribution function is given by the following Fokker-Planck equation,

$$\frac{\partial}{\partial t} \rho_t(q_1, q_2, p_1, p_2) = \left\{ H, \rho_t(q_1, q_2, p_1, p_2) \right\}$$

$$+ D \frac{\partial^2}{\partial p^2_1} \rho_t(q_1, q_2, p_1, p_2)$$

$$+ D \frac{\partial^2}{\partial p^2_2} \rho_t(q_1, q_2, p_1, p_2) \quad (7.15)$$

Just as in the case of closed classical ensembles, we need not to directly solve this
partial differential equation in a four-dimensional phase space. Instead, we further use the Monte-Carlo method in combination with a stochastic simulation of the environment for each classical trajectory. That is, in order to solve Eq. (7.15), we integrate the Langevin-Itô equations for each sample trajectory,

\[
\begin{align*}
\frac{dq_1}{dt} &= \frac{\partial H}{\partial p_1}, \\
\frac{dq_2}{dt} &= \frac{\partial H}{\partial p_2}, \\
\frac{dp_1}{dt} &= -\frac{\partial H}{\partial q_1} dt + \sqrt{2D\eta_1}, \\
\frac{dp_2}{dt} &= -\frac{\partial H}{\partial q_2} dt + \sqrt{2D\eta_2},
\end{align*}
\]

(7.16)

where \(\eta_1\) and \(\eta_2\) are two independent real differential stochastic variables satisfying \(\langle \eta_1 \rangle = \langle \eta_2 \rangle = 0\), \(\langle \eta_1^2 \rangle = \langle \eta_2^2 \rangle = dt\). Once again the Euler integration scheme for differential stochastic variables is employed. The convergence is generally faster than that in quantum calculations. Typically, \(2-4 \times 10^4\) sample trajectories and \(30-50\) realizations of \(\eta_1\) and \(\eta_2\) for each sample trajectory are sufficient.

### 7.4 Computational Results

#### 7.4.1 Expectation values

Let us begin with an examination of classical and quantum dynamics for the closed system (i.e., \(D = 0\)) case, as shown through expectation values of coordinates and momenta and "energy in a zeroth order mode". The energy of zeroth order mode is defined as \(E_1 = \langle p_1^2/2 + \beta q_1^4/4 \rangle\) and \(E_2 = \langle p_2^2/2 + \beta q_2^4/4 \rangle\), for the first and second degree
of freedom, respectively. Consider first an integrable system \((\alpha = \beta)\). Figures 7.1 and

\begin{align*}
\text{(a)} & \quad q_1(t) \\
\text{(b)} & \quad q_1^2(t) \\
\text{(c)} & \quad p_1(t) \\
\text{(d)} & \quad E_1(t)
\end{align*}

Figure 7.1: Time dependence of the four observables \(\langle q_1 \rangle, \langle q_1^2 \rangle, \langle p_1 \rangle\) and \(\langle E_1 \rangle\), for the closed integrable system case. The model is the quartic oscillator system described by Eq. (7.12) with \(\alpha = \beta\). Solid lines represent quantum results, dashed lines represent classical results. All variables are in dimensionless units.

7.2 show the time dependence of quantum and classical expectation values for four observables associated with each degree of freedom. It is seen that quantum classical agreement is spectacular even though the system is far from the classical limit and the potential is not harmonic. Evidently, correspondence in expectation values is not a problem for the integrable case.
Figure 7.2: Same as Fig. 7.1, but for the four observables \( \langle q_2 \rangle \), \( \langle q_2^2 \rangle \), \( \langle p_2 \rangle \) and \( \langle E_2 \rangle \) associated with the second degree of freedom.

By contrast, as shown in Figs. 7.3 and 7.4, when the system is strongly chaotic \((\alpha = 1.0, \beta = 0.01)\), there is strong quantum classical disagreement in expectation values for the same observables. In particular, all cases in Figs. 7.3 and 7.4 show qualitatively similar behavior, i.e., after an initial period \((t \approx 8.0)\) of quantum classical correspondence, the quantum results continue to oscillate while the classical results show smooth relaxation. Note that the quantum results do not always simply oscillate about the classical (e.g., see results for \( \langle q_1^2 \rangle \) in Fig. 7.3b and \( \langle q_2^2 \rangle \) in Fig. 7.4b). Note also that the quantum fluctuations about the mean are substantial (e.g., about
30% − 35% in the cases of $\langle E_1 \rangle$ in Fig. 7.3d and $\langle E_2 \rangle$ in Fig. 7.4d). The role of chaos in inducing interference effects is therefore clearly demonstrated. In addition, it should be pointed out that the appearance of large quantum classical discrepancies in expectation values is long after the logarithmic break time (according to the previous chapter, the break time of QCC in phase space structure is as short as $t = 1.5$ for even smaller $\hbar$).

