Coherence and Control in Photo-molecular Wave Packet Dynamics

by

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Abstract

Wave-mechanical phenomena such as resonance and interference, in both light and matter, are central to the principles of quantum coherent control over molecular processes. Focusing on the dynamical aspects, this dissertation is a compilation of studies on the interaction physics involving wave packets in molecules, the driving light field, and the underlying coherence and control. In each work, we will demonstrate interesting correlations between the properties of a carefully designed excitation light field and desirable outcomes of the molecules quantum dynamics.

We will analyze the dynamical effect of a Feshbach resonance in the adiabatic Raman photoassociation for ultracold diatomic molecule formation from ultracold atoms. A narrow resonance is shown to be able to increase the effective number of collisions, in an ultracold atomic gas, that are available for photoassociation. This results in an optimal resonance width much smaller than the atomic collision energy bandwidth, due to the balance between the effective collision rate and single-collision transfer probability. Next, we demonstrate the linear molecular response to high-intensity, broadband, shaped optical fields. We show that this originates from interferences based on intra-pulse Raman excitations, and thus response linearity is not unique to the first-order perturbative limit and can not be used to infer the strength of the field. In the last study, we simulate the stochastic vibrational wave packet and dissociation-flux dynamics in a molecule excited by light with temporal and spectral incoherent properties. Between this case and that using a coherent pulse with the same spectral profile, we compare the vibrational wave functions and the loss of electronic and vibrational coherence, and demonstrate the qualitative difference between coherently and incoherently driven dynamics in molecules.
Preface

A large portion of materials in Chapter 3 was published in the article: A.C. Han, E. Shapiro, M. Shapiro, *Pulsed adiabatic photoassociation via scattering resonances*, J. Phys. B: At. Mol. Opt. Phys. 44, 154018 (2011). This Chapter is a continuation from many previous studies by Evgeny Shapiro and Moshe Shapiro, where a large part of the analytical framework (some of section 2 of the publication), and some computational tools, have already been developed. The author contributed in combining some existing but previously separate analytical models (section 2), and building extended computational programs for these models (section 3). The author also carried out the numerical computations, whose results could not be trivially seen from the analytical framework (section 3). Other parts of the publication, not included in this thesis, have main contribution from Evgeny Shapiro and Moshe Shapiro.

Chapter 4 section 1 was published in the articles: A.C. Han, M. Shapiro, *Linear response in the strong field domain*, Phys. Rev. Lett. 108, 183002 (2012), and section 2 in: A.C. Han, M. Shapiro, *Linear response in the strong-field domain: ultrafast wave packet interferometry in the continuum*, J. Phys. B: At. Mol. Opt. Phys. 46, 085401 (2013). In the first publication, Moshe Shapiro conceived the idea and analytical framework. The author carried out the analytical derivation, chose the appropriate optical shaping methods, developed the numerical computational tool and carried out the numerical investigation, under the guidance of Moshe Shapiro. The second publication is by invitation from Journal of Physics B, as a continuation of the first article. The two authors together developed the conceptual setup, and the current author constructed the analytical time-domain model as an extension to the frequency-domain one in first publication. The au-
Author developed the computational program, and conducted the numerical analysis.

Chapter 5 is based largely on the publication: A.C. Han, M. Shapiro, P. Brumer, *Nature of quantum states created by one photon absorption: pulsed coherent vs pulsed incoherent light*, J. Phys. Chem. A, 117, 8199-8204 (2013). Moshe Shapiro developed a theoretical framework based on concepts conceived together with Paul Brumer. The author developed the analytical derivation and the computational tools, and tested the hypothesis on various model molecular potentials.
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To my parents and my wife
Chapter 1

Introduction

1.1 Motivation

The wave nature of matter is one of the central concepts in modern physical sciences. In particular, the quantum mechanical formulation of molecules has given rise to modern quantum chemistry, based on the Born-Oppenheimer structure for the constituent electrons and nuclei. Quantization of physical observables, a direction implication of the quantum theory, not only results in more accurate understanding of physical and chemical properties of molecules, at equilibrium and during the time-dependent evolution, but also opens up intriguing opportunities for experimentalists to actively influence, even to engineer, the outcome of physical and chemical processes, utilizing properties unique to their wave nature, such as resonances and interferences.

Among many approaches to tuning into the wave, or, as we will refer to throughout this thesis, coherent, aspects of molecules, is the molecular excitation using coherent electromagnetic wave, or simply light. This approach is rather intuitive, considering mechanically that light, in particular its time-varying electric field, exerts direct forces on most of constituent charged particles in the molecule, such as positively charged protons and negatively charge electrons. More naturally existing light-molecule interaction phenomena range from vision in almost all animals, to the very life-creating process of photosynthesis.

The strongest interaction between electromagnetic wave and matter is the action of the electric field on the molecule’s electronic and nuclear dipoles. At appropriate optical frequencies, such interaction can bring the molecule very efficiently into other quantum states with different physical properties. If the molecule is also quite isolated from the environment, its
structure and dynamics, in the presence of the effects of optical radiation, can be effectively and efficiently analyzed and understood via basic wave formulation of quantum mechanics. The classical treatment of light and quantum mechanical formulation of matter is commonly referred to as semi-classical theory of light-molecule interaction.

The principle of influencing molecular processes using electromagnetic waves is then sound, but the actual practice also requires the coherent manipulation of the electric field itself. Thanks to modern inventions of laser light sources, and technologies for the purposes of manipulating laser pulses, the laser excitation of molecules makes the \textit{coherent control} of molecular processes feasible. Lasing, in its most basic form, signifies our understanding and control over the light generation. In a classical (as opposed to quantum-optical) sense, it is exactly because of the control over the phase degree of freedom that gives us the generation of laser light: countless number of smaller, time-varying electric fields at the same frequency oscillate synchronously, to produce a very stable, large amplitude, sinusoidal total field. The extreme care given, in the first place, to produce such coherent light would then be utilized for coherent control of molecular waves.

The bandwidth of the excitation light, i.e. the range of frequencies or “colours” in its spectrum, suggests two categories for laser excitation of molecules. Considering the natural timescale for the motion of nuclei in molecules is femtoseconds \((10^{-15} \text{ second})\), laser pulses with duration a few order of magnitude higher (e.g. nanoseconds) are considered and commonly referred to as “continuous wave”, or CW for short. In the spectral domain, the long duration translates to a narrow bandwidth. Thus, the energy uncertainty in the molecular excitation is narrow, in comparison with the energy splittings in the quantized energy structure of the molecule. In most cases then, only single quantum eigenstate of a molecule is excited by CW light, while the phase of the light wave, imparted to the molecular wave function as a total phase, is unobservable and irrelevant for the excitation outcome.

However, the usage of CW light at more than one frequencies does enable us to influence molecular processes, via tuning the mutual phase between the two components. The early theoretical and experimental demonstra-
tions developed mainly by Moshe Shapiro and Paul Brumer, in the subfield between physics and chemistry known as *quantum coherent control*, involved techniques based on such multi-colour interference effects.

As technologies on producing and manipulating laser pulses with shorter and shorter durations mature, more researchers have turned to utilized broadband pulses to conduct coherent control studies. In most of today’s optics labs, it’s very convenient to produce short optical pulses with duration of a few tens of femtoseconds, if not shorter. This is comparable to the natural vibrational timescale of molecules, which, in the energy domain, corresponds to the pulse’s wide spectral band and the consequent ability to excite a number of vibrational eigenstates of the molecule with, more importantly, tuneable phase correlations. Such ultrashort, broadband, coherent pulses serve as an application of a large number of CW components, all exciting the molecule at the same time. Pulse shapers, either in the spectral or spatial domain, in particular, provides us with convenient spectral manipulation of such collection of CW components. Such superpositions of a large number of eigenstates, in both light and matter, corresponding to a large range of frequencies, are referred to as *wave packets*. So coherent control, in particular for molecular processes involving wave packets, has never been such an easy task if not for ultrafast laser sources and methods of pulse shaping.

On top of these two categories of CW vs. broadband optical excitation of molecules, additional regimes of light-matter interaction are divided according to the intensity of the excitation light. Such classification is, however, not new or unique to optical excitations. Perturbation, in any physical form, is well understood in the quantum theory, and can be classified according to its effect on changing the original quantized structure of the matter it is applied upon. We leave the detailed theoretical definition to the next section, since its physical interpretation can not stand alone without it. However, it is informative to outline that, with ever-increasing intensity of the optical excitation, the number of molecular eigenstates participating in any interference effect also increases. This can be due to the increased number of states the molecule can reach through various multiphoton processes, or, because
of the multiple times an eigenstate interfere with itself, while having reached some other intermediate states.

A third dimension in the categorization of photo-molecular interaction brings us back to the very quantification of coherence. If the phase correlation between the CW components of light, thus also between quantum eigenstates of molecules excited, is lost, what happens to the dynamics and controllability? It then becomes one of the goals of this thesis, to demonstrate some particular cases where we can very clearly observe the effects of photoexcitation of molecules under incoherent light.

In summary, what really motivates modern research, in the context of this doctoral dissertation, on coherent control of the complex dynamics of molecules and many aspects of molecular processes, is based on (1) the wave nature of molecules, and its very intimate relation to optical coherence during its photoexcitation, and (2) how utilizing the interference, i.e. the phase degree of freedom alone, can give us great influence over these molecular processes.

1.2 Thesis outline

In Chapter 2, we will first briefly outline the theoretical background as the foundation upon which all studies of this thesis are rooted. We will describe the quantum mechanical structure and dynamics of molecules, and the mathematical details of their interaction with electromagnetic waves.

A few topics concerning different physical systems, but with common underlying physical mechanism, principles and strategies are then presented in separate chapters. The first study of Chapter 3 aims to improve ultracold molecule production via photoassociating colliding ultracold atoms, utilizing scattering resonances. An optical excitation method rooted in the process of STIRAP (“STImulated Raman Adiabatic Passage”), has been developed by Moshe Shapiro prior to this study. But to also utilize the very versatile magnetic manipulation of Feshbach scattering resonances in the atomic gases, we wish to update the scheme by analyzing the role resonances play both in energy and time domains during the photoassociation. The result is both
counter-intuitive and insightful: there exists an optimal resonance width, balancing the competition between large photoassociation rate with short collision durations (large resonance width) and lowered rate with stretched collision time (narrow resonance width).

Two studies described in Chapter 4 share the same topic of linear molecular response in the strong-field regime of optical excitations. On the fundamental level, they originate from some core ideas and importance of coherent control, and the role it plays (actively or passively) in interesting physical phenomena. They are based on the fact that, although a first-order perturbative potential causes quantum state transition probabilities to depend linearly on the perturbation strength, the converse statement is not true. Namely, a linear response curve does not exclusively come from a perturbative excitation. We demonstrate, in the optical case, that such linearity can also come from a broadband, spectrally shaped, high-intensity field. We introduce various spectral shape modifications to the excitation pulse, both amplitude-only and phase-only, so that the multiple excitation pathways interfere, and we show that what follows may drastically differ in the response linearity.

The inseparable link between light and matter is again of central focus in the fourth study described in Chapter 5. With the rise of “quantum biology”, misconceptions and over-generalizations often occur in the booming new research area. Many heated debates ensued on whether experimental findings of long-lasting quantum coherence in light-harvesting molecule do exist in nature under sunlight. We approach this problem from the very initial stage of the physical process: the photo-absorption, and analyze electronic coherence in simple molecules created by coherent vs. incoherent light pulses. In the weak-field domain, an intuitive theory shows that the molecular vibration is directly and strongly influenced by the waveform of the incident light field that drives it, and hence acquires the same degree of coherence. Light as incoherent as sunlight would then create molecular vibrations that destroy interference between Born-Oppenheimer states of the molecule, hence also its electronic coherence, with a much faster rate than its coherent counterpart.
1.2. Thesis outline

Final conclusions are provided in the last chapter, both as a general summary overwviewing the studies covered, as well as to outline and motivate further topics that can be studied in the general theme of coherence, control, and wave packet dynamics.
Chapter 2

Theoretical background

2.1 Quantum structure and dynamics of molecules

2.1.1 Motion of a particle in central potential

Central to the quantum mechanical formulation of matter is the time-dependent Schrödinger’s equation

\[ i\hbar \frac{d}{dt} |\Psi(t)\rangle = H |\Psi(t)\rangle, \]  

(2.1)

where, in Dirac’s notation, |\Psi(t)\rangle is the time-dependent state of the physical system that evolves in time, whose first time derivative is given as the action of the Hamiltonian operator on the state. When expanded as a series of time-independent eigenstates of the Hamiltonian, multiplied with their respective time-dependent phase factor coefficients, the Schrödinger’s equation is effectively translated into a set of differential equations for the coefficients, using the orthonormality of the eigenstates,

\[ i\hbar \frac{d}{dt} \left( \sum_n c_n(t) |\psi_n\rangle \right) = H \left( \sum_n c_n(t) |\psi_n\rangle \right) = \sum_n c_n(t) E_n |\psi_n\rangle \]

\[ \Rightarrow \quad i\hbar \frac{d}{dt} c_n(t) = E_n c_n(t) \quad \Rightarrow \quad c_n(t) = c_n(0)e^{-iE_n t/\hbar}. \]  

(2.2)

So, eigenstates to the total Hamiltonian of the system not only serve as the quantum state with well defined energies, but also become the natural first steps to solve the dynamical problem.

Particularly relevant to molecular systems is the problem for the mo-
2.1. Quantum structure and dynamics of molecules

tion of a particle of mass \( \mu \) experiencing a potential energy \( V(\mathbf{r}) \), in three dimensions. The Hamiltonian includes the kinetic and potential energies \([1]\),

\[
H = \frac{\hat{p}^2}{2\mu} + V(\mathbf{r}),
\]  

(2.3)

and has eigenstate wave functions satisfying

\[
\left[ \frac{\hat{p}^2}{2\mu} + V(\mathbf{r}) \right] \Psi_E(\mathbf{r}) = E \Psi_E(\mathbf{r}).
\]  

(2.4)

The spatial representation of the momentum operator, in spherical coordinate system, is

\[
\frac{\hat{p}^2}{2\mu} = \frac{1}{2\mu} \left( \hat{p}_r^2 + \frac{L^2}{r^2} \right)
\]

\[
\hat{p}_r = \frac{\hbar i}{r} \frac{\partial}{\partial r} r = \frac{\hbar i}{r} \left( \frac{\partial}{\partial r} + \frac{1}{r} \right),
\]  

(2.5)

where the squared total angular momentum operator

\[
\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]
\]  

(2.6)

has eigenstate wave functions satisfying

\[
\hat{L}^2 Y_l^m = \hbar^2 l(l + 1) Y_l^m,
\]  

(2.7)

which are commonly known as the spherical harmonics.

A so-called central potential, which originates from conservative forces such as the Coulomb (electro-static) interaction force between charged particles, has an isotropic functional form, i.e. independent from the angular coordinates. We can then write \( V(\mathbf{r}) = V(r) \), making the energy eigenvalue relation

\[
\left[ \frac{1}{2\mu} \left( \hat{p}_r^2 + \frac{L^2}{r^2} \right) + V(r) \right] \Psi_E(r, \theta, \phi) = E \Psi_E(r, \theta, \phi).
\]  

(2.8)
In this case, \( \hat{L}^2 \) commutes with \( \hat{p}_z^2 \) and \( V(r) \) since neither has angular dependence, making it a compatible observable with the entire Hamiltonian. The consequence is that a state of the form

\[
\Psi_{E,l,m}(r, \theta, \phi) = Y_l^m(\theta, \phi) \frac{\phi_E(r)}{r},
\]

must be a simultaneous eigenstate to both the Hamiltonian and \( \hat{L}^2 \). Then, the \( \hat{L}^2 \) operator will be replaced by its eigenvalue in equation (2.8), and the factorization of \( 1/r \) will simplify the resulting equation

\[
\left[ \hat{p}_z^2 \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) \right] \frac{\phi_E(r)}{r} = \frac{\hat{p}_z^2}{2\mu} \frac{\phi_E(r)}{r} + \frac{h^2}{r} \left[ \frac{h^2 l(l+1)}{r^2} + V(r) \right] \phi_E(r)
\]

\[
= \frac{1}{r} \left[ - \frac{h^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{h^2 l(l+1)}{r^2} + V(r) \right] \phi_E(r)
\]

\[
= E \frac{\phi_E(r)}{r}
\]

(2.10)

to

\[
\left[ - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + U_l(r) \right] \phi_{E,l}(r) = E \phi_{E,l}(r),
\]

\[
U_l(r) = \frac{h^2 l(l+1)}{2\mu r^2} + V(r),
\]

(2.11)

an effective 1D problem in the radial direction that describes the motion of a mass \( \mu \), in angular momentum channel \( (l, m) \) with effective potential \( U_l(r) \), consisting of the original central potential plus a centrifugal term. Notice that the quantum number \( m \) does not enter the effective Hamiltonian, hence not determining the energy eigenvalues. So for brevity, the eigenstates are not labelled by \( m \), although in principle, do require its specification. The eigenvalues to this problem will then be the energy eigenvalues to the original central potential problem, and the set of eigenfunctions \( \phi_{E,l}(r) Y_l^m(\theta, \phi) \) solves any time-dependent motion of the particle in the central potential.
2.1. Quantum structure and dynamics of molecules

2.1.2 Born-Oppenheimer states of molecules

A molecule consists of a collection of electrons and nuclei, bounded in a localized region of space, with certain geometric configurations. In order to analyze the structure of a molecule, for example the geometric organization of the nuclei or electronic wave functions and energies, we need to start by defining its quantum mechanical Hamiltonian, and then solving it by finding the energy eigenstates in which the molecule has a stable structure. To the strongest effect, electrostatic potential energies govern the interactions between the constituent electrons and nuclei of the molecule. We therefore include, in addition to the kinetic energies, only Coulomb interaction in the molecular Hamiltonian

\[ H_{\text{mol}}(r,R) = \hat{T}_N(R) + V_{NN}(R) + \hat{T}_e(r) + V_{ee}(r) + V_{eN}(r,R) \]

\[ = \sum_j \frac{-\hbar^2}{2M_j} \nabla^2_R j + \frac{e^2}{4\pi\epsilon_0} \sum_{j\neq k} \frac{Z_i Z_j}{|R_j - R_k|} + \frac{-\hbar^2}{2m} \sum_j \nabla^2_r j \]

\[ + \frac{e^2}{4\pi\epsilon_0} \sum_{j\neq k} \frac{1}{|r_j - r_k|} + \frac{e^2}{4\pi\epsilon_0} \sum_{j,k} \frac{-Z_j}{|r_j - R_k|}, \] (2.12)

which has energy contributions from kinetic energies of nuclei \( \hat{T}_N(R) \) and electrons \( \hat{T}_e(r) \), electrostatic energy between nuclei \( V_{NN}(R) \), between electrons \( V_{ee}(r) \), and between nuclei and electrons \( V_{eN}(r,R) \). The set of all nuclear coordinates is denoted by shorthand notation \( R = \{R_j\} \), with \( j \) labelling each nucleus, and electronic coordinates by \( r = \{r_k\} \), with \( k \) labelling each electron. The effective electronic Hamiltonian then includes all terms involving the electrons,

\[ H_e(r,R) = \hat{T}_e(r) + V_{NN}(R) + V_{ee}(r) + V_{eN}(r,R), \] (2.13)

so that

\[ H_{\text{mol}}(r,R) = H_e(r,R) + \hat{T}_N(R). \] (2.14)

The Born-Oppenheimer formulation then proceeds to first solving the electronic problem, by looking for the electronic eigenstates to the electronic
2.1. Quantum structure and dynamics of molecules

Hamiltonian,

\[ H_e(r, R) \Phi_n(r, R) = W_n(R) \Phi_n(r, R) \]  \hspace{1cm} (2.15)

where the electronic energy eigenvalue is expected to be dependent on the
nuclear coordinates. The electronic energy eigenvalues \( W_n(R) \) are there-
fore a function of \( R \) as well, and are also known as the Potential Energy
Surfaces (PES), for the electronic state labelled by \( n \). Depending on the
nuclear degree of freedom of the molecule, namely the number of coordinate
variables in set \( R \), these PES’s in general are multi-dimensional. Therefore,
such “electronic structure” problem becomes an essential step towards ana-
lyzing any structural and dynamic properties of the molecule. In practice,
however, the main research effort on tackling the electronic problem lies
in the branch of quantum chemistry, where systematic and sophisticated
analytical and computational methods have been developed. For practical
considerations of this thesis, much of the electronic structural information
is therefore obtained using quantum chemistry softwares, or assumed from
previous studies.

Assuming such electronic problem is solved, i.e. the electronic wave
functions and the potential energy surfaces are known, then the well-known
Born-Oppenheimer approximation asserts that the total energy eigenstate
wavefunction \( \Psi(r, R) \) to the total molecular Hamiltonian is separated into a
nuclear and an electronic part,

\[ \Psi_{n,E}(R, r) = \chi_E(R) \Phi_n(r, R). \]  \hspace{1cm} (2.16)

Substituting it into the eigenvalue relation for the total Hamiltonian, we
have an equation for the nuclear part

\[
H_{mol}(r, R) \Psi_{n,E}(R, r) = \left[ \hat{T}_N(R) + H_e(r, R) \right] \chi_E(R) \Phi_n(r, R) \\
= \left[ \hat{T}_N(R) + W_n(R) \right] \chi_E(R) \Phi_n(r, R) \\
= E \chi_E(R) \Phi_n(r, R). \]  \hspace{1cm} (2.17)

The adiabatic approximation within the Born-Oppenheimer formulation
now assumes the electronic states are such that

\[
\int \Phi_n^*(r, R) \hat{T}_N \Phi_n(r, R) dr = 0,
\]
simplifying the above equation to a pure nuclear one,

\[
[\hat{T}_N(R) + W_n(R)] \chi_E(R) = E \chi_E(R). \tag{2.18}
\]

This equation becomes especially clear for diatomic molecules, where, upon changing to the centre of mass frame, the nuclear kinetic operator is for the reduced mass \( \mu \), and the PES is a function of only the bond length magnitude \( R = |R| \),

\[
\left[ -\frac{\hbar^2}{2\mu} \nabla^2 + W_n(R) \right] \chi_E(R) = E \chi_E(R). \tag{2.19}
\]

This amounts to the exact setup of the central potential problem, where the eigenstate solutions are known to be \( \chi_{n,l,\nu}(R) = \phi_{n,l,\nu}(R) Y_{m}^{l}(\theta, \phi) \), with \( \phi_{n,l,\nu}(R) \) being the vibrational eigenstate to the 1D problem

\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + U_{n,l}(r) \right] \phi_{n,l,\nu}(r) = E_{\nu} \phi_{n,l,\nu}(r), \tag{2.20}
\]

with effective potential

\[
U_{n,l}(R) = W_n(R) + \frac{\hbar^2 l(l + 1)}{2\mu R^2}.
\]

So, a full energy eigenstate of a molecule can then be uniquely referred to as the \( \nu' \)th vibrational level, belonging to the electronic state \( n \) and rotational channel \( l \) (sometimes symbol \( J \) is used in the place of \( l \)), in the absence of other mechanisms that may add further quantum numbers. We can then also write the wave function of the eigenstate as

\[
\Psi_{n,l,\nu}(r, R) = \frac{\phi_{n,l,\nu}(R)}{R} Y_{m}^{l}(\theta, \phi) \Phi_n(r, R). \tag{2.21}
\]

In some situations we analyze in this thesis, only a small number of
2.2. Photoexcitation of molecules

Born-Oppenheimer energy eigenstates of diatomic molecules are relevant to the physical process. In this case, the time-dependent quantity will be in fact the complex amplitude associated with each eigenstate, subject to the light-molecular interaction dynamics that we will outline in the next section. However, some cases can involve a large number of eigenstates, or continuum eigenstates which need to be included for a continuous range of energies. Then the direct analysis of the dynamics of complex amplitudes become less transparent, comparing with a rather more concise and convenient approach to simply combine vibrational states within the same rotational-electronic channel into a vibrational wave packet

$$\Psi_{n,l}(r,R) = \frac{\psi_{n,l}(t,R)}{R} Y_{l}^{m}(\theta,\phi)\Phi_{n}(r,R). \quad (2.22)$$

The time dynamics would be accounted for within the motion of the wave packet, and the initialization of molecular population in various eigenstates, would translate to the specification of spatial wave function for the initial vibrational wave packet.

The advantage of analyzing vibrational wave packets will become clear in the study in chapter 4 and 5, where spatial-temporal insights can be gained from looking at the wave packet dynamics. However, the wave packet methods does pose computational constraints, since for long times, care must be given to its spatial divergence, a problem absent when using energy eigenstate amplitudes.

### 2.2 Photoexcitation of molecules

#### 2.2.1 Dipole transitions

The Born-Oppenheimer structure of molecules tells us that the complex structure of molecules will be reflected in the additional quantum numbers labelling its full energy eigenstates. They refer to many degrees of freedom of molecular motions, such as vibration and rotation of nuclei, and motions of the electrons. Their wave functions can be, in principle, obtained via stages of solving the electronic and nuclear Hamiltonian problems. Once known,
2.2. Photoexcitation of molecules

these eigenstate wave function, in turn, would be very useful in analyzing interaction scenarios between the molecule and other mechanisms that can induce transitions between these Born-Oppenheimer states.

Central to all studies in this thesis is the photoexcitation of molecules. Due to the large difference in length scales, the electric field \( \mathbf{E}(t) \) of the excitation light (with wavelength at hundreds of nanometers) is considered to be spatially uniform across the molecule (sizes of angstroms to nanometers). To the strongest effects [2], the electric field interacts with the molecule’s total electric dipole \( \mu \) (a spatial vector). This calls for an additional term in the Hamiltonian of the system, describing light-molecule interaction energy

\[
H = H_{\text{mol}} - \mu \cdot \mathbf{E}(t),
\]

(2.23)

where the total dipole of the molecule consists of dipoles from each of the constituent electrons and nuclei

\[
\mu = \sum_j (-e \mathbf{r}_j) + \sum_j eZ_j \mathbf{R}_j = \mu_e(\mathbf{r}) + \mu_N(\mathbf{R}),
\]

(2.24)

where we use shorthand notation \( r \) and \( R \) to refer to the sets of electronic and nuclear position vectors.

This additional term’s time-dependence comes only from the time-varying electric field of light, which we require on physical ground to satisfy \( \mathbf{E}(t \to \pm \infty) = 0 \). The physical picture is then, for times long before and long after the photoexcitation, the asymptotic total Hamiltonians are simply \( H_{\text{mol}} \), the molecular Hamiltonian. During the light pulse, the molecule makes transitions between the energy eigenstates, because of the previously non-existing coupling between the energy eigenstates now provided by the field-dipole interaction term.

Therefore, it becomes essential to obtain the matrix elements of the interaction Hamiltonian, which is proportional to those for the dipole operator \( \mu \), in the basis of the molecular energy eigenstates \( |\Psi_{n,l,\nu}\rangle \) to \( H_{\text{mol}} \). Without writing out the full coordinate dependence, we only separate the molecular eigenstate into the electronic and nuclear parts as \( |\Psi_{n,l,\nu}\rangle = \)
2.2. Photoexcitation of molecules

\[ |\chi_{n,l,\nu}(R)\rangle |\Phi_n(r, R)\rangle, \text{ and calculate the matrix elements of the interaction as} \]

\[
\langle \Psi_{n',l',\nu'} | \mu | \Psi_{n,l,\nu} \rangle \\
= \int \int \left[ \chi_{n',l',\nu'}(R) \Phi_{n'}(r, R) \right]^* \mu(r, R) \left[ \chi_{n,l,\nu}(R) \Phi_n(r, R) \right] dR dr \\
= \int \chi_{n',l',\nu'}^*(R) \left\{ \int \Phi_{n'}^*(r, R) \mu_e(r) \Phi_n(r, R) dr \right\} \chi_{n,l,\nu}(R) dR \\
+ \int \chi_{n',l',\nu'}^*(R) \mu_N(R) \chi_{n,l,\nu}(R) \left[ \int \Phi_{n'}^*(r, R) \Phi_n(r, R) dr \right] dR.
\]

(2.25)

This very explicit expression for the matrix elements, especially off-diagonal ones with \((n', l', \nu') \neq (n, l, \nu)\), classifies dipole-induced transitions into two types:

(i) Vibrational transitions between electronic states, when \(n \neq n'\). The inner electronic integral between orthogonal electronic wave functions then makes the second term zero. So matrix element is determined solely by the first term, involving the integration of the two vibrational wave functions, and the electronic transition dipole moment, also known as transition dipole function. In many molecules, such transition dipole moment function is varying very slowly with nuclear coordinates \(R\), comparing with the vibrational functions themselves. Such situation gives rise to the \textbf{Franck-Condon approximation}, where the transition dipole function is taken out of the integration over \(R\), and the matrix element is proportional to the product \(D_{n',n} F_{(\nu',l',\nu,l)}\), where \(D_{n',n}\) is the approximated transition dipole function, and \(F_{(\nu',l',\nu,l)}\) is the \textbf{Franck-Condon factor} between the two vibrational levels. This type of transitions is the focus of this thesis.

(ii) Pure vibrational transitions within a single electronic state, when \(n = n'\). In this case, the inner integral in the second term between the electronic wave functions is nonzero. Thus the entire second term contributes, and represent, for the off-diagonal elements, the transitions due to the nuclear dipole. The electronic integral in the first term, on the other hand, now involves the same electronic wave function for the electronic state labelled
2.2. Photoexcitation of molecules

by $n$. For homonuclear diatomic molecules, the symmetries of the electronic wave function combined with that of the electronic dipoles make such integral zero, whereas it is not zero in principle for heteronuclear diatomic molecules.

A great part of the rich content of photo-molecular physics and chemistry is based on our understanding of and direct access to the details of such dipole-induced transitions in molecules. While conventional spectroscopy aims to investigate and discover molecular properties based on the observations from light emissions following these transitions, our ability to influence the light field, thus also the matrix elements of the light-molecule dipole interaction Hamiltonian, can also result in many selective manipulation of molecular processes. In the following sections, we will present some theoretical demonstrations of such control ability.

2.2.2 Perturbation theory

Perturbation theory is a mathematical framework that can be especially beneficial for the analytical calculations for light-induced transitions in molecules. The general setup for the time-dependent formulation starts, again, by identifying a molecular part and interaction part in the total Hamiltonian, as in equation (2.23),

$$H(t) = H_{\text{mol}} + H_{I}(t),$$

where $H_{\text{mol}}$ has Born-Oppenheimer eigenstates $|E_j\rangle$ with shorthand index $j$ including all relevant quantum numbers.

Assuming a general molecular state as an expansion

$$|\Psi(t)\rangle = \sum_{j} b_j(t)e^{-iE_jt/\hbar} |E_j\rangle,$$  \hspace{1cm} (2.26)

the Schrödinger’s equation for the total Hamiltonian

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = H(t) |\Psi(t)\rangle,$$  \hspace{1cm} (2.27)

can be rewritten, using the molecular and interaction parts of the Hamiltonian.
nian, in the so-called interaction picture as

\[ i\hbar \frac{d}{dt} b(t) = H_I(t) b(t), \]  

(2.28)

with eigenstate amplitude vector

\[ [b(t)]_j = b_j(t) \]

(2.29)

and interaction Hamiltonian matrix

\[ [H_I(t)]_{ij} = \langle E_i | H_I(t) | E_j \rangle e^{i(E_i - E_j)t/\hbar}. \]

(2.30)

Then, the perturbation expansion proceeds by presenting a recursive solution for the state amplitude vector in the form

\[ b(t) = b(-\infty) + \frac{-i}{\hbar} \int_{-\infty}^{t} H_I(t_1) b(t_1) dt_1, \]

(2.31)

where we see the value of \( b(t) \) at time \( t \) depends on not only its initial condition \( b(-\infty) \) but also its entire history from the beginning until time \( t \) inside the integral. Then, repeatedly applying this formula to the “history” state amplitudes inside the integral, we can generate the infinite series

\[
\begin{align*}
\mathbf{b}(t) &= \mathbf{b}(-\infty) + \frac{-i}{\hbar} \int_{-\infty}^{t} H_I(t_1) \left[ \mathbf{b}(-\infty) + \frac{-i}{\hbar} \int_{-\infty}^{t_1} H_I(t_2) \mathbf{b}(t_2) dt_2 \right] dt_1 \\
&= \mathbf{b}(-\infty) + \frac{-i}{\hbar} \int_{-\infty}^{t} H_I(t_1) \mathbf{b}(-\infty) dt_1 \\
&\quad + \left( \frac{-i}{\hbar} \right)^2 \int_{-\infty}^{t} H_I(t_1) \int_{-\infty}^{t_1} H_I(t_2) \mathbf{b}(t_2) dt_2 dt_1 \\
&= \mathbf{b}(-\infty) + \frac{-i}{\hbar} \int_{-\infty}^{t} H_I(t_1) \mathbf{b}(-\infty) dt_1 \\
&\quad + \left( \frac{-i}{\hbar} \right)^2 \int_{-\infty}^{t} H_I(t_1) \int_{-\infty}^{t_1} H_I(t_2) \mathbf{b}(-\infty) dt_2 dt_1 \\
&\quad + \left( \frac{-i}{\hbar} \right)^3 \int_{-\infty}^{t} H_I(t_1) \int_{-\infty}^{t_1} H_I(t_2) \int_{-\infty}^{t_2} H_I(t_3) \mathbf{b}(t_3) dt_3 dt_2 dt_1 \\
&= \ ...
\end{align*}
\]

(2.32)
which can compactly written as

\[
\begin{align*}
\mathbf{b}(t) &= \left[ 1 + \sum_{n=1}^{\infty} U^{(n)}(t) \right] \mathbf{b}(-\infty), \\
U^{(n)}(t) &= \left( -\frac{i}{\hbar} \right)^n \int_{-\infty}^t \int_{-\infty}^{t_1} \ldots \int_{-\infty}^{t_{n-1}} H_I(t_1)H_I(t_2) \ldots H_I(t_n) dt_n \ldots dt_1.
\end{align*}
\]

(2.33)

In most cases, such Dyson series [3] converges, with higher \( n \) terms contributing negligibly to the values of \( \mathbf{b}(t) \). Accordingly, we refer to \( U^{(n)}(t) \) as being responsible for the “\( n \)'th order” perturbation or transition.

With this formulation, we can analyze a very particular type of the photoexcitation of a “ladder” \( N \)-state system, where \( H_I \) has nonzero element only for neighbouring states, and initial population is completely in \( |E_1\rangle \), i.e. \( \mathbf{b}(-\infty) = (1 \ 0 \ldots \ 0)^T \equiv \hat{\mathbf{e}}_1 \) in the basis of \( \{ |E_1\rangle, |E_2\rangle \ldots |E_N\rangle \} \). In this case, \( H_I \) can in fact be written in the form of “ladder operators” due to its matrix element arrangement, \( H_I(t) = A^\dagger(t) + A(t) \), where \( A(t) \) has only nonzero element at its lower sub-diagonal. We can then calculate arbitrary \( b_{m>1}(t) \) as

\[
b_m(t) = \hat{\mathbf{e}}_m \left[ 1 + \sum_{n=1}^{\infty} U^{(n)}(t) \right] \hat{\mathbf{e}}_1 = \hat{\mathbf{e}}_m \sum_{n=1}^{\infty} U^{(n)}(t) \hat{\mathbf{e}}_1 = \hat{\mathbf{e}}_m \sum_{n=m}^{\infty} U^{(n)}(t) \hat{\mathbf{e}}_1
\]

(2.34)

where unit vector \( \hat{\mathbf{e}}_m \) has 1 at element \( m \) and 0 elsewhere. The change in the summation is because only perturbation terms higher than \( m \) include product of \( m \) or more “raising” ladder operators \( A^\dagger(t) \), in the expansion in equation (2.33), that can connect \( \hat{\mathbf{e}}_1 (|E_1\rangle) \) to \( \hat{\mathbf{e}}_m (|E_m\rangle) \).

As a result, for such “ladder climbing” excitation scenarios, we can quantify the strength of the interaction Hamiltonian, e.g. the intensity of the excitation field incident to a molecule, according to its influence on the magnitude of population \( |b_m(t)|^2 \) for molecular eigenstate \( |E_m\rangle \). The comparison of population in each eigenstate is in fact very efficient and unambiguous, since the system is closed (or possibly open only to leaking of population) and total population is normalized to unity. Any further interference effect
involving the amplitude or populations would not change such comparison.

This is going to be quite relevant to our study in Chapter 4, in terms of determining the strength of the field. “Weak field” is used interchangeably with a “first-order perturbative field”, where excited populations of molecular eigenstates in the “ladder” higher than the second one are much smaller than unity and thus negligible. A “strong field” refers exclusive to a field strong enough that perturbations with order higher than 2 cause significant population transfer. Conversely, if we found significant population excited to the 3rd eigenstate in the “ladder” or higher, the field is then definitively qualified as a strong field.

2.2.3 Principle of coherent control

The area of study on coherent control, in principle, is to utilize the optical phases of the excitation field, to achieve selectivity in the molecule’s transition among the energy eigenstates. In order to gain some quantitative understanding about how the transition dynamics can be influenced by various properties of the excitation field, let’s next analyze an explicit situation. Consider only two Born-Oppenheimer energy eigenstates, for simplicity labelled as $|0\rangle$ and $|1\rangle$, of a diatomic molecule interacting with a pulse of laser light $E(t)$. Although in practice, such field is expected to be convergent in time, i.e. $E(t \to \pm\infty) = 0$, it is however theoretically instructive to first analyze the more elemental molecular excitation by monochromatic field of the form $E(t) = \hat{E}\epsilon_0 \cos(\omega_L t + \phi)$. Here $\hat{E}$ is its polarization direction, $\epsilon_0$ is the amplitude, and $\omega_L$ is the angular frequency of the light assumed to be very close to the energy separation between the two states ($\omega_L \simeq |E_1 - E_0|/\hbar$).