Figure 7.3: Time dependence of the four observables $\langle q_1 \rangle$, $\langle q_1^2 \rangle$, $\langle p_1 \rangle$ and $\langle E_1 \rangle$, for the closed chaotic system case. The model is the quartic oscillator system described by Eq. (7.12) with $\beta = \alpha/100 = 0.01$. Solid lines represent quantum results, dashed lines represent classical results. All variables are in dimensionless units.
Figure 7.4: Same as Fig. 7.3, but for the four observables $\langle q_2 \rangle$, $\langle q_2^2 \rangle$, $\langle p_2 \rangle$ and $\langle E_2 \rangle$ associated with the second degree of freedom.

Parallel results for the same observables, after introducing decoherence into the chaotic system, are shown in Figs. 7.5 and 7.6. A comparison of Figs. 7.5 and 7.6 with Figs. 7.3 and 7.4 shows substantially improved QCC upon introducing decoherence. In particular, Figs. 7.5a, 7.5c, 7.6a and 7.6c show that quantum oscillations in the first-order moments are strongly suppressed by decoherence. More remarkable is the observed correspondence for the case of $\langle q_1 \rangle$ and $\langle q_2 \rangle$ (see Figs. 7.5b and 7.6b), in which the long term classical average in the closed system can deviate significantly from the long term quantum average by more than 45%. This
indicates that decoherence delocalizes quantum distribution functions within the energy shell, a conservative-system analogue of the noise-induced delocalization seen in one-dimensional quantum chaotic systems [13]. Finally, the improved correspondence in \( \langle E_1 \rangle \) and \( \langle E_2 \rangle \) is shown in Figs. 7.5d and 7.6d. The quantum classical discrepancies in the energy of zeroth order mode decrease from as large as 30\% in the closed system to less than 5\% upon introducing decoherence. This suggests that the energy transfer between different degrees of freedom is also strongly affected by decoherence effects. This observation may be of particular interest in understanding intramolecular vibrational energy flow in polyatomic molecules.

Figure 7.5: Same as Fig. 7.3, but for the open chaotic system case.
Figure 7.6: Same as Fig. 7.4, but for the open chaotic system case.

7.4.2 Individual realizations

As mentioned earlier, the stochastic evolution of pure state vectors described by Eq. (7.10) could be regarded as fundamental according to the spontaneous wavefunction collapse models. This being the case, then each stochastic realization of our computations could simulate a real individual situation even when the system is not subject to any environmental decoherence or quantum continuous measurement. This makes it even more interesting to examine the decoherence effects on the wavepacket dynamics of the stochastic Schrödinger equation using our quantum state diffusion-split
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operator approach.

Figure 7.7: Contours of constant wavefunction intensity at $t = 25$ for propagation, for the integrable system case, from the same initial state. (a) shows results for the closed system ($D = 0$); (b), (c), (d) show results for three different realizations with $D = 6.0 \times 10^{-4}$. The wavefunction intensity increases linearly at a constant spacing 0.001. All variables are in dimensionless units.

Figure 7.7 shows the contour plot of four quantum wavefunctions for the integrable case studied earlier (see Figs. 7.1 and 7.2), each evolving from the same time zero initial wavefunction. Figure 7.7a shows the result of propagation for $D = 0$ and Figs. 7.7b-d show three different $|\psi(\xi_m(t), t)\rangle$ for the nonzero $D$ at $t = 25$. Inter-
Interestingly, it is seen that in the presence of decoherence the wavepacket structure has been drastically suppressed. In particular, in Figs. 7.7c and 7.7d the wavefunctions have almost evolved into perfectly Gaussian wavepackets. Thus, for integrable systems, even though there is already very good QCC in expectation values, decoherence could still have large impact on individual realizations.

We present in Fig. 7.8 the results of similar examinations for the chaotic case at \( t = 25 \), a time by which decoherence appears to have restored considerable correspondence (see Figs. 7.5 and 7.6). A comparison of Figs. 7.8b-d with Fig. 7.8a shows that the former tend to be more localized and less distorted than the
latter. Indeed, Fig. 7.8d shows that decoherence has changed the complex structure in Fig. 7.8a into a single significant peak and some small fluctuations. In essence, the competition between chaos-induced rapid spreading and distortion of quantum wavepackets and decoherence-induced suppression of wavepacket structure is vividly demonstrated here.