The Schrödinger’s equation, in the basis of $|0\rangle$ and $|1\rangle$, can then be written as

$$i\hbar \frac{d}{dt} \begin{pmatrix} b_0(t)e^{-iE_0t/\hbar} \\ b_1(t)e^{-iE_1t/\hbar} \end{pmatrix} = \left[ \begin{pmatrix} E_0 & 0 \\ 0 & E_1 \end{pmatrix} - \begin{pmatrix} 0 & \mu_{12} \\ \mu_{21} & 0 \end{pmatrix} \epsilon_0 \cos(\omega_L t + \phi) \right] \begin{pmatrix} b_0(t)e^{-iE_0t/\hbar} \\ b_1(t)e^{-iE_1t/\hbar} \end{pmatrix}, \quad (2.35)$$
where $E_{0,1}$ are the energy eigenvalues for the two states, and $\mu_{ij} = \langle i | \hat{\mu} | j \rangle = \langle i | \mu \cdot E | j \rangle$ are the matrix elements of operator representing the molecular dipole in the field’s polarization direction, in the same basis. The diagonal elements for the interaction are commonly assumed to be zero, which can be for example due to wave function parity in molecules. Notice that, here, the amplitudes for the two states have time-dependence in addition to the phase factor of time as found in equation (2.2), due to the interaction term. Carrying out the time differentiation, the above equation simplifies to

$$\frac{d}{dt} \begin{pmatrix} b_0(t) \\ b_1(t) \end{pmatrix} = \frac{i}{\hbar} \epsilon_0 \cos(\omega_L t + \phi) \begin{pmatrix} 0 & \mu_{01} e^{-i\omega_{10} t} \\ \mu_{10} e^{i\omega_{10} t} & 0 \end{pmatrix} \begin{pmatrix} b_0(t) \\ b_1(t) \end{pmatrix}, \quad (2.36)$$

where we define the shorthand notation $\omega_{10} = (E_1 - E_0) / \hbar$.

It is common, at this stage, to make the so-called rotating-wave approximation for the excitation field, to further simply the above equation. We retain only the term with smallest oscillation frequency, i.e. the $e^{i\omega t}$ term with smallest $|\omega|$, on the right hand side. The cosine function can be expressed as $\cos \theta = (e^{i\theta} + e^{-i\theta}) / 2$. The reason for such approximation is a quantitative one: Considering the general solution given as the perturbation expansion from equation (2.33), each $U^{(n)}(t)$ would have matrix element in the form

$$\sum_j \int_0^t e^{-i\omega_j t'} dt' = \sum_j \left. \frac{1 - e^{-i\omega_j t}}{i\omega_j} \right|_0^t = \sum_j \frac{1 - e^{-i\omega_j t}}{i\omega_j}, \quad (2.37)$$

where we can see, the largest contribution comes from the term in the summation with greatest $1/\omega_j$, i.e. smallest $\omega_j$.

In equation (2.36), the smallest oscillation frequency is $|\omega_L - \omega_{10}|$, since $\omega_L$ is assumed to be near-resonance with the state energy separation. For a numerical example, the central laser frequency used to optically couple a ground vibrational state to an excited one, for our study on IBr molecule in chapter 5, is around 538 THz. But the value for $|\omega_L - \omega_{10}|$, i.e. possible laser frequency’s detuning from the energy separation between the two states, is no more than 3 THz. This results in $(1/3)/(1/538) \approx 180$ times...
bigger contribution from the small-frequency component.

Therefore, with the rotating-wave approximation, and denoting \( \Delta \omega = \omega_L - \omega_{10} \), equation (2.36) effectively becomes

\[
\frac{d}{dt} \begin{pmatrix} b_0(t) \\ b_1(t) \end{pmatrix} = \frac{i \epsilon_0}{2 \hbar} \begin{pmatrix} 0 & \mu_{10} e^{i \Delta \omega t + i \phi} \\ \mu_{10} e^{-i \Delta \omega t - i \phi} & 0 \end{pmatrix} \begin{pmatrix} b_0(t) \\ b_1(t) \end{pmatrix} 
= \frac{i \epsilon_0}{2 \hbar} \begin{pmatrix} \mu_{10} e^{i \Delta \omega t + i \phi} b_1(t) \\ \mu_{10} e^{-i \Delta \omega t - i \phi} b_0(t) \end{pmatrix}. 
\tag{2.38}
\]

If the molecule completely resides in state \(|0\rangle\) at \( t = 0 \), and the electric field is first-order perturbative, we can assume for all subsequent times that \( \frac{db_0(t)}{dt} \equiv 0 \), hence \( b_0(t) \equiv 1 \) ([I] and section 2.2.2). This way, above equation gives us, in the case of nonzero detuning \( \Delta \omega \neq 0 \),

\[
\frac{d}{dt} b_1(t) = \frac{i \epsilon_0}{2 \hbar} \mu_{10} e^{-i \Delta \omega t - i \phi} 
\Rightarrow \ b_1(t) = \frac{i \epsilon_0 \mu_{10}}{2 \hbar} - i \phi \int_0^t e^{-i \Delta \omega t'} dt' = \frac{\epsilon_0 \mu_{10}}{2 \hbar \Delta \omega} e^{-i \phi} (1 - e^{-i \Delta \omega t}). 
\tag{2.39}
\]

The oscillation of the excited state population is then

\[
|b_1(t)|^2 = \epsilon_0^2 \mu_{10}^2 / \hbar^2 \Delta \omega^2. 
\tag{2.40}
\]

For \( \Delta \omega = 0 \), we have

\[
\frac{d}{dt} b_1(t) = \frac{i \epsilon_0 \mu_{10}}{2 \hbar} e^{-i \phi} \Rightarrow \ b_1(t) = \left( \frac{i \epsilon_0 \mu_{10}}{2 \hbar} e^{-i \phi} \right) t
\tag{2.41}
\]

where the rate of linear increase in \( |b_1(t)|^2 \) is \( \epsilon_0^2 \mu_{10}^2 / 4 \hbar^2 \). The linear dependence in time is a consequence of the assumption that \( b_0(t) \equiv 1 \) for all times, which, of course, will be unphysical at arbitrarily long time. Therefore, this solution is for short time only.

In both cases, the characteristic rates of change in the excited state population are proportional to the intensity of the excitation field \( \epsilon_0^2 \) and the strength of the transition dipole moment \( |\mu_{10}|^2 \), both very reasonable since
2.2. Photoexcitation of molecules

A stronger excitation, or a stronger coupling would be expected to increase transition rate. However, in either case, the transition rates are insensitive to the initial phase of the field \( \phi \), a coherence property of the excitation field. Therefore, varying the phase of the electric field of the perturbative, monochromatic excitation light would not affect the transition dynamics between two energy eigenstates. This forms the basis of the principle that there can be no phase-only coherent control, when a single eigenstate is excited by a first-order perturbative field. If the single eigenstate is excited by a broadband pulse, the same derivation as above follows for each monochromatic component of the pulse, coupling state 0 to a different excited state, thus reconfirming such no-control principle in the first-order perturbative domain. We will discuss such principle again as the motivation behind the study in Chapter 4.

To get around the no-control scenario with first-order perturbative field, one can either utilize another field with second order perturbative strength, amounting to the classic 1- vs. 2-photon coherent control technique, or, excite from an additional source state using first-order perturbative field, which is known as bichromatic control scheme [4]. Both cases rely on the establishment of multiple “excitation pathways” to the same target excited state, and can offer us control over the transition dynamics via only the phases of the fields. For the bichromatic control, assume the excitation of \( |1\rangle \) involves an additional source eigenstate \( |0'\rangle \), which for example can be a different vibrational eigenstate with all quantum numbers identical to \( |0\rangle \) except vibrational. Accordingly, another electric field \( E'(t) \) appropriate for their energy separation is used. The direct application of the above perturbation analysis would give us, for the nonzero detuning case,

\[
b_1(t) = \frac{\epsilon_0 \mu_{10}}{2 \hbar \Delta \omega} e^{-i\phi}(1 - e^{-i\Delta \omega t}) + \frac{\epsilon'_0 \mu_{10'}}{2 \hbar \Delta \omega'} e^{-i\phi'}(1 - e^{-i\Delta \omega' t}).
\] (2.42)
2.2. Photoexcitation of molecules

The oscillation in the excited population is then (assuming $\mu_{ij}$ are real)

\[ |b_1(t)|^2 = \left| \frac{\epsilon_0 \mu_{10}}{2\hbar \Delta \omega} e^{-i\phi}(1 - e^{-i\Delta \omega t}) + \frac{\epsilon'_0 \mu'_{10}'}{2\hbar \Delta \omega'} e^{-i\phi'}(1 - e^{-i\Delta \omega' t}) \right|^2 \]

\[ = \left| \frac{\epsilon_0 \mu_{10}}{2\hbar \Delta \omega} \right|^2 \sin \frac{\Delta \omega t}{2} + \left| \frac{\epsilon'_0 \mu'_{10}'}{2\hbar \Delta \omega'} \right|^2 \sin \frac{\Delta \omega' t}{2} + 2 \frac{\epsilon_0 \mu_{10}}{2\hbar \Delta \omega} \frac{\epsilon'_0 \mu'_{10}'}{2\hbar \Delta \omega'} \sin \frac{\Delta \omega t}{2} \sin \frac{\Delta \omega' t}{2} \cos \left( \frac{(\Delta \omega - \Delta \omega') t}{2} + (\phi - \phi') \right), \quad (2.43) \]

where, if the field frequencies are chosen such that $\Delta \omega - \Delta \omega' = 0$, the relative phase angles $\phi - \phi'$ between the two fields can, now, alter the amplitude of the population oscillation. The at-resonance case is even more clearly dependent on the relative phases:

\[ b_1(t) = \left( \frac{i\epsilon_0 \mu_{10}}{2\hbar} e^{-i\phi} + \frac{i\epsilon'_0 \mu'_{10}'}{2\hbar} e^{-i\phi'} \right) t \]

\[ \Rightarrow |b_1(t)|^2 = \left| \frac{i\epsilon_0 \mu_{10}}{2\hbar} e^{-i\phi} + \frac{i\epsilon'_0 \mu'_{10}'}{2\hbar} e^{-i\phi'} \right|^2 t^2 \]

\[ = \left[ \frac{\epsilon_0 \mu_{10}}{2\hbar \Delta \omega} \right]^2 + \left[ \frac{\epsilon'_0 \mu'_{10}'}{2\hbar \Delta \omega'} \right]^2 + 2 \frac{\epsilon_0 \mu_{10}}{2\hbar \Delta \omega} \frac{\epsilon'_0 \mu'_{10}'}{2\hbar \Delta \omega'} \cos(\phi - \phi') \right] t^2. \quad (2.44) \]

This demonstrates the principle of how altering the relative phases between two monochromatic field components, connecting two different Born-Oppenheimer states to the same target state, can give us control over the transition dynamics in a molecule. Such interference effects between photoexcitation pathways will be discussed in many places in this thesis.

2.2.4 Adiabatic processes

When the excitation field is pulsed, i.e. convergent for $t \to \pm \infty$, and the modulation varies very slowly with time, the adiabatic theorem of quantum mechanics [1] tells us the system will remain in its time-dependent energy eigenstate throughout the process. Transition processes in molecules satisfying such condition are known as adiabatic processes.
2.2. Photoexcitation of molecules

One particularly successful technique of adiabatic manipulation of quantum state transitions in molecules is known as the stimulated Raman adiabatic passage (STIRAP) \[5\]. With STIRAP, the molecule under the excitation of two pulsed laser fields can transition between two energy eigenstates, say \(|0\rangle\) and \(|2\rangle\), with no direct optical coupling, i.e. \(\mu_{02} = 0\), by utilizing a third state with coupling to both. The appropriate design of the pair of excitation pulses can result in 100% transfer, namely, without the excitation of the intermediate state at all times.

We briefly outline the mathematical reasons as below. The field-dipole interaction Hamiltonian matrix in the basis of \{|0\rangle, |1\rangle, |2\rangle\}, under rotating-wave approximation, is

\[
H_I(t) = \begin{pmatrix}
0 & V_{01}(t)e^{i\omega_{01}t} & 0 \\
V_{01}^*(t)e^{-i\omega_{01}t} & 0 & V_{12}(t)e^{i\omega_{12}t} \\
0 & V_{12}^*(t)e^{-i\omega_{12}t} & 0
\end{pmatrix}
\]

(2.45)

where the two electric fields are assumed to be at-resonance with the energy separations, \(\omega_{01} = (E_1 - E_0)/\hbar\) and \(\omega_{12} = (E_2 - E_1)/\hbar\). The dynamical equation for such three-state problem can be derived in a very similar way to the derivation from equation (2.35) to (2.36), but now we would have

\[
\frac{d}{dt} \begin{pmatrix} b_0(t) \\ b_1(t) \\ b_2(t) \end{pmatrix} = \frac{i}{\hbar} \begin{pmatrix}
0 & V_{01}(t) & 0 \\
V_{01}^*(t) & 0 & V_{12}(t) \\
0 & V_{12}^*(t) & 0
\end{pmatrix} \begin{pmatrix} b_0(t) \\ b_1(t) \\ b_2(t) \end{pmatrix}.
\]

(2.46)

Given that the field modulation \(V_{ij}(t)\) varies slowly enough for the process to be adiabatic, the system remains in one of the time-dependent eigenstates

\[
|E_{\pm}(t)\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix}
\pm \frac{1}{\sqrt{(V_{12}(t)/V_{01}(t))^2 + 1}} \\
\frac{1}{\sqrt{(V_{01}(t)/V_{12}(t))^2 + 1}} \\
\end{pmatrix}, \quad |E_0(t)\rangle = \begin{pmatrix}
\frac{1}{\sqrt{(V_{01}(t)/V_{12}(t))^2 + 1}} \\
0 \\
\frac{1}{\sqrt{(V_{12}(t)/V_{01}(t))^2 + 1}}
\end{pmatrix}.
\]

(2.47)
2.3 Wave coherence

to the total time-dependent Hamiltonian, with time-dependent eigenvalues

\[ E_{\pm}(t) = \pm \sqrt{V_{01}^2(t) + V_{12}^2(t)}, \quad E_0 = 0. \]

Key to the optimal \( |0\rangle \) to \( |2\rangle \) transition is the so-called “counter-intuitive” arrangement of excitations, where \( V_{12}(t) \) proceeds \( V_{01}(t) \), ensuring \( V_{12}(t) \gg V_{01}(t) \) as \( t \to -\infty \), and \( V_{12}(t) \ll V_{01}(t) \) as \( t \to \infty \). This way,

\[
|E_{\pm}(t \to -\infty)\rangle \cong \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}, \quad |E_0(t \to -\infty)\rangle \cong \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad (2.48)
\]

and after the excitation,

\[
|E_{\pm}(t \to \infty)\rangle \cong \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}, \quad |E_0(t \to \infty)\rangle \cong \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (2.49)
\]

The net effect is that, if the initial state of the molecule is entirely \( |0\rangle \), the molecule occupies the \( |E_0\rangle \) state in the time-dependent picture. So when the interaction is finished, the molecule, remaining in \( |E_0\rangle \), is now entirely in \( |2\rangle \). An “adiabatic passage” from \( |0\rangle \) to \( |2\rangle \) is thus formed using the time-dependent energy eigenstate \( |E_0\rangle \). In our first study, in Chapter 3, we will encounter a similar three-state transfer problem in the context of ultracold molecule production. We will extend such STIRAP technique, to include continuum eigenstates with resonances.

2.3 Wave coherence

For either matter waves, arisen from the quantum mechanical formulation, or the electromagnetic waves which are solutions to the Maxwell wave equation, eigenstate decomposition technique for solving the dynamics of the wave packet, similar to equation (2.2), can be applied. For so-called linear problems, the complex amplitudes for the eigenstate evolves trivially in
2.3. Wave coherence

time, according to phase factor $e^{-i\omega t}$ where $\omega$ is the characteristic frequency of the eigenstate describing energy eigenvalues for matter, and angular frequency for light. For problems involving eigenstate transitions, dynamics can also be solved by analyzing the coupling between amplitudes of eigenstates, i.e. calculating the off-diagonal matrix elements of the term in the Hamiltonian responsible for transition among eigenstates. In this case, both the magnitude and the phase of the complex amplitudes evolve in time.

In both light and matter, essential to controlling the time evolution of wave packets of eigenstates is the interferences between the complex amplitudes. We have conducted analysis, so far, under the assumption that the amplitudes are deterministic variables. This gives us full information about the relative phases between eigenstate amplitudes, at any given time. However, in order to analyze situations of incoherence, another important concept for later studies in this thesis, in both light and matter, we consider each amplitude’s evolution as a stochastic one, meaning that the complex amplitude is modelled by random variables instead. Effectively, the quantum state vector, written in certain basis of dimension $N$ as $|\Psi\rangle = (c_1 c_2 \ldots c_N)^T$ also becomes a random vector.

The implication of such incoherence is often loss of mutual coherence between eigenstates to a certain degree, and goes to any situation where the cross-correlation between eigenstate is important. For a specific example, consider when the spatial probability density, i.e. the magnitude-squared wave function, of a wave packet of excited eigenstates is of concern, similar to the case for our study in Chapter 5. If the eigenstate amplitudes maintain constant magnitude, but are frequently disturbed in the phase values, then we can model $c_n = |c_n|e^{i\phi_n}$, where $|c_n|$ is deterministic but $\phi_n$’s are independent, uniform random variables in the range $[-\pi, \pi]$, with probability
density functions \( f_n(\phi_n) = \frac{1}{2\pi} \). The statistically averaged result is then

\[
\langle |\Psi(x,t)|^2 \rangle = \langle \sum_n |c_n|^2|\psi_n(x)|^2 \rangle + \sum_{i \neq j} |c_i||c_j|\langle e^{i(\phi_i-\phi_j)}e^{-i(E_j-E_i)t}|\psi_i(x)\psi_j^*(x)\rangle
\]

\[= \sum_n |c_n|^2|\psi_n(x)|^2 \quad (2.50)\]

since

\[
\langle e^{i(\phi_i-\phi_j)} \rangle = \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} e^{i(\phi_i-\phi_j)} \frac{1}{2\pi} \frac{1}{2\pi} d\phi_i d\phi_j = 0. \quad (2.51)
\]

Namely, the wave packet loses any time-dependent movement, originally due to the coherent interference between eigenstates.

Similar results apply to optical waves, and to the bichromatic coherent control as well. In equations (2.43) (with \( \Delta \omega - \Delta \omega' = 0 \)) and (2.44), if the optical phases \( \phi \) and \( \phi' \) are the random variables as described above, statistical averaging would also make \( \langle \cos(\phi - \phi') \rangle = 0 \), since \( \langle \cos(\phi - \phi') \rangle = \frac{1}{2} [\langle e^{i(\phi-\phi')} \rangle + \langle e^{-i(\phi-\phi')} \rangle] \). Therefore, incoherence, exhibited in the randomization of phases for eigenstates, would be expected to destroy any coherent wave packet motion, and coherent control abilities utilizing laser lights.

2.4 Numerical computations

All studies included in this thesis have some parts involving numerical computations. Since the material systems are based on diatomic molecules, we use the atomic unit system in all numerical studies, where fundamental constants such as Bohr radius \( a_0 \), electron mass and charge \( m_e \) and \( e \), Planck constant \( h \) and Coulomb constant \( 1/4\pi\epsilon_0 \) become base units (numeric values of 1) for related physical quantities. Unit conversion into atomic units from other unit systems can then be derived based on these base units. It’s also a common practice, in many places in this thesis, where “atomic unit” or “a.u.” is used to denote the unit of a numeric value; the underlying physical
2.4. Numerical computations

quantity, e.g. energy or length\(^{1/2}\), is implied by the variable taking on the numeric value.

In solving for the numeric solutions to partial or ordinary differential equations, functions of a spatial coordinate is represented by an array of numeric values (e.g. complex numbers), with predefined, equal spacing. For example, a wave function \(\psi(R)\) in the range of \(R \in [1, 11] \text{a.u.}\), with spatial resolution of 0.1a.u. is represented by a sequence of complex values \(\psi_j = \psi(R_j)\), with \(R_j = (1.0 + 0.1j)\text{a.u.}, j = 0...100\). First and second derivatives of the function are calculated using finite-difference, two-point formula

\[
\frac{d\psi}{dR}\bigg|_{R_j} = \frac{\psi_{j+1} - \psi_{j-1}}{2h}, \quad \frac{d^2\psi}{dR^2}\bigg|_{R_j} = \frac{\psi_{j+1} - 2\psi_j + \psi_{j-1}}{h^2}
\]

(2.52)

where \(h = R_j - R_{j-1}\). End points use appropriate single-point formulas, or approximated from neighbouring ones, and they are of less importance in determining the solutions to the differential equations.

To solve the next value in time also using finite-difference methods, either for a discretized function as above, or simply a complex value, a number of methods ranging from Euler’s method to 4th order Runge-Kutta methods are used. For any of these methods, the time increment is decreased until convergent results are obtained for a finite time propagation.

Matrix diagonalization is also used when appropriate, such as solving for the eigenstates to a time-independent Hamiltonian matrix, representing the kinetic energy and a known potential function \(-\frac{1}{2\mu}\frac{d^2}{dR^2} + V(R)\). According to equation (2.52), using the array of spatial points as basis, the matrix for \((h^2)\frac{d^2}{dR^2}\) is tri-diagonal, with \(-2\)’s on the diagonal and 1’s left and right to it, and that for \(V(R)\) is diagonal, with \([V(R)]_{jj} = V(R_j)\).

The programming languages and visualization tools used for numerical studies include FORTRAN, Python, C++, Mathematica and Gnuplot. For electronic structure calculations, GAUSSIAN quantum chemistry software is used.
Chapter 3

Adiabatic photoassociation of ultracold molecules via scattering resonances

3.1 Introduction

In recent years, the production of translationally and internally cold ($\leq 1$K) and ultracold ($\leq 1$mK) molecules has become a very popular and intriguing subject of research [6–11], due to the very novel and interesting physics involving ultralow energy atomic collisions and Feshbach resonances [12–14], field-matter interactions [15–20], its relevance to ultracold chemistry [21, 22], as well as potential applications these ultracold molecular systems can provide, for example, for testing fundamental laws [23, 26] or implementing quantum computers [27–31].

Many methods to produce ultracold molecules exist. They can be based on cooling previous hot molecules, such as buffer gas cooling [32], or Stark [33] and Zeeman [34–36] decelarators. Alternatively, many methods rely on associating atoms already at ultracold temperatures into ultracold molecules, including, for example, one-colour photoassociation [37, 38], Feshbach resonance magneto-association [39–43], Feshbach-optimized photoassociation [44, 45], broadband femtosecond photoassociation [46–48], and many more. These techniques have various advantages and disadvantages, in terms of technologies required, efficiencies, and constraints on properties of the material systems.

Of particular interests to our current theoretical and numerical study is
3.1. Introduction

the Adiabatic Raman Photoassociation (ARPA), introduced \[49-51\] as an extension of the Stimulated Raman Adiabatic Passage (STIRAP) \[5, 52-55\] to atomic scattering continuum states. This technique has unique characteristics from the dynamics of multicolour pulsed photoexcitation and photoassociation, and meanwhile is also closely related to the mechanics of scattering resonances. In this perspective, both static and dynamic aspects of the photoexcitation and collision would play important roles in the process. Accordingly, our main inspiration and focus of the current study is really the interesting dynamical phenomena as well as its effect on improving the efficiency of the technique. Comprehensive analysis for many aspects on the practicality of the ARPA technique, or its comparison with existing methods on producing ultracold molecules, calls for future research based on many references above.

In the ARPA technique, as illustrated in Figure 3.1, the two-atom system initially consists of two separate freely colliding atoms, at ultralow temperatures, or equivalently ultralow collision energies. This is reflected in assuming that the initial quantum state of the system consists of continuum eigenstates in a very small energy range, just above the dissociation threshold of the ground electronic potential energy surface with zero angular momentum (\(J = 0\) channel or the s-wave channel). Under the irradiation of a combination of a dump and a pump laser pulse, the two-atom scattering continuum is then coupled optically to single bound state in the excited electronic manifold, which in turn is coupled to the absolute ground vibrational level of the ground electronic manifold. The use of full Born-Oppenheimer energy eigenstates, also the small number of them, is ensured by the very narrow energy bandwidth of the atomic collision, and the corresponding narrow bandwidth of the optical excitation field.

The pulse pair is mutually coherent and partially overlapping in space and time. Similar to the three-level STIRAP, the two pulses are ordered “counter-intuitively” \[5\]. The dump pulse precedes the pump (see section \[2.2.4\]), and has a central frequency appropriate for transition between the final bound state and an intermediate excited bound state. The pump pulse in turn has frequencies appropriate for coupling the continuum to the interme-
3.1. Introduction

Figure 3.1: A schematic display of the Adiabatic Raman Photoassociation (ARPA) process. **Left panel:** Atoms colliding in the near-threshold energy range are excited by the “pump” laser to the vibrational state $|2\rangle$ on an excited electronic potential. The latter is coupled by the “dump” laser to the deeply bound target state $|1\rangle$. **Right panel:** The same setup but with the inclusion of a hyperfine-manifold bound level interacting with the previous continuum, resulting in a Feshbach resonance.

The main limitation for the above approach to work efficiently is the small Franck-Condon factors, i.e. the spatial wave functions overlaps, between the intermediate bound state and the ground potential. To overcome this difficulty, Feshbach scattering resonances are then introduced, to provide more spatially localized continuum wave functions, hence better overlap. Figure 3.1 also illustrates a fundamental setup of such a Feshbach resonance: A different hyperfine electronic ground potential (green curve) with slightly higher dissociation threshold enables the interaction between one of its high-lying vibrational level and the initial continuum states. Further, the energy difference between the two ground potentials is magnetically tuneable, thus offering us a choice of the structure of the Feshbach resonance, particularly its width, based on which vibrational level is put into the energy range.

The use of wide resonances has been shown to be able to alleviate
the small-overlap limitation, in the Feshbach-optimized Photoassociation (FOPA) technique [44], which relies on the CW vibrational de-excitation of heteronuclear diatomic molecules, and in the first single-collision analysis of the ARPA technique with resonance [56]. However, dynamic effects of the resonance become important, especially in the setting of pulsed photoexcitation, for a collection of colliding atoms: Since the lifetime or duration of the atomic collision is inversely proportional to the width of the resonance, one can not overlook the increased number of atomic collisions in progress, hence available to enter the adiabatic passage, due to narrower resonances. A wide resonance, accordingly, shortens the collision time despite having an improved overlap factor. This becomes a key factor on choosing resonance width for best ultracold molecular production efficiency, when a gaseous ensemble of atoms is considered.

In the following, we first develop the underlying dynamical equations that describe the ARPA process. The effective mode expansion [57] method is introduced, to aid to efficient numerical calculations for the ARPA population dynamics, both for a single pair of ultracold $^{85}$Rb atoms (a single collision event), and for an atomic ensemble. There we demonstrate how the collision lifetime is extended by narrow resonances, which can then leverage the increased number of combining atoms during the photoexcitation, and provide better overall efficiencies than wider resonances.

3.2 Dynamics of quantum-state amplitudes

3.2.1 Equations for bound-continuum population transfer

As illustrated in Figure 3.1 the ARPA process involves the ground and first-excited electronic potential energy surfaces of the two-atom system. The initial state of the system consists entirely of energy eigenstates $|E\rangle$ in the ground manifold, with energies above the dissociation threshold. The dipole matrix element (transition amplitudes) are non-negligible between vibrational levels (one of which is $|2\rangle$) in the first excited electronic manifold and initial continuum states, as well as vibrational levels in the ground
3.2. Dynamics of quantum-state amplitudes

manifold, specifically, its lowest level $|1\rangle$.

With the presence of a pair of optical pulses with (scalar) electric field $E = \epsilon_n(t)\cos(\omega_n t)$ ($n = 1$ for dump and $n = 2$ for pump), the system undergoes transitions into both bound manifolds, provided that the two-atom continuum wave packet comes in close internuclear distances during the onset of the fields. The bandwidth of the pulses (determined by the durations of $\epsilon_n(t)$) are chosen to match the ultracold temperature range of the atomic gas, centred around 100 $\mu$K and going down to tens of nK. This way, by choosing the appropriate centre frequencies $\omega_{1,2}$, we effectively need to include no other bound states than $|1,2\rangle$, since the vibrational energy separations in the electronic manifolds concerned are much larger.

The effective Hamiltonian, therefore, can be written as (in atomic units),

$$\hat{H} = \hat{H}_0 - 2\hat{\mu} \sum_{n=1,2} \epsilon_n(t) \cos(\omega_n t), \quad (3.1)$$

$$\hat{H}_0 = E_1 |1\rangle \langle 1| + E_2 |2\rangle \langle 2| + \int_{E_{th}}^{\infty} E |E\rangle \langle E| dE, \quad (3.2)$$

where $E_{th}$ is the dissociation (threshold) energy of the electronic manifold hosting the continuum, and $\hat{\mu}$ is the dipole operator of the molecule along the electric fields’ direction. We assume, as usual, that the spatial variation (i.e. wavelength) of the optical field is much larger than the sizes of the atoms or molecules, and hence is considered constant over spatial coordinates in the Hamiltonian.

The main feature of the atomic continuum we wish to explore is a Feshbach-type resonance, originating from the interaction between a high-lying vibrational bound level in one ground hyperfine electronic manifold, with the continuum portion of another hyperfine manifold with slightly higher dissociation threshold. We treat the two hyperfine manifolds together as one continuum (“the atomic continuum”) with each energy eigenstate $|E\rangle$ accounting for bound and continuum states in both the closed and open hyperfine channels. This, in the time domain, simplifies the collision dynamics to only linear combination of continuum states $|E\rangle$ with time-dependent phase factors. It also leads to, in the energy domain, the expression of a
3.2. Dynamics of quantum-state amplitudes

resonance as the sharp energy dependence of the transition-dipole matrix elements \( \mu_{2,E} = \langle 2 | \hat{\mu} | E \rangle \) \cite{44, 56, 58}.

Expanding the total, time-dependent state of the molecule in terms of the material eigenstates involved,

\[
|\Psi(t)\rangle = \sum_{i=1,2} b_i(t) e^{-iE_i t} |i\rangle + \int_{E_{th}}^{\infty} b_{E}(t) e^{-iEt} |E\rangle \, dE, \tag{3.3}
\]

and using their orthonormality and the Rotating Wave Approximation (RWA), the time-dependent Schrödinger’s equation \( i \frac{d}{dt} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \) can be translated into a set of dynamical equations for the eigenstate amplitudes

\[
\dot{b}_1(t) = i \Omega_1^*(t) b_2(t), \tag{3.4}
\]

\[
\dot{b}_2(t) = i \Omega_1(t) b_1(t) - \Gamma_f b_2(t) + i \int_{E_{th}}^{\infty} \Omega_E(t) b_E(t) e^{i\Delta_E t} \, dE, \tag{3.5}
\]

\[
\dot{b}_E(t) = i \Omega_E^*(t) b_2(t) e^{-i\Delta_E t}, \tag{3.6}
\]

where \( \Delta_E = E_2 - E - \omega_2 \) and \( \Delta_1 = E_2 - E_1 - \omega_1 \) are the energy detuning of the pulses, \( \Omega_1(t) = \epsilon_1(t) \mu_{2,1} e^{i\Delta_1 t} \) and \( \Omega_E(t) = \epsilon_2(t) \mu_{2,E} \) are the Rabi frequencies, and \( \Gamma_f \) is a spontaneous decay rate we artificially added, at which amplitude of \(|2\rangle\) is lost.

We further reduce the number of dynamical equations by incorporating a formal solution of equation (3.6)

\[
b_E(t) = b_E(0) + i \int_0^t \Omega_E^*(t') b_2(t') e^{-i\Delta_E t'} \, dt', \tag{3.7}
\]

into the integral of equation (3.5),

\[
\dot{b}_2(t) = i \Omega_1(t) b_1(t) - \Gamma_f b_2(t) + i \int_{E_{th}}^{\infty} \Omega_E(t) b_E(0) e^{i\Delta_E t} \, dE
\]

\[
- \epsilon_2(t) \int_{-\infty}^{\infty} \left[ |\mu_{2,E}|^2 \int_0^t \epsilon_2(t') b_2(t') e^{-i\Delta_E t'} \, dt' \right] e^{i\Delta_E t} \, dE, \tag{3.8}
\]

which can be further simplified by defining a source function and a spectral
3.2. Dynamics of quantum-state amplitudes

Auto-correlation function

\[
\begin{align*}
    f_{\text{source}}(t) & = \int_{E_{\text{th}}}^{\infty} \Omega_E(t)b_E(0)e^{i\Delta_E t}dE, \quad (3.9) \\
    F(t - t') & = \int_{E_{\text{th}}}^{\infty} |\mu_{2,E}|^2 e^{i\Delta_E(t-t')}dE. \quad (3.10)
\end{align*}
\]

This makes the overall dynamical equations for the two bound states

\[
\begin{align*}
    \dot{b}_1(t) & = i\Omega_1^*(t)b_2(t), \quad (3.11) \\
    \dot{b}_2(t) & = i\Omega_1(t)b_1(t) - \Gamma_f b_2(t) + i f_{\text{source}}(t) - \epsilon_2(t) \int_0^t \epsilon_2(t')b_2(t')F(t - t')dt'. \quad (3.12)
\end{align*}
\]

Note that so far, these integro-differential equations are very difficult to solve numerically. We will next further explore physical assumptions, especially those related to the inclusion of resonances, that can greatly reduce the complexity.

3.2.2 The effective modes expansion

In the case of a flat continuum or “slowly varying continuum approximation” (SVCA), $\mu_{2,E}$ varies sufficiently slowly with energy $E$, and we replace it by an averaged value without the energy dependence. This eliminates the integral in the spectral auto-correlation function, reducing it to $F(t - t') = 2\pi |\mu_{2,E}|^2 \delta(t' - t)$. Consequently, the entire last term in equation (3.12) depends only on $b_2(t)$, and the dynamical equation set becomes more compact in matrix notation

\[
\frac{d}{dt} \mathbf{b} = iH \cdot \mathbf{b} + if_{\text{source}}, \quad (3.13)
\]
3.2. Dynamics of quantum-state amplitudes

with

\[ b(t) \equiv \begin{pmatrix} b_1(t) \\ b_2(t) \end{pmatrix}, \quad f_{\text{source}}(t) \equiv \begin{pmatrix} 0 \\ f_{\text{source}}(t) \end{pmatrix}, \]

\[ H = \begin{pmatrix} 0 & \Omega_1^* \\ \Omega_1 & i\Gamma_{\text{eff}}(t) \end{pmatrix}, \quad \Gamma_{\text{eff}}(t) = \pi |\mu_2, \pi|^2 \epsilon_2^2(t). \quad (3.14) \]

A more detailed discussion of the solutions under SVCA was made in Refs. [49–51].

The flat continuum or SVCA assumption becomes invalid with the presence of collisional resonances, in which case \( \mu_{2,E} \) changes rapidly near the resonance energy [44, 58]. The effective mode expansion then starts by treating \( \mu_{2,E} \) as an expansion of Lorentzian profiles [57]. Compact matrix form and efficient computation will then follow and greatly simplify the dynamical equations. Specifically, let’s write

\[ \mu_{2,E} = \sum_{s=1}^{M} \frac{i\mu_s \Gamma_s/2}{E - E_s + i\Gamma_s/2}, \quad (3.15) \]

where \( \mu_s \) represents the electronic transition dipole moment, \( \Gamma_s \) the full-width-at-half-maximum (FWHM), and \( E_s \) the centre energy for each resonance labelled by \( s \). This form is capable of approximating well both wide and narrow resonances [56, 58, 59], meanwhile also evaluating the autocorrelation function integral analytically to

\[ F(t - t') = \sum_{s=1}^{M} \alpha_s f_s^+(t)f_s^-(t'), \quad (3.16) \]

with

\[ \alpha_s = \sum_{s'} \frac{-i\mu_s \mu_{s'} \Gamma_s \Gamma_{s'}/4}{E_s - E_{s'} - i(\Gamma_s + \Gamma_{s'})/2}, \quad f_s^\pm(t) = \sqrt{2\pi} e^{\mp i\chi_s t}, \]

\[ \chi_s = E_s - E_2 + \omega_2 - i\frac{\Gamma_s}{2}. \quad (3.17) \]
3.2. Dynamics of quantum-state amplitudes

Using equation (3.16) we now define the effective modes variables as [57],

\[ B_s^-(t) = i \int_0^t \epsilon_2(t') b_2(t') f_s^-(t') dt', \] (3.18)

which transforms the dynamical equations into

\[ \dot{b}_1(t) = i \Omega_1^*(t) b_2(t), \]
\[ \dot{b}_2(t) = i \Omega_1(t) b_1(t) - \Gamma f b_2(t) + i f_{source}(t) + i \epsilon_2(t) \sum_{s=1}^{M} \alpha_s f_s^+ B_s^-(t), \]
\[ \dot{B}_s^-(t) = i \epsilon_2(t) f_s^-(t) b_2(t), \quad s = 1, ..., M. \] (3.19)

This way, we eliminated the integration in the original equation set at the (very limited) expense of increased number of equations. Further changing variables \( B_s(t) = \sqrt{\alpha_s/2\pi f_s^+} B_s^-(t) \) and \( \Omega_2^{(s)} = \epsilon_2(t) \sqrt{2\pi \alpha_s} \), we have

\[ \dot{b}_1(t) = i \Omega_1^*(t) b_2(t) \]
\[ \dot{b}_2(t) = i \Omega_1(t) b_1(t) - \Gamma f b_2(t) + i f_{source}(t) + \sum_s i \Omega_2^{(s)}(t) B_s(t) \]
\[ \dot{B}_s(t) = -i \chi_s B_s(t) + i \Omega_2^{(s)}(t) b_2(t), \] (3.20)

which can now again be put into matrix notation,

\[ \frac{d}{dt} \mathbf{b} = i \mathbf{H} \cdot \mathbf{b} + i \mathbf{f}_{source}, \] (3.21)

where

\[ \mathbf{b}(t) = \begin{pmatrix} b_1(t) \\ b_2(t) \\ B_1(t) \\ B_2(t) \\ \vdots \end{pmatrix}, \quad \mathbf{f}_{source}(t) = \begin{pmatrix} 0 \\ f_{source}(t) \\ 0 \\ 0 \\ \vdots \end{pmatrix}, \] (3.22)
3.2. Dynamics of quantum-state amplitudes

and

\[
H = \begin{pmatrix}
0 & \Omega_1^* & 0 & 0 & \cdots \\
\Omega_1 & i\Gamma_f & \Omega_2^{(1)} & \Omega_2^{(2)} & \cdots \\
0 & \Omega_2^{(1)} & -\chi_1 & 0 & \cdots \\
0 & \Omega_2^{(2)} & 0 & -\chi_2 & \cdots \\
: & : & : & : & : & \cdots
\end{pmatrix}.
\] (3.23)

The effective modes amplitudes \(B_s(t)\) thus effectively describes some bound states of energies \(E_s\), coupled by the Rabi frequencies \(\Omega_2^{(s)}(t)\) to state |2⟩, with detuning \(E_s - E_2 + \omega_2\), and decay at rates \(\Gamma_s/2\) as contained in \(\chi_s\). They reflect exactly the nature of bound-continuum interaction behind the existence of scattering resonances. Note that the non-Hermiticity of the Hamiltonian is due not just to the decay of the effective modes, appearing as the imaginary part of \(\chi_s\), but also to \(\alpha_s\) in the Rabi frequencies \(\Omega_2^{(s)}\), which are in general complex numbers due to the summation in its definition.