7.5 Approaching the Classical Limit

Our results in this chapter so far are concerned with the deep quantum regime. As the system approaches the classical limit, correspondence in open systems is expected to improve further. However, different levels of quantum classical correspondence could lead to totally different understandings of how classical dynamics eventually emerges from quantum dynamics. First, on the level of correspondence in expectation values of some observables, results in Chap. 6 suggest that decoherence may not be necessary for correspondence even long after the logarithmic break time. Second, on the level of correspondence in phase space structure, Zurek's condition (7.5) suggests that the required decoherence strength $D$ scales with $\hbar^2$. Thus, as $\hbar \to 0$, the classical Liouville equation is restored from von Neumann's equation with the decoherence strength $D$ being vanishingly small. Third, on the level of correspondence in individual realizations, results shown in Fig. 7.8 suggest that decoherence-induced localized wavepackets in individual realizations could correspond to classical chaotic trajectories as $\hbar \to 0$.

Here we are particularly interested in the third viewpoint of correspondence.
The important problem is then on the scaling behavior of the required decoherence strength \( D \) versus \( \hbar \) for such correspondence-of-trajectory scenario. Our quantum state diffusion-split operator approach offers an opportunity for such investigations. Below we extend the previous calculations in the subsection 7.4.2 to the regimes much closer to the classical limit and then examine the localization behavior of individual realizations of the solution to the stochastic Schrödinger equation. In particular, we characterize the degree of coordinate space localization of the evolving wavepackets by the average variances of \( q_1 \) and \( q_2 \), i.e., \( [(q_1^2) - \langle q_1 \rangle^2]^{1/2} \) and \( [(q_2^2) - \langle q_2 \rangle^2]^{1/2} \), over the time interval \( 15 \leq t \leq 30 \). Note that, due to the underlying classical chaos, the wavepackets unitarily evolving from an initial minimum-uncertainty-product state would have essentially spread over the entire available phase space, even for very small \( \hbar \) considered below. Thus, any observed localization behavior of the evolving wavepackets \( |\psi(t)\rangle \) in Eq. (7.10) is due to the nonunitary terms.

We shall compare two scaling laws of \( D \) in terms of \( \hbar \), i.e.,

\[
D(\hbar) = \tilde{D}(\frac{\hbar}{0.1})^2
\]

and

\[
D(\hbar) = \tilde{D}(\frac{\hbar}{0.1})^1,
\]

where \( \tilde{D} \equiv D(\hbar = 0.1) \) is chosen to be \( 6.0 \times 10^{-4} \), a value previously shown to be large enough to substantially improve correspondence in expectation values for \( \hbar = 0.1 \). Note also that for both scaling laws \( D \) goes to zero as \( \hbar \to 0 \), with the former corresponding to Zurek’s condition Eq. (7.5). One could also consider other
scaling laws which requires much stronger $D$. For instance, one could consider

$$D(\hbar) = \tilde{D}(\frac{\hbar}{0.1})^q, \quad q \leq 0. \quad (7.19)$$

However, none of the scaling laws described by Eq. (7.19) are of interest here since they give a non-vanishing diffusion constant $D$ even in the $\hbar \to 0$ limit.

![Graphs showing scaling laws](image)

Figure 7.9: The average variance of $q_t$ over the time interval $15 \leq t \leq 30$, for three individual realizations of the evolving wavefunctions satisfying the stochastic Schrödinger equation [see Eq. (7.6)]. The Hamiltonian is given by Eq. (7.12) with $\beta = \alpha/100 = 0.01$. The initial state is the same as in the previous calculations. The scaling of $D$ in terms of $\hbar$ is chosen as (a) $D = \tilde{D}(\hbar/0.1)^2$, and (b) $D(\hbar) = \tilde{D}(\hbar/0.1)^4$.