Equation (3.21) resembles a multi-state STIRAP [60] process with \(\Omega_1(t)\) and \(\Omega_2^{(s)}(t)\) coupling respectively |1⟩ with |2⟩, and |2⟩ with each of the effective modes (Figure 3.2). However, the transfer dynamics differs in a significant way: in our current case the effective modes are initially empty, and get gradually populated. We can see this most explicitly for a single resonance, for which the dynamical equations assume the form,

\[
\begin{align*}
\dot{b}_1(t) &= i\Omega_1^*(t)b_2(t) \\
\dot{b}_2(t) &= i\Omega_2(t)b_1(t) - \Gamma_f b_2(t) + i\Omega_2^{(1)}(t)\left[f_{\text{source}}(t)/\Omega_2^{(1)}(t) + B_1(t)\right] \\
\dot{B}_1(t) &= -i\chi_1 B_1(t) + i\Omega_2^{(1)}(t)b_2(t).
\end{align*}
\] (3.24)
3.2. Dynamics of quantum-state amplitudes

Figure 3.2: **Left panel:** Three bound states STIRAP. The population which starts in the initial bound state $|3\rangle$ is transferred into state $|1\rangle$ by following the evolution of the “dark” field-dressed state. The process avoids population loss due to spontaneous emission from state $|2\rangle$ because the latter remains unpopulated. **Middle panel:** ARPA via a collisional resonance. The population gradually feeds the resonances as the continuum wave packet (shaded area) arrives (at time $t_0$). **Right panel:** The resonance-dominated continuum of the middle panel is replaced by a single (or several) effective mode(s) with decaying amplitude(s) $B_1(t)$ ($B_s(t)$).

Let $B(t) = \frac{f_{\text{source}}(t)}{\Omega_2^{(1)}}(t) + B_1(t)$, we obtain

\[
\begin{align*}
\dot{b}_1(t) &= i\Omega_1^{(1)}(t)b_2(t) \\
\dot{b}_2(t) &= i\Omega_1(t)b_1(t) - \Gamma_j b_2(t) + i\Omega_2^{(1)}(t)B(t) \\
\dot{B}(t) &= -i\chi_1 B(t) + i\Omega_2^{(1)}(t)b_2(t) + \left[i\chi_1 f_{\text{source}}(t)/\Omega_2^{(1)}(t) + f_{\text{source}}'(t)\right].
\end{align*}
\]

(3.25)

where $f_{\text{source}}'(t) \equiv \frac{1}{\sqrt{2\pi\chi_1}} \int_{-\infty}^{\infty} \Delta E \mu_{2,E} b_E(0)e^{i\Delta E t}dE$.

Here, we can observe that this new effective mode variable $B(t)$ has decaying behaviour at a rate indicated by the imaginary part of $\chi_1$. The source of population going into this effective mode comes from the terms in the square bracket (see Figure 3.2). There the first term is especially important, since it represents the field-free population source, as the Fourier transform of the product of the resonant transition dipole moment and the energy distribution of the initial scattering wave packet. The width of the resonance in comparison with the atomic scattering energy bandwidth will
3.3. Numerical computation for Rb-Rb collisions

then determine the characteristic time duration of this field-free source term.

Such contrast with traditional bound-state STIRAP implies the possibility of population loss from the “dark” state. In three-state counter-intuitive pulse ordering adiabatic passage \cite{5}, the population resides initially in the adiabatic “dark” state, which is a superposition of the initial and target states only. The adiabaticity of the pulses guarantees the completeness of the transfer from the initial to the target state, leaving the intermediate state unpopulated at all times. Since, in our case, the effective mode gets populated in a gradual fashion, the system wave function may contain non-negligible contributions from other “bright” states that have a small overlap with $|2\rangle$, allowing population loss via spontaneous emission. The way to counter the effect of increased spontaneous emission at higher atomic gas temperatures is discussed in section 3.3.3.

3.3 Numerical computation for Rb-Rb collisions

In this section we employ the above formulation and perform some numerical computations on the resonance-enhanced photoassociation of ultracold $^{85}$Rb atoms to form $^{85}$Rb$_2$ in its ground vibrational state. In keeping with our view of the process, we divide the computations into two parts: the population transfer for a single collision event involving one pair of atoms, and that for a thermal gaseous ensemble of atoms.

3.3.1 Single-event transfer efficiency

Following the model of Refs. \cite{50, 51}, we consider a pair of $^{85}$Rb atoms colliding on the ($J = 0$) ground electronic potential. We assume that at $t = 0$ (before the onset of the pulses) the total molecular state wave packet has non-zero amplitudes only in the continuum eigenstates

$$
|\Psi(0)\rangle = \int_{E_{th}}^{\infty} b_E(0) e^{-iEt} |E\rangle dE,
$$

(3.26)
Figure 3.3: A single resonance is used for the computation, with magnitude $|\mu_{2,E}| = |\mu_{res} \Gamma_{res} / [2(E - E_{res}) + i\Gamma_{res}]|$ as a function of energy, shown for various choices of $\Gamma_{res}$ and $E_{res} = 100 \mu K$. The resonance height is $\mu_{res} = 300$ a.u., but can be made even larger to favour lower laser intensities. The Franck-Condon factor involving eigenstate $|E\rangle$ follows the same shape.

and the continuum wave packet is an energetically-narrow Gaussian \cite{49,51}

$$b_E(0) = \frac{1}{(2\pi \delta_0^2)^{1/4}} \exp \left[ -\left( \frac{E - E_0}{2\delta_0^2} \right)^2 + i(E - E_0)t_0 \right], \quad (3.27)$$

with $\delta_0 = 70 \mu K$ and $E_0 = 100 \mu K$ (temperature is converted to energy in atomic units with $E = k_B T$). The threshold energy $E_{th}$ will from now on be taken as $-\infty$ for effective evaluation of the integrals, based on the assumption that $b_E(0)$ has essentially decayed to negligible values much before the true $E_{th}$. With this choice of parameters, the wave packet’s temporal peak occurs at a numeric value $t_0 = 1.2 \mu s$ \cite{49,50}. Of course, in practice timing the excitation pulses with respect to a single collision event is unrealistic. However, since we will calculate in the next section the total photoassociation efficiency for an ensemble of atoms colliding at different times, the specification of such timing is important. Lastly, in order for the pulse pair’s spectral widths to have a good overlap with the energetic spread of the atomic wave packet, the pulses in the time domain have $\mu s$ durations.

The scattering continuum is assumed to contain a single resonance, whose shape is given by equation (3.15). Figure 3.3 shows this resonance centred at $E_{res} = E_0 = 100 \mu K$ for three different width choices. Since $E_{res}$
3.3. Numerical computation for Rb-Rb collisions

can be tuned in practice (e.g. magnetically), we can optimize the transfer by making it always equal to $E_0$. This is confirmed by by the numerical calculation (Figure 3.5 bottom panel) to improve the maximal overlap enhancement.

The bound-to-bound matrix element is chosen to have a numeric value $\mu_{21} = 0.0051\text{a.u.}$ This numeric value can be different depending on the actual experimental set-up, but our results only depend on the Rabi frequency $\Omega_1(t)$, which is proportional to the product of this bound-to-bound matrix element with the dump pulse amplitude. A increase (or decrease) of the matrix element translates into a proportional decrease (or increase) in the laser amplitude required. The spontaneous decay rate from $|2\rangle$ is $\Gamma_f = (30\text{ns})^{-1}$ [49–51]. The centre frequency of the dump pulse is chosen to coincide with $E_2 - E_1$, and that of the pump pulse with $E_2 - E_0$. The field envelopes $\epsilon_{1,2}(t)$ are taken as Gaussian functions, peaking respectively at 1.05 $\mu$s and 1.55 $\mu$s. The duration of both fields is 0.22 $\mu$s, peaking at intensity $3 \times 10^5$ W/cm$^2$ [50].

With these specifications, Eqs. (3.20) become

\begin{align}
\dot{b}_1(t) &= i\Omega_1^*(t)b_2(t), \\
\dot{b}_2(t) &= i\Omega_1(t)b_1(t) - \Gamma_f b_2(t) + i f_{\text{source}}(t) + i\Omega_2^{(1)}(t)B_1(t), \\
\dot{B}_1(t) &= -(\Gamma_{\text{res}}/2)B_1(t) + i\Omega_2^{(1)}(t)b_2(t),
\end{align}

where $\Omega_1(t) = \epsilon_1(t)\mu_{2,1}$ and $\Omega_2^{(1)} = \epsilon_2(t)\mu_{\text{res}}\sqrt{2\pi\Gamma_{\text{res}}}/2$. Notice here that the Franck-Condon factors contained in $\mu_{2,1}$ and $\mu_{\text{res}}$ always appear as product with the field amplitudes $\epsilon_{1,2}(t)$. So the intensities of the fields really need to be chosen according to the Franck-Condon factors between states involved. An enhancement of either one of them will result in the same order decrease required for the other.

Figure 3.4 shows the results of numerically propagating the equations for $b_{1,2}(t)$ and $B_1(t)$, given that $b_1(0) = b_2(0) = B_1(0) = 0$. We plot the populations of states $|1,2\rangle$ for a wide (100$\mu$K) and a narrow (6$\mu$K) resonance. The wide resonance results in an essentially complete population transfer ($> 90\%$), while that of the narrow one is only $\sim 23\%$. No loss of population.
3.3. Numerical computation for Rb-Rb collisions

Figure 3.4: The target $|1\rangle$ and intermediate $|2\rangle$ state populations as a function of time for two resonance widths. **Top panel:** the pump and dump field amplitudes. **Middle panel:** The target state population $|b_1(t)|^2$. The transfer efficiency is 90% for the wide (100µK) resonance, but only 23% for the narrow (6µK) resonance. **Bottom panel:** The intermediate state population $|b_2(t)|^2$. (Notice the large difference in the vertical scale relative to the middle panel.)
3.3. Numerical computation for Rb-Rb collisions

Figure 3.5: Top panel: The target population, $|b_1(t \to \infty)|^2$, for different resonance widths. Bottom panel: $|b_1(t \to \infty)|^2$ as a function of the centre of the resonance $E_{res}$, for $E_0 = 100\mu K$; this shows transfer is optimal when the centre of the resonance coincides with the central energy of $bE(0)$.

in the target ground state can occur in a single atom-pair photoassociation event, but it is possible in practice, due to either atomic collisions that populate other vibrational levels, or multiple pulse pairs that subsequently move population back or away. As shown in the lower panel, due to the adiabatic nature of the process and the “counter-intuitive” pulse ordering, the population of the intermediate level $|2\rangle$ remains very low.

3.3.2 Ensemble transfer efficiency

In agreement with Ref. [56], for each single atom-pair photoassociation event, the transfer efficiency via a wide resonances is always better than that of a narrow one (Figure 3.5 top panel). The situation is however different
3.3. Numerical computation for Rb-Rb collisions

Figure 3.6: The magnitude of the window functions $f^W(t)$ for different resonance widths $\Gamma_{res}$ and fixed height $\mu_{res}$. Longer tails of $|f^W(t)|$ are observed for narrower resonances.

for an ensemble of colliding atoms due to previously mentioned dynamical effects. An alternative way of viewing this effect is to examine the discrete effective modes which replace the continuum in our theory. These modes are, to all intents and purposes, resonances\cite{61}. As clearly seen in equation (3.30), the rate of de-populating an effective mode is $\Gamma_{res}$, the resonance-width of that mode. Hence narrower resonances correspond to smaller rates of depopulation, and increased interaction duration of the effective modes with $|2\rangle$.

In Figure\[3.6\] we examine these trends in a quantitative way by displaying $f^W(t)$, the field-normalized source term (or a window function), given as,

$$f^W(t) = f_{source}(t)/\epsilon_2(t) = \int_{-\infty}^{\infty} \mu_{2,E} b_E(0) e^{i\Delta E t} dE,$$ \hspace{1cm} (3.31)

for resonances of changing widths. Clearly in evidence is the prolonged duration of $f^W(t)$ when switching to narrower resonances.

The temporally stretched population source is also beneficial when we consider the action of a pulse pair that is delayed relative to $t_0$, the arrival time of the incoming wave packet. Figure\[3.7\] shows the transfer efficiency as a function of such delay times for 3 different resonance widths. For a narrow resonance, despite the drop in the peak value, the single collision transfer efficiency remains large for longer times. This means that atom-pairs that
started their collision prior to the peak fields can still be transferred into bound molecules with significant probability.

Figure 3.7: Target state transfer efficiency $|b_1(t \to \infty)|^2$ for different resonance widths as a function of the delay time $\delta t = t_0 - t_P$, where $t_P = 1.2\mu$s is the pulses’ overlap peak time, and $t_0$ is the incoming wave packet peak time.

Figure 3.8: The time-averaged molecular production efficiency for a single pulse pair for an atom ensemble at $100\mu$K, calculated by integrating the delay plots of Figure 3.7.

In order to obtain the delay-time averaged efficiency for an atomic ensemble, we need to calculate the area under the transfer-efficiency curves in Figure 3.7. Figure 3.8 displays the dependence of the delay-time averaged efficiency for various resonance widths. We first notice that the efficiency changes relatively slowly for resonance width larger than $1000\mu$K. This is because in this case the resonance width far exceeds $\delta_0$, the energetic
spread of the initial atomic ensemble, thus approaching the flat-contiuum (SVCA) limit. But as the width of the resonance drops to a few $\mu$K, the molecular production efficiency rises to a maximum value, then drops significantly due to prolonged collision time making spontaneous emission more pronounced. Therefore, there really exists an optimal resonance width for which the molecular production efficiency is maximal. Comparing the optimal molecular production efficiency, obtained for a (narrow) resonance value of $\sim 8\mu$K, with the efficiency in the flat-contiuum limit, we see an improvement factor around 1.56.

3.3.3 Scaling behaviour with ensemble temperature

We now explore, as was done in Ref. [49], how the process varies as the average ensemble energy $E_0$ and energy spread $\delta_0$ are scaled down by a factor of $s > 1$, namely, $E_0 \rightarrow E_0/s$, and $\delta_0 \rightarrow \delta_0/s$.

The equations have been shown to be invariant under this scaling [49], provided that the peak time was scaled up by the same factor $t_0 \rightarrow st_0$, and the initial wave packet amplitude is scaled as $b_E(0; E_0, t_0) \rightarrow \sqrt{s}b_E(0; E_0/s, st_0)$. We now consider the effect, in addition to the above, of scaling the resonance shape as $\mu_{2, E}(E, \Gamma_{res}) \rightarrow \mu_{2, E}(E/s, \Gamma_{res}/s)$. In order to match the spectral profile to the scaled $b_E(0)$, we need to scale up the centre frequencies and durations of the two pulses by the same $s$ factor. Since we can choose the intensities of the fields, we let $\epsilon_1(t) \rightarrow \epsilon_1(ts)/s$ and $\epsilon_2(t) \rightarrow \epsilon_2(ts)/\sqrt{s}$ [49] As a result, the source function scales like $f_{source}(t, t_0, \Gamma_{res}) \rightarrow s^{-1} \cdot f_{source}(st, st_0, \Gamma_{res}/s)$. The above scaling choices leave the dynamical equations [3.28][3.30] essentially unchanged, only except for the spontaneous decay rate. As we scale the relevant times by a factor of $s$, the effect of the spontaneous emission becomes more pronounced.

In Figure 3.9, we display the dependence of the single collision photoassociation efficiency on the spontaneous decay rate. Note that a change in one order of magnitude for the spontaneous decay rate only affects our results negligibly. When we compare the results to those in Figure 3.5, where the transfer efficiency is plotted as a function of the resonance width, we see
3.3. Numerical computation for Rb-Rb collisions

Figure 3.9: Top panel: The single collision photoassociation efficiency $|b_1(t \to \infty)|^2$ as a function of resonance width, for four different values of the spontaneous decay rate. Bottom panel: The same plot at stronger laser intensities. The photoassociation efficiency now becomes insensitive to the spontaneous decay rates.
3.3. Numerical computation for Rb-Rb collisions

that the transfer efficiency is not significantly affected at ensemble temperatures of a few $\mu$K to a few $10^2$ $\mu$K. As the ensemble temperature goes down by three orders of magnitude, the single collision transfer efficiency goes down too, by $\sim 67\%$ of its original value. The effect is more pronounced for narrower resonances, because the longer interaction times enhance the effect of the spontaneous decay. However, as shown in the lower panel of Figure 3.9, it is possible to counter the effect of spontaneous decay at very low temperatures, e.g. in nK range, by increasing the intensity of both laser fields.

So in short, the optimal resonance width seems to be in most cases around $\sim 8\%$ of the ensemble temperature. The corresponding molecular production efficiency is $\sim 56\%$ higher than that of the wide resonance (flat continuum) case.

3.3.4 Thermalization and practical matters

So far, we have considered the molecular production efficiency for a single collision event, and for an ensemble of colliding atoms, under the excitation of a single pulse pair. In practice, one might also need to consider the effect of a train of such pulse pairs, carrying out the photoassociation on the same atomic ensemble. Although this is not the focus of our current study, we nevertheless provide some qualitative comments on the difficulties and their possible solutions.

Firstly, the cumulative action of a train of pulse, at longer timescales, can in fact change regions in phase space corresponding to the recombining atoms, thereby affecting the initial wave packet amplitude $b_E(0)$. However, an atomic ensemble can thermalize sufficiently fast, on the order of milliseconds, to yield the typical atomic trap setting of $100\mu$K temperature and $10^{11}/\text{cm}^3$ density [62]. This means, depending on the repetition rate of the pulses, that after a few thousand $\mu$s pulse-pairs, the atomic ensemble can thermalize back to its original phase-space distribution, re-validating the ensemble-averaged form we used for $b_E(0)$.

According to previous estimates [49, 50], the total number of pulse pairs
needed to transfer an entire atomic ensemble of density $10^{11}/\text{cm}^3$ (at a temperature of 100 $\mu$K) is around of $10^7$. Therefore a few thousand pulses is indeed a very small fraction of total number of pulses needed, and the thermalization is fast enough comparing with the ensemble size molecular conversion time.

Another practical difficulty is how to hide the newly formed molecule, either from subsequent pulse pairs that may transfer them back to the atomic continuum, or from surrounding atomic collisions that can impart temperature to the ultracold molecules. In accordance with more detailed discussions in Refs. [49, 50], this can be done, for example, by allowing the newly formed molecules to physically “leak” away from the laser focus, which is possible because they react differently from the atoms to the confining laser frequency. A molecular trap can then be placed just below the atomic trap. Such solution, however, imposes constraints on the time separation between pulse pairs in the pulse train; their separation needs to be long enough for such molecule-atom separation process to happen. Further quantitative analysis, as future extension to this study, is then required.