The computations are expensive in both memory and CPU time. For the smallest $\hbar = 0.0015625$ we considered, a grid size of $2048 \times 2048$ is used. Figures 7.9 and 7.10 present the degree of wavepacket localization versus $\hbar$, for the two scaling laws of $D$ versus $\hbar$ described by Eqs. (7.17) and (7.18). The initial condition is still described by Eq. (7.14) with $\bar{q}_1 = 0.40$, $\bar{q}_2 = 0.60$, $\bar{p}_1 = 0.50$, and $\bar{p}_2 = 0.414$. 
Two key observations can be made from the results in Figs. 7.9 and 7.10. First, for the scaling law $D \propto \hbar^2$, the degree of localization of individual realizations of the evolving wavefunctions essentially remains the same as $\hbar$ goes to zero. In particular, the average variance in $q_1$ [Fig. 7.9a] stays around 0.8 for all three realizations, whereas the average variance in $q_2$ [Fig. 7.10a] is seen to be fluctuating significantly with different realizations, but still essentially scales with $\hbar^0$ as $\hbar$ becomes small. Thus, even in the semiclassical limit, individual wavefunctions evolving stochastically can still occupy an enormous part of the phase space due to classical chaos. This makes it clear that Zurek's condition [see Eq. (7.5)] for the correspondence in distribution functions does not guarantee the emergence of a classical macroscopic world comprised of extremely localized individual events. Second, for the scaling law $D \propto \hbar^1$, the degree of localization of individual realizations of the evolving wavefunctions is seen to go to zero as $\hbar$ goes to zero. Indeed, a closer examination of the results...
in Figs. 7.9b and 7.10b suggests that the average variance in $q_1$ or $q_2$ actually scales with $\hbar^{1/2}$. Thus, even with the underlying classical chaos, due to the nonunitary and nonlinear terms in the stochastic Schrödinger equation, an initial localized state can remain highly localized all the time. More significantly, due to Ehrenfest's theorem, the vanishingly small coordinate variances in the $\hbar \to 0$ limit necessarily ensure the emergence of classical chaotic trajectories satisfying Newton's equation. It can not be over-emphasized that such dramatic correspondence is achieved with the decoherence strength $D$ being also vanishingly small as $\hbar$ goes to zero.

Clearly, we have now a new picture of quantum classical correspondence in classically chaotic systems. However, it should be noted that we also have to pay a high price by discarding the linear Schrödinger equation as the fundamental law of nature.

### 7.6 Conclusion and Discussion

In this chapter we have successfully studied decoherence effects in conservative non-linear dynamics. The development of a generally useful and powerful numerical approach makes it possible to extend previous studies in the literature from one-degree-of-freedom chaotic systems to conservative chaotic systems.

To see clear-cut decoherence effects on quantum classical correspondence in expectation values, our model quantum system is chosen to be far from the semiclassical limit. Thus, (1) in the closed system case, chaos-induced quantum coherence effects shortly appear, and (2) in the open system case, decoherence effects are seen to
be able to remarkably improve quantum classical correspondence. In particular, the energy flow between different degrees of freedom, which is absent in one-degree-of-freedom systems, can also be strongly affected by decoherence. The results strongly imply that decoherence is of importance to understand the classicality of nonlinear molecular systems.

Indeed, the parameters chosen in this chapter lie in the range expected of typical molecule, which suggests the possibility of experimentally observing decoherence effects in the vibrational motion of excited polyatomics. To see this, note that a convenient dimensionless unit to compare systems is the fraction $F(t)$ of energy absorbed per degree of freedom from the bath per vibrational oscillatory period $2\pi/\omega$, relative to the level spacing $\hbar\omega$, where $\omega$ is the vibrational period. That is, $F(t) = (D/m)(2\pi/\omega)(1/\hbar\omega)$. From Eq. (7.5) we have:

$$
F(t) = \frac{2\pi D}{m\hbar^2\omega^2} > \frac{\pi \hbar \lambda}{m\chi^2\omega^2} \approx \frac{\pi \hbar}{\chi^2 m\omega}
$$

where we have assumed [25] $\lambda \approx \omega$. Typical sizes of the right hand side of Eq. (7.20) for a small molecule are on the order of $10^{-3}$, in the same range as that obtained for the model adopted in this paper. With the right hand side of Eq. (7.20) being the ratio of $\hbar$ to a typical system action, the small molecule is seen to be of the same order of “quantumness” as the adopted model.

This chapter also stresses that quantum classical correspondence in expectation values does not necessarily imply the emergence of chaotic trajectories from the quantum dynamics. Aided by the quantum state diffusion approach, this chapter also presents interesting results on the localization behavior of individual realizations.
of the evolving wavefunctions satisfying the stochastic Schrödinger equation. In particular, it is computationally shown that, while Zurek's scaling law of decoherence strength \( D \propto \hbar^2 \) can not guarantee the emergence of classical trajectories, the scaling law \( D \propto \hbar \) seems sufficient to give chaotic classical trajectories as \( \hbar \) approaches 0. Thus, quantum classical correspondence in chaotic systems is studied from both the ensemble perspective and the trajectory perspective.