3.4 Conclusions

In this study we have shown that Adiabatic Raman Photoassociation of ultracold atoms, assisted by collisional resonances, is an efficient way of producing ultracold diatomic molecules in deeply bound states. By replacing the atomic scattering continuum with resonances by a discrete set of effective modes, we derived an analytical framework for the dynamics that both reveals the factors contributing to the final molecular production efficiency clearly and concisely, and makes convenient computational implementations. Then through numerical simulations, we confirmed the improvement of molecular production efficiency, in the single atom-pair collisional event, using wide resonances. When an ensemble of atoms is considered, on the other hand, there exists an optimal, yet very narrow, value of resonance width for best transfer efficiency. The underlying physical mechanism is the dynamic interplay and balanced competition between large Franck-Condon
3.4. Conclusions

overlap factors, which improve single collision transfer efficiency, and pro-
longed collisional lifetimes, which increase the number of collision events
during the optical pulses.

Quantitatively, the narrow-resonance molecular production efficiency can
be as much as \( \sim 56\% \) higher than the wide resonances efficiency. For atomic
temperatures in the \( \mu \text{K} \) range, we find that the optimal conditions are at-
tained for resonances whose widths are about one order of magnitude smaller
than that of the ensemble temperature. In the case of lowered atomic tem-
peratures, ARPA scheme is shown to also work efficiently. The only non-
scalable, or non-controllable, factor is the spontaneous decay rate, which in
the decreased temperature setting, amplifies its harm to the final produc-
tion efficiency. It is shown, however, that it can be effectively countered by
increasing intensities of the optical fields used.

Interesting future applications would include time-dependent resonances.
We envision combining ARPA with dynamical sweeping Feshbach resonances
across the threshold energy range. As the sweep will render the resonances
narrower, the laser pulses will be made narrower in order to transfer the
atomic gas into molecules in an optimal piecewise manner.
Chapter 4

Linear molecular response in the strong field domain

In this chapter, we discuss the dynamical behaviour of quantum transitions of simple molecules under the excitation by broadband, high-intensity, femtosecond pulses that are subject to coherent spectral shaping. The interesting physics resides in the interference effects in the photo-response of the molecule, specifically how the transition into a number of previously unoccupied quantum states can be correlated and controlled by the coherent aspects of the incident light pulse.

The original motivation behind the studies is the following. In time-dependent quantum mechanics, the probability for a material system to transition to a new energy eigenstate of the unperturbed Hamiltonian, due to a first-order perturbation (see Section 2.2.2), is linearly dependent on the strength of such perturbation [1]. However, in practice, the strength of the perturbing force is usually difficult to classify in relation to the quantities of the system it applies to. Therefore, the linearity in the material response has been commonly used, although incorrectly, to deduce whether the perturbation is of the first order. It is then one of our motivations to clarify this fallacy by demonstrating that such linearity is not exclusive to first order perturbative fields: linear response can also be present with strong field (non-first order) due to dynamical interference effects.

In addition, some recent experiments during the time of the original publication also claimed phase-only coherent control using weak optical fields [63] - an impossibility according to traditional coherent control theory (section 2.2.3 and [4, 64, 65]). Although, later on, these experiments stimu-
4.1. Linear response via Raman transitions in a three-potential model

![Diagram](image)

Figure 4.1: The model molecular system has two energy-degenerate excited electronic potentials of continuum nature, coupled with a number of bound vibrational levels in the ground potential by a broadband light pulse.

lated the even richer topic of coherent control over open quantum systems [66–69], where such phase-only control is shown possible, they did employ above incorrect linear-response argument to produce its conclusions about the strength of the light fields. We therefore consider our studies also as a possible alternative explanation to these experimental findings, by presenting response linearity, high-intensity perturbation, as well as phase-only coherent control in the same picture.

4.1 Linear response via Raman transitions in a three-potential model

The first study below presents a rather general formulation, describing the response of a molecular quantum system under a strong optical perturbation. We will reveal the linear response of the material system under high-intensity excitation signified by higher order excitation, accompanied by coherent control. Specifically, the molecular system initially resides in a bound manifold along a certain internal coordinate (e.g. vibration of a diatomic molecule), and the incident optical pulse interacts with the molecule's dipole, and excites it electronically into a pair of energy-degenerate excited potentials that host continuum or quasi-continuum states (e.g. for dissociation or isomerization), as illustrated in Figure 4.1.
4.1. Linear response via Raman transitions in a three-potential model

With the electric field of the pulse $E(t) = 2\hat{\epsilon}(t) \cos(\omega_L t)$ being polarized in $\hat{\epsilon}$ direction, having envelope modulation $\epsilon(t)$ and centre frequency $\omega_L$, the effective Hamiltonian in atomic units is

$$H = H_M + H_I,$$

$$H_M = \sum_{j=1}^{N} E_j |E_j\rangle \langle E_j| + \sum_n \int E |E, n^-\rangle \langle E, n^-| dE,$$

$$H_I = -\mu \cdot E(t),$$

(4.1)

where $\mu$ is dipole operator of the molecule, $|E, n^-\rangle$ are the aforementioned continuum eigenstates of energy eigenvalue $E$, and $n$ denotes one among the two potentials (the “channel”) which is also the main quantity we wish to control. $N$ is the number of bound states that are effectively coupled by (continuum-mediated) resonance Raman transitions as enabled by the bandwidth of the excitation pulse.

As usual, the time-dependent state of the material system is expanded in relevant energy eigenstates,

$$|\Psi(t)\rangle = \sum_{j=1}^{N} b_j(t) e^{-iE_j t} |E_j\rangle + \sum_n \int b_{E,n}(t) e^{-iEt} |E, n^-\rangle dE.$$  (4.2)

The Schrödinger’s equation for the time evolution of this state then translates into the following differential equations (with Rotating Wave Approximation)

$$\dot{b}(t) = i \sum_n \int \Omega_{E,n}(t) b_{E,n}(t) dE,$$

$$\dot{b}_{E,n}(t) = i \Omega_{E,n}^\dagger(t) \cdot b(t),$$

(4.3)

where we have organized the bound level amplitudes and Rabi frequencies as vectors $[b(t)]_j = b_j(t)$ and $[\Omega_{E,n}(t)]_j = \epsilon(t) \mu_{j,n}(E) e^{-i\Delta_{E,j} t}$. The transition dipole matrix elements are $\mu_{j,n}(E) = \langle E_j | \mu \cdot \hat{\epsilon} | E, n^- \rangle$, and the laser detuning from resonance is $\Delta_{E,j} = E - E_j - \omega_L$. The time evolution of the bound state amplitudes is obtained by formally
4.1. Linear response via Raman transitions in a three-potential model

integrating $b_{E,n}(t)$, and substituting the expression into the first part of equation (4.3), assuming that $b_{E,n}(-\infty) = 0$ for all $E$ and $n$:

$$\dot{b}_j(t) = -\epsilon(t)e^{iE_jt} \int_{-\infty}^{t} \epsilon^*(t') \sum_{k,n} F_{j,k}^{(n)}(t-t')b_k(t')e^{-iE_k t'} dt',$$

(4.4)

where

$$F_{j,k}^{(n)}(t-t') = \int \mu_{j,n}(E)\mu_{n,k}(E)e^{-i(E-\omega L)(t-t')}dE.$$  

(4.5)

The matrix spectral correlation function $F_{j,k}^{(n)}(t-t')$ can be further simplified by applying the “slowly varying continuum approximation” (SVCA) [4], in which we replace each energy-dependent transition dipole matrix element by some average value $\mu_{j,n}(E) \approx \mu_{j,n}(\omega L) \equiv \bar{\mu}_{j,n}$, and it follows that $F_{j,k}^{(n)}(t-t') \approx 2\pi \bar{\mu}_{j,n}\bar{\mu}_{n,k}\delta(t-t')$. This approximation is valid whenever the bound-continuum transition dipole matrix element change little over the energies covered by the pulse’s bandwidth. The result is a simplified set of equations for the bound amplitudes

$$\dot{\mathbf{b}}(t) = -\Omega^f(t)\mathbf{b}(t),$$

(4.6)

$$[\Omega^f(t)]_{j,k} = \pi|\epsilon(t)|^2 \sum_n \bar{\mu}_{j,n}\bar{\mu}_{n,k}e^{i(E_j-E_k)t},$$

(4.7)

which can be readily propagated numerically. With bound coefficients known, imposing $b_{E,n}(-\infty) = 0$, we have the probability amplitude of excitation (or, photodissociation or photoisomerization) to channel $n$ as

$$P_{E,n} = |b_{E,n}(t \rightarrow \infty)|^2,$$

$$b_{E,n}(t) = i \int_{-\infty}^{t} \Omega_{E,n}^\dagger(t') \cdot \mathbf{b}(t')dt'.$$

(4.8)

We now assume that two bound vibrational states $|E_1\rangle$ and $|E_2\rangle$ in the ground potential are coupled to two continuum channels $n = \alpha, \beta$, and coherent control is then reflected in our ability to change the energy-averaged branching ratio

$$\rho_{\alpha,\beta} = \int_{-\infty}^{\infty} P_{E,\alpha}dE/\int_{-\infty}^{\infty} P_{E,\beta}dE.$$  

(4.9)
4.1. Linear response via Raman transitions in a three-potential model

The generality of our formulation lies partly in the way that we can define dimensionless parameters $q_n = \bar{\mu}_{2,n}/\bar{\mu}_{1,n}$, and $Q = \bar{\mu}_{1,\beta}/\bar{\mu}_{1,\alpha}$. Although $q_{\alpha,\beta}$ and $Q$ are complex in general, we simplify the analysis by choosing them to be real. We note that when $q_{\alpha} = q_{\beta}$, writing out equation (4.8) would give us the branching ratio as $\rho_{\alpha,\beta} = 1/Q^2$, which is independent of the field, thus no optical control is possible in this case. Therefore, we assume $q_{\alpha} \neq q_{\beta}$, a very reasonable assumption in most molecular systems.

In a typical experimental setup, a pulse shaper [70] is used to specify the amplitudes and phases of each frequency component of the excitation pulse. Here we consider a class of pulses consisting of two equally wide, linearly chirped sub-pulses. The interaction Hamiltonian that follows has general form

$$H_I = -2\mu[\epsilon(t + t_0) + \epsilon(t - t_0)] \cos[\omega(t)t]$$

$$\approx -\mu \epsilon_s(t) e^{-i\omega_L t},$$

$$\omega(t) = \omega_L + a_0 t,$$

$$\epsilon_s(t) \equiv [\epsilon(t + t_0) + \epsilon(t - t_0)] e^{-i a_0 t^2}. \quad (4.10)$$

For our analysis, we have devised a specific pulse form, as the following, which includes a pair of Gaussian-shaped sub-pulses

$$\epsilon_s(t) = \frac{1}{2} \left[ 2(1 + 2iA)(1 + e^{-t_0^2/\tau^2}) \right]^{-1/2} \cdot \left\{ \exp \left[ \frac{-(t + t_0)^2}{2\tau^2(1 + 2iA)} \right] + \exp \left[ \frac{-(t - t_0)^2}{2\tau^2(1 + 2iA)} \right] \right\} \quad (4.11)$$

which results in a convenient, analytical expression for the spectrum

$$\tilde{\epsilon}_s(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \epsilon_s(t) e^{-i\omega t} dt$$

$$= \cos (\omega t_0) \frac{(2I)^{1/2} \exp[i\phi/2 - iA\tau^2\omega^2 - \omega^2\tau^2/2]}{[1 + \cos \phi \exp(-t_0^2/\tau^2)]^{1/2}}. \quad (4.12)$$

The purpose of such analytical construction is to guarantee the conservation of total pulse energy, for all dimensionless parameters related to shaping
4.1. Linear response via Raman transitions in a three-potential model

Figure 4.2: Sample photo-products population dynamics for different time delays and chirping parameters. The intensity value is $\mu^2 \tau I = 0.01$. 
4.1. Linear response via Raman transitions in a three-potential model

defined as the following. Firstly, \( W = \tau |E_1 - E_2| \) is used to represent the duration for both sub-pulses, in the unit of the inverse of the energy separation between the vibrational states. The time delay between the two sub-pulses is then controlled by the value of \( T_0 \equiv t_0/\tau \), where \( 2t_0 \) the is the separation in time between the peaks of the sub-pulses. Lastly, \( A \) determines any potential linear chirp rate via \( a_0 = A/|\tau^2(1+4A^2)| \). Such parameterization allows separate control of the spectral amplitude via \( T_0 \) and the spectral phase via \( A \). Note that the choice \( (T_0 = 0, A = 0) \) corresponds to a transform-limited pulse with temporal profile \( \epsilon_s(t) = I_1/2 \exp[-t^2/(2\tau^2)] \).

Given the pulse shape, the probabilities of photodissociation (photoisomerization) into the \( n = \alpha, \beta \) channels are calculated using equation (4.8). For the case where we use \( Q = 2, q_{\alpha} = 0.6, q_{\beta} = 1.2 \) and \( W = 0.5 \), Figure 4.2 shows the probabilities as functions of time. Because of the assumed “flatness” of the continuum, the changes in the probability are rather monotonic in time. Also, having started with state \( |E_1\rangle \), state \( |E_2\rangle \) is populated by continuum-mediated resonance Raman transitions. Figure 4.3 displays \( P(I) \), the photoexcitation yield given as the total population removed from the bound state manifold after the pulse is over, with \( P(I) = \sum_n P_{E,n} \), where \( P_{E,n} \) are obtained from equation (4.8). We see that the response curves, in subplots (a,c), start saturating after displaying a linear dependence. At moderately strong intensities, (substantial) control over the branching ratio, in subplots (b,d), as a function of \( T_0 \) and \( A \) is clearly in evidence. For example, at the higher end of intensity values \( (\mu^2 \tau I = 0.01 - 0.02) \), the yield for the \( (T_0 = 0, A = 0) \) pulse in subplot (a) displays a short bout of linear \( I \) dependence followed by the onset of saturation. In contrast, the yield for the \( (T_0 = \pi, A = 0) \) case in subplot (a), or \( (T_0 = 0, A = \pi) \) cases in subplot (c), displays a much more protracted linear phase prior to saturation.

In spite of the nearly linear photoexcitation yield, for example, at intensity values around \( \mu^2 \tau I = 0.01 \), the branching ratios exhibit rather extensive range of control, of about 16% for shaped pulses (middle non-flat branching ratio curves, in second and fourth panels in Figure 4.3). Even at around \( \mu^2 \tau I = 0.005 \) (lowest non-flat branching ratio curves), where all the yield curves are essentially the same and highly linear, the range of branching
4.1. Linear response via Raman transitions in a three-potential model

Figure 4.3: The photoexcitation yields or “response curves” (subplots a,c) as functions of the field intensity, at particular shaping parameter choices, and the branching ratios as functions of shaping parameters, at fixed intensities (subplots b,d). The response curves are made more linear due to shaping.
4.1. Linear response via Raman transitions in a three-potential model

Figure 4.4: The nonlinearity of the intensity response curves vs. $\mu^2\tau I_0$.

ratio control is still about 8%, obviously a non-first-order behaviour. Only when the intensity approaches zero (e.g. at $\mu^2\tau I = 0.0001$) where the yield approaches zero too, does the variation in the branching ratio due to shaping disappear.

In order to quantify the visibly evident high degree of linear intensity dependence, we have also calculated a nonlinearity factor

$$\frac{\left( \frac{d^2P}{dI^2} \right)_{I_0}}{\left( \frac{2dP}{dI} \right)_{I_0}},$$

the ratio between the second-order and the first-order terms in the Taylor series expansion about $I_0$. Figure 4.4 shows the degree of nonlinearity calculated in this manner, plotted against $\mu^2\tau I_0$. We see that until $\mu^2\tau I_0 = 0.02$, where all the curves begin to saturate significantly, pulses whose shapes are defined by $(T_0 = \pi, A = 0)$ or $(T_0 = 0, A = \pi)$ exhibit a greater degree of linearity, as compared to transform-limited pulse (i.e. $(T_0 = 0, A = 0)$). Up to $\mu^2\tau I_0 = 0.01$, the nonlinear factors of the above pulses are about half their transform-limited values.
4.1. Linear response via Raman transitions in a three-potential model

The physical reason for this enhanced linearity of the molecular response to pulse shaping is due to the coherent interplay between the two sub-pulses. Essentially, the first sub-pulse creates, by a (continuum-mediated) Raman process, a superposition of the $|E_1\rangle$ and $|E_2\rangle$ bound states. The second sub-pulse then dissociates this superposition state in the usual bichromatic control scenario [4, 64]. We verify this mechanism by looking at the intensity responses, a subset of which is shown in subplot (a) of Figure 4 as a function of $T_0$. For each $T_0$ value, when it’s displaced by an integer multiple of $2\pi$ (as a result of our choice of numerical parameters), we found an identical response curve. This matches the periodicity of the vibrational superposition. However, when we set $q_\alpha$ and $q_\beta$ to zero, the variations in $T_0$ no longer alter the intensity response curves, nor do such variations affect the branching ratio. For cases involving chirping, the response curves can only mainly a certain degree of “recurrence” for $A$ smaller than $2\pi$, at $T_0 \ll 1$.

Finally, we also examine here the case in which the initial state is composed of a coherent superposition of the two bound states, $c_1 |E_1\rangle + e^{i\phi_0}c_2 |E_2\rangle$ with $c_1^2 + c_2^2 = 1$, subject to the action of a simple transform-limited excitation pulse, for which ($T_0 = 0, A = 0$). This time, it is the variation in $c_2$, or the relative phase $\phi_0$, that affects the intensity response curves. In Figure 4.5 we see changes to linearity of the curves, now due to change in the $c_2$ and $\phi_0$ parameters. The variation in the branching ratio, due to changes in these variables, is quite significant. The branching ratios are however insensitive to the laser intensity because control is mainly derived from the variation in the initial superposition rather than the field.

In summary, here we have been able to probe how pulse shaping affects the intensity dependence of the photoexcitation, by first developing a time-dependent, non-perturbative model of coherent control of a three-potential molecular system interacting with a broadband pulse. We have shown that shaped pulses may exhibit a wide range of linear response of the overall photoexcitation yield, even at moderately high intensities. The mechanism responsible for this behaviour is bichromatic control in conjunction with continuum-mediated Raman transitions between bound states. Secondly,
4.1. Linear response via Raman transitions in a three-potential model

Figure 4.5: The intensity response curves for an initial superposition of two bound states $\psi_i = c_1 |E_1\rangle + e^{i\phi_0} c_2 |E_2\rangle$. Upper two panels are the intensity response and control for $\phi_0 = 0$ and variable $c_2$; lower two panels are the response and control at fixed $c_2^2 = 0.4$ and variable $\phi_0$. 
we have shown that extensive coherent control over the branching ratio can co-exist with extended linear intensity regimes. Thus, linear intensity response, which we have shown to occur even for moderately strong pulses where non-perturbative effects are present, is not a necessary indicator for the weak-field regime nor the validity of employing first order perturbation theory.