Previous theoretical studies on quantum state diffusion have suggested that \( D \propto \hbar^{3} \) could lead to the emergence of chaotic trajectories from quantum dynamics [26]. Here we have taken a step further. We have employed a weaker scaling law of \( D \), i.e. \( D \propto \hbar^{1} \), with \( D \) vanishing in the \( \hbar \to 0 \) limit, and still obtain the emergence of highly localized wavepacket evolving chaotically. Note that, the diffusion constant \( D \) in the GRW and GPR wavefunction collapse models scales with \( \hbar^2 \), whereas \( D \) in the GGR gravity-induced collapse model scales with \( \hbar^1 \) [27]. Thus, our numerical results suggest that, of the three spontaneous wavefunction collapse theories, the GRW and GPR models are not favored as far as quantum classical correspondence in chaotic systems is concerned, and the GGR model could potentially explain the chaotic classicality of the macroscopic world.

To conclude, we have developed a generally useful quantum state diffusion-split operator approach to study decoherence effects in Hamiltonian systems. Applying this approach to a generic conservative chaotic system, we have shown that decoherence does indeed lead to significant improvement in classical-quantum correspondence in expectation values, i.e., quantum mechanics plus decoherence effects is in far better
agreement with the classical mechanics plus decoherence effects than is the analogous comparison in the absence of decoherence. Connecting this approach with the spontaneous wavefunction collapse models, we further show that it is possible to obtain the emergence of chaotic classical trajectories from the modified Schrödinger equation with the decoherence strength being vanishingly small as $\hbar$ goes to zero.
Bibliography


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Chapter 8

Summary and Outlook
In this thesis we have made the following significant contributions:

- Based on both a paradigm of Hamiltonian chaos and a model of kicked diatomic system, we have shown that under certain conditions even a very simple scenario can give extensive coherent control of quantum chaotic dynamics, thus opening up new directions for both coherent control and quantum chaos.

- After analyzing a variety of coherent control scenarios, we have achieved a better understanding of quantum interference effects therein. In particular, we have demonstrated the crucial role of laser-matter interaction in coherent control and concluded that the key difference between phase insensitive and phase sensitive control lies in the nature of the indistinguishability of multiple pathways to the same target state.

- We have shown, for the first time, both theoretically and computationally, that manipulating quantum interference effects in bimolecular scattering of identical molecules can have a large impact on both differential and total cross sections.

- For both closed and open chaotic systems, we have obtained substantial analytical and/or numerical results which yield many interesting and complementary perspectives on quantum classical correspondence in chaotic molecular dynamics.

Our progress in the study of coherent control, quantum chaos and decoherence in molecular dynamics suggests that much exploratory work related to their overlap remains to be done. In particular, we believe that the following directions are
attractive and important:

- **The control of quantum chaos in conservative systems.** This direction is a natural extension of the work in this thesis. On one hand, the formal controllability of all quantum systems (which of course includes conservative chaotic systems) has been well established in the literature [1]; on the other hand, simple scenarios of coherent control of conservative chaos are unavailable. Our work on coherent control of quantum chaotic diffusion suggests that controlling quantum chaos in conservative systems may also be relatively easy by taking advantage of quantum interference effects. In particular, for chaotic molecular systems the main control objective is to suppress (1) the extremely fast intramolecular energy flow and (2) the extremely fast dephasing for each individual degree of freedom. To a certain extent, these future studies will rely on the present work on quantum classical correspondence in conservative chaotic systems.

- **Quantum control based on non-unitary dynamics.** The traditional quantum control approach assumes unitary dynamics. Indeed, the superposition principle is at the heart of coherent control. However, unitarity is not the entire story of quantum physics. A complete quantum picture of molecular processes includes both unitary evolution and nonunitary wavefunction collapse (quantum measurement). While the non-unitary dynamics caused by decoherence is usually deemed as an obstacle to quantum control, it is possible that introducing quantum measurements (and, if applicable, feedback based on the results of quantum measurements [2]) in a controlled fashion can bring about new possibilities of
quantum control. Stimulated by a recent research topic called quantum Zeno and quantum anti-Zeno effects [3], one could even conceive that a chemical reaction in the quantum regime may be controlled at will by designing different ways of watching it.

- *Active control of decoherence phenomena.* The control of decoherence is a prerequisite for the extensive use of quantum interference and even quantum entanglement. A well established passive approach is to manipulate the quantum dynamics within the so called decoherence free subspace [4], which is a result of certain symmetries of system-environment interaction. However, the ultimate goal, which is of extreme importance to coherent control and quantum information processing, is active control of decoherence. During the completion of this thesis, we noted that a number of active scenarios for the control of decoherence were discovered [5]. A common feature of these scenarios is that they require that the external control fields strongly affect the system in order to be controlled on a time scale much shorter than that of the system-environment interaction. Such requirement is not necessarily expensive, and may be indispensable for controlling decoherence.
Bibliography