4.2 Linear response in $H_2^+$

As we have understood from the above section, there are cases in which the response of a molecule in a single eigenstate to the effects, especially coherent ones, of a high-intensity, broadband laser field is linear. The underlying mechanism can be attributed to quantum interferences between multiple-eigenstate excitation pathways. In this second study, we demonstrate the extended appearance of such response linearity in the realistic hydrogen cation molecule, $H_2^+$, that undergoes extensive rotational and electronic excitation by a femtosecond pulse. This study relates to and extends the previous one in two aspects:

(i) The quantum structure of $H_2^+$, although being the “simplest molecule”, is more complex and realistic than the three-potential model before. Molar rotation now provides a “ladder” of degenerate potential energy surfaces within each electronic manifold. We tackle the problem accordingly by simulating the dynamics of vibrational wave packets, rather than full Born-Oppenheimer energy eigenstate amplitudes, in these rotational-electronic channels. It turns out to be conceptually compact, analytically concise, computationally straightforward and non-demanding, and meanwhile also reveals the much richer wave packet interference effects.

(ii) The initial state of the molecule is assumed to be a vibrational wave packet in one particular rotational-electronic channel, as a continuation from the last case analyzed in the previous study. Such wave packet is assumed to be created from a single vibrational eigenstate by some earlier pulse via Raman-type transitions. As such, it’s important to point out that in our current case, we always have bichromatic control even with first-order pertur-
bative field due to the simultaneous excitation of multiple vibrational eigenstates. Nevertheless, we will consider and demonstrate non-perturbative regime exclusively. The excitation pulse used is thus high-intensity and broadband, and its timing with respect to the initial wave packet can be tuned. Various intensity response and population dynamics behaviour will then follow, in every relevant rotational-electronic channel, as a result of such time delay.

The time-delayed optically probing of wave packet interference effects is commonly known as a Wave Packet Interferometry (WPI) technique [4, 64, 71–75]. The WPI in our current setup differs from a conventional one in that the photoexcitation is delayed with respect to a pre-existing material wave packet, rather than a precursor pulse. The resultant wave packet interference is nevertheless similar: Due to the high intensity of the excitation pulse, the initial vibrational wave packet interferes with part of itself, via Raman-type transitions, differently at different delay times. Also, the wave packets created by the excitation pulse originating from each eigenstate within the initial wave packet also interfere differently at different delay times, and do so in an extended number of bound and continuum channels.

As before, not only do we reveal linear response (now as a result of WPI-type excitation), we will also show the coexisting ability of coherent control. It also represents a simple yet effective control mechanism: the time delay translates, in the spectral domain, to a linear tilt of the spectral phase of the excitation pulse. Although such linear shaping may not affect the two-photon spectrum of the pulse, it does so for higher order multiphoton spectral components.

### 4.2.1 Vibrational wave packet method

The molecule under consideration, \( \text{H}_2^+ \), interacts with an incident coherent laser pulse with centre wavelength at 304nm (32900 cm\(^{-1}\)), chosen to overlap well energetically with the transition frequencies between the ground 1s\(\sigma_g\) electronic state and the first-excited 2p\(\sigma_u\) electronic state of the molecule (Figure 4.6). We denote the \( \text{H}--\text{H}^+ \) inter-nuclear separation vector by \( \mathbf{R} \),
4.2. Linear response in $H_2^+$

Figure 4.6: Schematic illustration for the photoexcitation of $H_2^+$ by an optical electric field with bandwidth covering three vibrational states of the ground $1s\sigma_g$ state.

the collective electronic coordinate by $r$, and the electronic wave function by $\Phi_\alpha(R, r)$, where $\alpha = g, e$ refers to the ground or excited electronic state. The vibrational wave packet approach starts by expanding the total molecular wave function in the $Y_{JM}(\theta, \phi)\Phi_\alpha(R, r)$ rotational-electronic basis,

$$\Psi(t, R, r) = \sum_{\alpha, J, M} \psi_{\alpha, J, M}(t, R)Y_{JM}(\theta, \phi)\Phi_\alpha(R, r)/R,$$

where $J$ and $M$ denote respectively the quantum number for total angular momentum of the nuclei and its $z$-projection. Instead of vibrational eigenstates, time dependent “vibronic coefficients” $\psi_{\alpha, J, M}(t, R)$ are used to represent the vibrational wave packet in the channel specified by $(\alpha, J, M)$, and thus depend on time non-trivially. The additional choice of linear field polarization ensures that $\Delta M = 0$, and that $\Delta J = \pm 1$.

Dropping the conserved $M$ index for brevity, we consider the molecule starting in the $J = 0, M = 0$ ground electronic state $g$. The molecule’s quantum dynamics is governed by the time dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi,$$
4.2. Linear response in $H^\dagger_2$

where as usual $H$ is the total light-matter dipole interaction Hamiltonian

$$H = H_{\text{mol.}} - \mu \cdot E(t) = H_{\text{mol.}} - \mu \cdot \hat{E}E(t), \quad (4.15)$$

with $\mu$ being the dipole operator and $\hat{E}E(t)$ the electric field of the excitation light. Substituting the state expansion and the Hamiltonian into equation (4.14), we thus obtain a set of coupled differential equations in matrix form

$$i\hbar \frac{d}{dt} \psi(t, R) = H(t, R)\psi(t, R). \quad (4.16)$$

where $\psi(t, R)$ is represented by a vector of vibrational wave packets, defined to have components $\psi_J = \psi_{e,J}$ for odd $J$, and $\psi_J = \psi_{g,J}$ for even $J$, with $J = 0, 1, 2, 3...$ The Hamiltonian matrix $H$ is a tridiagonal matrix, with $H_{J,J} = H_{e,J}$ for odd $J$, and $H_{J,J} = H_{g,J}$ for even $J$, with diagonal elements being

$$H_{(g,e),J}(R) = -\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + \frac{J(J+1)}{2mR^2} + W_{g,e}(R), \quad (4.17)$$

and off-diagonal elements

$$H_{J,J+1} = H_{J+1,J} = -\langle Y_{J+1}^0 | \langle \Phi_e | \mu | \Phi_g \rangle \cdot E(t) | Y_J^0 \rangle$$

$$= -D(R)E(t) \langle Y_{J+1}^0 | \cos \theta | Y_J^0 \rangle, \quad (4.18)$$

where $m$ is the reduced mass for the molecule, and $\theta$ is the angle between $\hat{E}$ and the transition dipole momentum $\langle \Phi_e | \mu | \Phi_g \rangle$, a spatial vector assumed to be along the internuclear axis direction. The ground and excited potential energy surfaces $W_{g,e}(R)$, and the magnitude of the electronic transition dipole function $D(R)$, accurate for $R \leq 17$ Bohr, are calculated using GAUSSIAN with TD method and 6-311+G(3df,3pd) basis set. Using properties of the associated Legendre polynomials, we also have simplification

$$\langle Y_{J+1}^M | \cos \theta | Y_J^M \rangle = \sqrt{\frac{(J+1+M)(J+1-M)}{(2J+1)(2J+3)}}. \quad (4.19)$$

In the dipole interaction, the electric field amplitude $E(t)$ is spatially
uniform on the molecular scale, and has only time dependence. We choose a transform-limited pulse,

$$E(t) = E_0 \exp \left[-\frac{(t - t_c)^2}{2t_p^2}\right] \cos \left[\omega_L(t - t_c)\right],$$  

(4.20)

with peak intensity $$I = c\epsilon_0|E_0|^2$$. The pulse duration is chosen to be $$t_p = 3$$ fs, so that its width in energy ($$\sim h/t_p$$) is comparable to the differences in energy between the $$v = 4, 5, 6$$ vibrational levels that make up the initial wave packet in the $$J = 0$$ channel (Figure 4.6).

$$\psi_{g,J=0}(t = 0, R) = \left[\phi_4(R) + \phi_5(R) + \phi_6(R)\right]/\sqrt{3}$$

$$\psi_{\alpha,J>0}(t = 0, R) = 0,$$

(4.21)

created at some initial time $$t = 0$$. Here $$\phi_v(R)$$ are the formal vibrational eigenstates of the channel-Hamiltonian $$H_{g,J=0}(R)$$.

We then apply the laser pulse of equation (4.20) and follow the wave packet dynamics, governed by the Schrödinger’s equation, using a 4th order Runge-Kutta numerical method, with 0.0006 fs time steps and a spatial grid mesh of 0.02 Bohr. With such short pulse duration, accurate numerical propagation of vibrational wave packets can be achieved at moderate computer times. An advanced numerical method utilizing effective mode expansion [76] provides an efficient, full-eigenstate alternative to our vibrational wave packet method, especially in the case when the excitation pulse has much longer duration.

### 4.2.2 Response analysis

The propagation of vibrational wave packets enables us to directly obtain the molecular population in each specific channels they belong, as a function of the intensity of the excitation field. In Figures 4.7 to 4.10 we display the molecular populations in rotational channels up to $$J = 10$$, for a wide range of peak intensity values. The populations are obtained by integrating the magnitude-squared vibrational wave packets over the internuclear distance $$R$$. The upper bound for rotation $$J = 10$$ is chosen to be appropriate for the
peak intensity of the field, which is verified by gradually increasing the peak intensity until the excited population in $J = 10$ channel is approaching, but kept below, 1%.

As shown in Figure 4.7 and 4.8 for $9 < t_c < 20$ fs range of delay times we observe a variable degree of near linear response of the population to the field intensity. This is observed for all the rotational channels, as well as in the initially unoccupied $v = 3, 7$ vibrational states. The response becomes more linear for example at $t_c \approx 18$ fs, when suppression of excitation, such as in the $J = 0 \rightarrow J = 2, 4$ case discussed below, exists. An additional case of essentially perfect linear response occurs for $t_c \approx 18$ fs where the $v = 3$ state exhibits excitation enhancement. Strong linearity accompanied by excitation enhancement is also observed in $v = 7$ state and $J = 1, 3$ channels, at around $t_c \approx 9$ fs. At relatively high rotational channels $J > 5$, response can still be very linear close to $t_c \approx 15$ fs, but this occurs only at moderate to high intensities ($> 200$TW/cm$^2$).

Such essentially linear response curves can persist up to a few hundred TW/cm$^2$ of peak intensity. This is despite the fact that at such intensities the fields display all the features of being strong: For example, starting at the ground rotational level, the field induces extensive rotational excitation by multiple Raman transitions, populating channels up to $J = 10$. In addition, coherent control over the branching ratios between rotational, or ro-vibrational, channels, is also present as a function of $t_c$ alone (as shown in Figure 4.11). This amounts to a part, or a second stage, of the phase-only (referring to the molecular phases determined by $t_c$) coherent control over the excitation of a single eigenstate [4], that, again, is only present in the non-perturbative regime. We have thus conclusively demonstrated our original claim [77] that essentially linear response curves can in fact exist within the strong-field regimes, accompanied by phase-only coherent control over the population branching ratio.

In Figures 4.8 and 4.10, we display the response of the system when the delay times assume values displaced by $\sim 20$ fs relative to the values of Figures 4.7 and 4.9. They are almost identical, hence implying a periodic behaviour. This periodic behaviour is best demonstrated in Figure 4.12 and
4.2. Linear response in $H^+_2$

where clear population beating, at about the same period $\sim 20$ fs, is displayed in all the rotational and vibrational states under consideration. The period of $\sim 20$ fs matches that of the vibrational motion of the initial wave packet, which is determined by the energy separation between nearest vibrational levels. Specifically, this period is given as $2\pi h/\Delta E \cong 2\pi h/0.008$ Hartree $\cong 18.8$ fs, with $\Delta E$ being the average energy difference between the $v = 4, 5$ and $v = 5, 6$ levels.

A similar beating phenomenon to the one described here was observed experimentally by Ohmori et al. [78], (see also [79]) where a strong delayed near-infrared excitation pulse, analogous to our second excitation pulse, was seen to cause beatings in the populations of individual vibrational levels belonging to the $B$-state of diatomic iodine, due to the interference between the elastic $|v\rangle \rightarrow |v\rangle \rightarrow |v\rangle$ Rayleigh scattering and the inelastic $|v \pm 1\rangle \rightarrow |v'\rangle \rightarrow |v\rangle$ Raman scattering.

The present oscillatory behaviour is similar to the above mechanism [78], except for the important difference that the intermediate state is the $|E, n^-\rangle$ dissociative continuum. We are thus seeing interference between the elastic $|v\rangle \rightarrow |E, n^-\rangle \rightarrow |v\rangle$ resonance Rayleigh scattering and the inelastic $|v \pm 1\rangle \rightarrow |E, n^-\rangle \rightarrow |v\rangle$ resonance Raman scattering.

Aside from such periodicity, the population beating in Figure 4.12 and 4.13 is also influenced by the initial vibrational wave packet motion. In Figure 4.14 we plot the spatio-temporal profile of the initial field-free wave packet:

$$\left|\phi_4(R)e^{-iE_4 t/h} + \phi_5(R)e^{-iE_5 t/h} + \phi_6(R)e^{-iE_6 t/h}\right|^2.$$

We observe that at $t_c = 10, 30, \text{and } 50$ fs delay times for which the population of the entire $J = 0$ channel is minimal, the field-free wave packet reaches its classical turning point, and is mostly concentrated at the Franck-Condon region close to $R = 3 - 4$ Bohr. This in turn increases the Franck-Condon overlap and thus enhances the total population removal from the entire $J = 0$ channel.
4.2. Linear response in $H_2^+$

Figure 4.7: State populations as a function of laser peak intensity, and of delay times for various $J$-channels, and for the $v = 3$ and $v = 7$ states of the $J = 0$ channel.
4.2. Linear response in $H_2^+$

Figure 4.8: State populations plots similar to Figure 4.7 but for a different band of delay times approximately 20 fs later. The response curves show almost identical behaviour.
Figure 4.9: Similar state population plots as in Figure 4.7 and 4.8 but for channels of higher $J$, with the same bands of delay times (same colour schemes for the plots).
4.2. Linear response in $H_2^+$

Figure 4.10: Continued from Figure 4.9 for the later time band.
4.2. Linear response in $H_2^+$

Figure 4.11: Branching ratio of populations in some pairs of vibrational and rotational states are plotted, signifying coherent control.
4.2. Linear response in $H_2^+$

Figure 4.12: Population in various vibrational eigenstates $v = 3 - 7$ in the $J = 0$ channel, and first three rotational channels, as functions of delay time $t_c$. Superimposed are such scans with different field intensities, with the same intensity range and colour scheme as Figure 4.11.
4.2. Linear response in $H_2^1$

Figure 4.13: Similar to Figure 4.12 but for higher rotational channels.
4.2. Linear response in $H_2^+$

Figure 4.14: The field-free probability-density for the initial vibrational wave packet as a function of $R$ and $t$. The beat frequency ($\approx 5 \times 10^{13}$ Hz) is in agreement with the average vibrational spacing $(E_{v=6} - E_{v=4})/(2\hbar)$.

4.2.3 Conclusions

We have studied the regimes of linear response of the $H_2^+$ molecule subject to a high-intensity ultrafast pulse, which is delayed with respect to an assumed precursor Raman-type excitation that creates a vibrational superposition state. We have demonstrated that the photoexcitation yield as a function of the pulse’s intensity can vary greatly in shape, and exhibit essentially linear dependence at certain delay times. At moderately strong laser intensities, the molecular population in a number of rotational-electronic channels also oscillate with this delay time, with a period corresponding to the vibrational period determined by the nearest vibrational eigenstates. Strong-field linear response is linked to the suppression of excitation during the destructive interference periods of this oscillatory behaviour, where excitation saturation is “postponed” to even larger field intensities. This effectively makes the linearity of the response curves an ineffective indicator of the strength of the field, comparing with, for example, the extent of rotational or electronic excitation.

This study complements the first study on a three-state model, and affirms our previous findings concerning phase-shaped excitation pulses [77]: While the existence of weak fields can justify the use of first-order pertur-
4.2. Linear response in $H_2^+$

Electron excitation and imply linear response, the converse is not true. Namely, linear response does not necessarily imply the perturbative weak field domain.

It’s also important to point out that, in the context of high-intensity excitation of the $H_2^+$ molecule, many other interesting phenomena such as non-adiabatic wave packet dynamics around light-induced conical intersections [80–84] are not considered in this study, mainly due to the very short time-scale of the photoexcitation considered. For strong, broadband photoexcitations with much longer durations, the molecular wave packet created via multiphoton transitions, would be able to traverse the field-dressed two-dimensional potential energy surface in both the bond length and rotational angle degrees of freedom, with a conical intersection formed due to the ground and excited electronic manifolds intercepting in energy. Our current method, which accounts for the coupling between the vibrational and rotational wave packet motion, would then in principle be able to analyze such non-adiabatic wave packet dynamics.
Chapter 5

Quantum dynamics under incoherent photoexcitation

5.1 Electronic decoherence via random vibration

5.1.1 Motivation

In previous studies, we have focused on methods of manipulating and controlling molecular quantum dynamics through coherent properties of the optical fields, e.g. their spectral phases and timing, in relation to the coherent quantum mechanical wave packets in molecules. Crucial to achieving the final control is our ability to affect the coherent aspects of the field, which in practice is enabled by coherent light sources such as lasers, and experimental tools for spectral manipulation such as pulse shapers. Thus, the molecular control is in its nature inseparable from the coherence of the excitation light.

In recent years, an increasing number of studies have identified surprisingly long-lived coherences in biological systems, especially in photosynthetic light harvesting molecules [85–93]. Such long-lived coherences were detected in studies in two-color photon echo spectroscopy [86, 88], angle-resolved coherent optical wave-mixing [87], and phase-stabilized 2D electronic spectroscopy [94]. Following these findings, it has been suggested that quantum coherence may play an important role in biological processes, for example in the energy transfer that follows the photo-excitation step. An important question to ask is, then, to what extent the dynamics observed in such experiments, which utilize coherent laser light sources, are relevant for natural processes induced by incoherent light sources such as sunlight, even when the
two types of light share the same central frequency and spectral bandwidth.

It is the objective of this study to demonstrate the loss of quantum coherence and control, found in setups similar to our previous studies or the light-harvesting experiments, when the molecular system is excited by incoherent light sources. Several previous studies, analyzing various effects of incoherent excitation sources on the resultant molecular dynamics, include an analysis of the excited state survival probability as a function of the incoherence of the light \([95, 96]\), effects of incoherent fields on the photoisomerization yields \([97]\), a quantum-optical formulation of the state of the molecule after photon-absorption \([98]\), studies of open system dynamics relevant to photosynthetic complexes \([99]\), and general features of the response of open systems to incoherent excitation \([100]\). However, none of these studies looked directly at the spatial shape of the wave packets and the associated temporal evolution and coherence properties resulting from excitation with incoherent vs. coherent light sources. Such studies are particularly important in comparing the nature of the excited quantum state prepared by these light sources.

Therefore, we will concentrate on the actual spatio-temporal shape of the wave functions resulting from photo-excitation, a primary entity that effectively brings out the differences between the two types of light-induced excitations mentioned above. Our main analytical tool is a time-dependent quantum-theoretic calculation of the different nuclear wave packets resulting from the photo-excitation step. Optical incoherence is then simulated by introducing random jumps in the phase and central frequency of the excitation pulse, with the degree of optical incoherence being controlled by the frequency and amplitudes of these random jumps.

We will consider first the photo-excitation of a model molecule into a superposition of two electronic states, and contrast the calculated coherences induced by incoherent light with the outcome of excitation by an ultrashort coherent pulse with the same central frequency and spectral band- width. The spatial structure and time dependence of the resultant wave packet dynamics is then analyzed for a variety of potential energy surfaces. Following it, we will present the similar random wave packet dynamics in the real-
istic IBr molecule, in which the energy-degenerate electronic states are of bound-continuum nature. In this case, the photodissociation flux will also be analyzed for the coherent vs. incoherent cases.

5.1.2 Stochastic Schrödinger’s equation for random wave packet

In this section, we develop a time-dependent theory describing the dynamics of vibrational wave packets of a molecule under weak-intensity optical field that may be incoherent.

Consider, first, the case in which the molecule resides in the ground electronic manifold with \((J = 0, M = 0)\), and is photo-excited to a single electronic excited state that can be of dissociative or bound nature. The light source is again treated as a classical time-varying electric field. The time-evolution of the quantum state of the molecule can then be described by a stochastic Schrödinger’s equation,

\[
i \hbar \frac{d}{dt} \Psi(t, R) = H(t) \Psi(t, R),
\]

(5.1)

where the state vector is written in the basis of rotational-electronic channels as

\[
\Psi(t, R) = \frac{1}{R} \begin{pmatrix}
\psi_g(t, R) \\
\psi_x(t, R)
\end{pmatrix},
\]

with \(\psi_{g,x}(t, R)\) denoting the vibrational wave packets in the ground and excited electronic manifold. The total Hamiltonian matrix consists of a time-independent molecular part and a time-dependent interaction part describing electric-dipole interaction

\[
H(t) = H_{mol} + H_I(t),
\]

\[
H_{mol} = \begin{pmatrix}
H_g & 0 \\
0 & H_x
\end{pmatrix} = \begin{pmatrix}
\hat{T}_N + W_g & 0 \\
0 & \hat{T}_N + W_x
\end{pmatrix},
\]

\[
H_I(t) = \begin{pmatrix}
0 & V^*(t) \\
V(t) & 0
\end{pmatrix}.
\]

(5.2)
5.1. Electronic decoherence via random vibration

The nuclear kinetic energy operator $\hat{T}_N$, and the ground and excited PES functions $W_{g,x}$, are by definition functions of the set of nuclear coordinates $\mathbf{R}$. The matrix element describing interaction has a general form of

$$V(\mathbf{R}, t) = -\left[ \int \Phi_x(\mathbf{R}, q_e)\mu(\mathbf{R}, q_e)\Phi_g(\mathbf{R}, q_e)dq_e \right] \cdot \hat{\epsilon}E(t), \quad (5.3)$$

where $\Phi_{g,x}$ are electronic eigenstate wave functions involving collective electronic coordinates $q_e$, $E(t) = E_L(t)\cos(\omega t + \phi)$ is the electric field, $\mu(\mathbf{R}, q_e)$ is the dipole operator, and $\hat{\epsilon}$ is the unit polarization vector.

It is most convenient to solve the Schrödinger equation in the interaction representation (with the $\mathbf{R}$ variable temporarily suppressed for brevity)

$$i\hbar \frac{d}{dt} \left[ U^\dagger(t - t_0)\Psi(t_0) \right] = H'_I(t) \left[ U^\dagger(t - t_0)\Psi(t_0) \right], \quad (5.4)$$

where $t_0$ represents some initial time long before the onset of $H_I(t)$, and

$$H'_I(t) \equiv U^\dagger(t - t_0)H_I(t)U(t - t_0),$$

with the evolution operator in the interaction representation defined as

$$U(t_f - t_i) \equiv e^{-iH_{mol}(t_f - t_i)/\hbar} \equiv \begin{pmatrix} U_g(t_f - t_i) & 0 \\ 0 & U_x(t_f - t_i) \end{pmatrix}. \quad (5.5)$$

Assuming the laser field intensity is weak enough so that first-order perturbation theory is valid, the state in the interaction representation assumes the form

$$U^\dagger(t - t_0)\Psi(t) = \Psi(t_0) + \frac{1}{i\hbar} \int_{t_0}^{t} H'_I(t')\Psi(t_0)dt', \quad (5.6)$$
or in the Schrödinger’s representation,

$$\Psi(t) = U(t - t_0)\left[ 1 + \frac{1}{i\hbar} \int_{t_0}^{t} H'_I(t)dt' \right] \Psi(t_0) \quad (5.7)$$

In order to gain physical insight, we now consider excitation by a $E(\tau)\delta(t-...
5.1. Electronic decoherence via random vibration

\( \tau \) pulse, for which

\[
V(R, t) = D(R)E(\tau)\delta(t - \tau),
\]

\[
D(R) \equiv -\hat{\epsilon} \cdot \int \Phi_x(R, q_e)\mu(R, q_e)\Phi_g(R, q_e)dq_e.
\]  \( (5.8) \)

The assumption that the molecule is initially in the ground electronic manifold,

\[
\Psi(t_0, R) = \frac{1}{R} \begin{pmatrix} \psi_g(t_0, R) \\ 0 \end{pmatrix},
\]

reduces equation \( (5.7) \) to

\[
\psi_x(t, R)/R = \frac{h(t - \tau)}{ih}U_x(t - \tau)D(R)E(\tau)U_g(\tau - t_0)[\psi_g(t_0, R)/R], \]  \( (5.9) \)

where

\[
h(t - \tau) = \begin{cases} 
1 & \text{for } t > \tau \\
\frac{1}{2} & \text{for } t = \tau \\
0 & \text{for } t < \tau
\end{cases}
\]  \( (5.10) \)

is the Heaviside function. The physical picture that emerges is that no population is excited before the arrival of the delta pulse, and exactly at \( t = \tau \), where \( h(0) = 1/2 \), and \( U_e(\tau - \tau) = 1 \), we have

\[
\psi_x(\tau, R)/R = \frac{D(R)}{2ih}E(\tau)U_g(\tau - t_0)[\psi_g(t_0, R)/R]
\]

\[
= \frac{D(R)}{2ih}E(\tau)\psi_g(\tau, R)/R.
\]  \( (5.11) \)

Thus, at \( t = \tau \), a replica of the ground state wave packet (multiplied with \( D(R)E(\tau)/2ih \)) is formed on the excited PES, and evolves at \( t > \tau \) as

\[
\psi_x(t > \tau, R)/R = U_x(t - \tau)[\psi_x(\tau, R)/R].
\]  \( (5.12) \)

Using the above insight, we can consider any time-dependent function for the electric field, as a series of delta functions with the strength equal to

\[
83
\]
the field at that time point

\[ E(t) = \int_{-\infty}^{\infty} E(\tau) \delta(t - \tau) d\tau. \] (5.13)

This generalizes equation (5.9) for an arbitrary pulse, to obtain

\[ \psi_{x}(t, R)/R = \int_{-\infty}^{t} \frac{U_{x}(t - \tau)}{i\hbar} D(R) E(\tau) U_{g}(\tau - t_{0}) |\psi_{g}(t_{0}, R)/R| d\tau. \] (5.14)

The excited wave packet can then be viewed, equivalently, as a sum of replicas launched by all delta pulses until time \( t \), evolving according to the excited state Hamiltonian \( H_{x} \) \[101, 102\]. The differential form of equation (5.14),

\[ i\hbar \frac{d}{dt} \frac{\psi_{x}(t, R)}{R} = H_{x} \frac{\psi_{x}(t, R)}{R} + D(R) E(t) U_{g}(t - t_{0}) \frac{\psi_{g}(t_{0}, R)}{R}, \] (5.15)

is exactly an inhomogeneous Schrödinger’s equation for the excited state wave packet \( \psi_{x}(t, R) \), “driven” by a source term which is the product of the dipole strength along the polarization direction, the replication of the ground electronic state wave packet at the given time, and a potentially stochastic (incoherent) electric field.

Equation (5.15) not only reveals the very direct relationship between the excited wave packet and the electric field of the light, therefore also their coherence, but also has the great advantage of allowing us to easily vary the degrees of incoherence in the light sources. In particular, we can conveniently introduce random jumps in the central frequency and the carrier-envelope phase of the field, at any given time point. This is equivalent to doing so for a selected number of the \( \delta \) function components of the field in equation (5.13), with magnitude

\[ E(\tau) = \mathcal{E}_{L}(\tau) \cos \{ [\omega_{L} + \Delta \omega(\tau)]\tau + \phi(\tau) \}. \] (5.16)

The real-valued \( \Delta \omega(\tau) \) and \( \phi(\tau) \), which are taken to be constant (zero) in time for coherent fields, become random variables for incoherent light. An
5.1. Electronic decoherence via random vibration

![Figure 5.1](image.png)

Figure 5.1: A realization of the incoherent light, and its magnified view, with central wavelength at \( \sim 455\text{nm} \) (0.1 Hartree), and envelope function \( \mathcal{E}_L(t) \sim [\sin(\pi t/200 \text{fs})]^0.1 \) for \( 0 < t < 200 \text{ fs} \), and zero elsewhere, chosen to simulate CW behaviour without “sudden” numerical turning on and off. A random phase jump in the \([-\pi, \pi]\) range, and a central frequency shift in the \( \pm 0.0175 \) Hartrees range, is introduced every 7 fs on average.

An example is shown in Figures [5.1] for such a field suffering phase and frequency interruptions, with intervals averaging about 7 fs. The field correlation function \( \langle E(\tau + t)E(t) \rangle \) is tested to fall off rapidly, becoming essentially zero on the order of a few femtoseconds. In comparison, the coherence time of solar radiation is 1.32 fs [103]. However, such incoherent field, although convenient to construct, is considered more coherent than true solar radiation, due the very flat and well defined envelope function. Therefore, this reduced and very elementary model of incoherent light can be thought of as rather describing a single, atomic light emitter, e.g. from a thermal body, that suffers from relatively regular collisions that induce the phase and frequency interruptions [104]. In contrast, true solar light originates from thermal ra-
5.1. Electronic decoherence via random vibration

Figure 5.2: The coherent pulse has transform-limited envelope function $E_L(t) \sim \exp\left[-(t - 6 \text{ fs})^2/2(1.6 \text{ fs})^2\right]$. A portion of the incoherent pulse is also shown for comparison. The spectra of the pulses of coherent and a single realization of incoherent light are also shown. The total energy flux, $\int_{-\infty}^{\infty} |E(t)|^2 dt$, is kept the same for the two types of pulses.

diation from a large number of emitters, each of which is expected to have field properties similar to our current one. On such basis, we would expect any results following true solar radiation would only be an amplified version of our conclusions.

A coherent pulse is constructed from a spectrum matching that of the incoherent one, in central frequency and bandwidth, as shown in Figure 5.2. In the time domain, the coherent field is seen to be much shorter in duration than the incoherent one, but with much larger peak amplitude, in order to carry the same energy flux.

The method adopted below is similar in spirit to the “quantum trajectories” approach[105, 106] where the ensemble associated with the electric field correlation function is built up of a collection of individual realizations,
5.1. Electronic decoherence via random vibration

Each one given by excitation with different random parameters. Two different types of results are shown: those from sampling individual realizations, and those obtained as an average over the ensemble of realizations.

5.1.3 Wave packet simulations and electronic decoherence

To conduct a detailed numerical simulation for the quantum wave packet dynamics under the photoexcitation described in Figure 5.1 and 5.2, we consider a model molecular system, built from the parameters from the PES of the $H_2^+$ molecular ion. The initial wave packet is assumed to be in the ground $1\sigma_g$ electronic state with angular momentum $J = 0$, and is photoexcited to two model excited states that can each be dissociative or bound. We also assume that these two excited states are decoupled from one another, in order to reduce the dynamics to that of a sum of the individual ground-to-excited-state transitions, each described by equation (5.15).

At $t_0 = 0$, we assume for simplicity that the ground state wave packet is a vibrational eigenstate, making its time-evolution trivial, and that the excitation field is linearly polarized, making the transition from $(J = 0, M = 0)$ only to $(J = 1, M = 0)$. The transition dipole function is modelled according to $H_2^+$ [107], as $D(R) = D(R) \approx R/2$ in atomic units. Equation (5.15) then becomes

$$
\frac{d}{dt} \frac{\psi_x(R,t)}{R} = -i H_x(R) \frac{\psi_x(R,t)}{R} + D(R) E(t) e^{-iE_g t} \frac{\psi_g(R)}{R}.
$$

(5.17)

with

$$
H_x(R) = -\frac{1}{2\mu} \left( \frac{d^2}{dR^2} + \frac{2}{R} \frac{d}{dR} \right) + \frac{1}{\mu R^2} + W_x(R),
$$

(5.18)

where $\mu$ is the molecule’s reduced mass, and $W_x(R)$ is the potential energy surface for the excited state, which will take various shapes for different cases in the following. Now the $1/R$ factorization conveniently transforms the above equation to a one-dimensional Schrödinger’s equation

$$
\frac{d}{dt} \psi_x(R,t) = -i \left[ -\frac{1}{2\mu} \frac{d^2}{dR^2} + W_x(R) \right] \psi_x(R,t) + D(R) E(t) e^{-iE_g t} \psi_g(R),
$$

(5.19)
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which is ready for numerical computation.

Using the same electric field $E(t)$ as in Figures 5.1 and 5.2, and choosing $\psi_g(R)$ as the $v = 5$ vibrational state, we used equation (5.19) to propagate the excited radial wave functions $\psi_x^{(1)}(R, t)$ and $\psi_x^{(2)}(R, t)$ in electronic states 1 and 2, from $t = 0$ to 300 fs, using time steps of 0.003 fs and radial steps of 0.02 Bohrs. We analyze the motion of the $\psi_x^{(1)}(R, t)$ and $\psi_x^{(2)}(R, t)$ pair that has originated from the same ground electronic state for two cases: (A) Continuum dynamics for a pair of purely repulsive exponentially-decaying excited potentials, and (B) Bound state dynamics for a pair of Morse potentials, where a heavier reduced mass, $\mu = 5 \times 918$ a.u. is used. Sample plots of the wave packets, for these two cases, subject to the coherent and incoherent modes of excitation, are presented in Figures 5.3 and 5.4. In the case of the incoherent excitation, the results of a single random realization is shown.

The completed wave packets resulting from incoherent light excitation are seen to be choppy and highly unstructured. In the case of the repulsive potentials, following the excitation step, these wave packets spread out much more rapidly, while covering much larger extensions, than do the coherently excited cases. The situation is even more dramatic in the bound state excitation cases where the wave packets resulting from the incoherent light excitation exhibit a significantly smaller number of coherent oscillations as compared to the excitation by coherent pulses, and a highly irregularly structured wave function is seen.

The above results show characteristics of the excited state wave functions on individual electronic states. Also of interest, in particular with respect to experimental studies of long-lived coherences, is the persistence of electronic coherence, a property related to several electronic levels. To examine this, we quantify the electronic coherence by the off-diagonal element of the density matrix of the two electronic states, traced over the nuclear spatial coordinate,

$$\rho_{1,2}(t) = \int [\psi_x^{(1)}(R, t)]^* \psi_x^{(2)}(R, t) dR.$$  \hspace{1cm} (5.20)

Because the coherence is obtained via first-order perturbation theory, it is
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![Graph showing spatio-temporal plots of modulus-squared radial wave functions](image)

Figure 5.3: The spatio-temporal plots of the modulus-squared radial wave functions of the vibrational wave packets, $\psi_x^{(1,2)}(R, t)$. Top row is for case (A): purely repulsive excited state-1 and state-2 potentials, and bottom row is for case (B): bound Morse wells. The functional forms for both types of PES correspond to the first and third cases in Figure 5.5.
Figure 5.4: Same as Figure [5.3] but for photoexcitation with a single realization of the incoherent pulse.
convenient to normalize $\rho_{1,2}(t)$ by dividing it by $\rho_{1,1}(t) + \rho_{2,2}(t)$, the density matrix trace, giving

$$C(t) = \frac{\rho_{1,2}(t)}{\rho_{1,1}(t) + \rho_{2,2}(t)}.$$  \hspace{1cm} (5.21)

In this way we factor out the effects of the total excitation yield that are of no interest for this comparative study. Note also that equation (5.20), by averaging over vibrations, includes the effect of decoherence due to the vibrational degree of freedom on the electronic coherences. The resultant normalized coherences $C(t)$ are plotted in Figure 5.5, for different choices of the PES for the two electronic states, under the action of the two types of fields. Interestingly, in the case of incoherent light, convergence for the results shown were obtained with averaging over only ten realizations of the electric field.

These plots clearly show that for incoherent field excitations the magnitude of the coherence $C(t)$ decays at a much faster rate than that of the coherent pulse, approaching a much lower asymptotic value than that of the coherent case. This is especially so, as shown in the middle row of Figure 5.5, when coherence $C(t)$ is not significant to begin with, in the coherent case, due to small Franck-Condon overlap regions of the two surfaces. In the case of the bound Morse potential wells, clear and gradual decoherence of the two wave packets is observed for the case of coherent excitation. This is in strong contrast with the incoherent pulse excitation, where the coherence $C(t)$ decays almost immediately.

In all of the three cases, the final electronic coherence induced by the incoherent field is a small fraction of the coherence generated by the coherent case. Thus we find that the incoherence of the light eliminates long lived coherences when the excitation is carried out with pulses of solar-like incoherent sources.

Several comments are in order. First, note that decoherence observed here does not include additional environmental effects, since the molecule is isolated, i.e. the system is closed. Rather, the observed fast coherence loss arises, in the incoherent light case, from the nature of the two wave packets as they lose mutual coherence. That is, the molecular vibration serves as the
Figure 5.5: The left column shows three pairs of PES’s, and the \( v = 5 \) vibrational wave function. The repulsive PES on the top has functional form \( W^{(i)}_x(R) = W_0^{(i)} \exp\left[-\frac{(R - R_0^{(i)})}{a^{(i)}}\right] + W_\infty^{(i)} \), and the Morse potentials in the bottom panel have \( W^{(i)}_x(R) = W_0^{(i)} \left[1 - e^{-\left(R - R_0^{(i)}/a^{(i)}\right)}\right]^2 + W}_\infty^{(i)} \), both described by a parameter vector \( v_n = (W_0^{(n)}, R_0^{(n)}, a^{(n)}, W_\infty^{(n)}) \). For the top panel, \( v_1 = (0.1, 3.3, 1.0, 0.0) \), \( v_2 = (0.1, 3.0, 1.2, 0.005) \). In the middle panel, \( v_1 \) is the same but \( v_2 = (0.1, 2.5, 1.0, 0.01) \). In the bottom panel, \( v_1 = (0.1, 5.0, 2.5, 0) \) and \( v_2 = (0.1, 5.01, 2.53, 0.01) \). All numerical values are in atomic units. In the right column is the absolute value of \( C(t) \), the normalized electronic coherence resulting from coherent and incoherent light excitation for the three different PES of the left column. The results for the incoherent light were averaged over a set of 10 realizations. (Additional realizations did not significantly alter the results.)
5.1. Electronic decoherence via random vibration

decohering environment [108, 109], and it is particularly effective in this case due to the highly unstructured and choppy nuclear wave functions created by incoherent light. If, then, we consider low degree of coherence as in true solar radiation, or additional coupling to an external environment, the decay of electronic coherence will reflect the change accordingly [100], and as a consequence, be expected to be much faster, and to levels much closer to zero. Long lived electronic coherences are thus not expected to persist in realistic open systems irradiated with incoherent sources.

Second, note that the incoherent light source used above acts over a 200 fs time scale. Thus, although the short coherence time of natural incoherent light is represented in this computation, there are two significant differences between the results here and that which would result from true solar radiation, which acts over far longer times (effectively CW): (1) Due to, again, the smooth pulse envelope, the incoherent pulse used here possesses more coherence than would natural solar radiation that is incident for minutes or longer [95]; (2) At such long times, as discussed elsewhere [95, 98], long time excitation of isolated molecules using natural incoherent light leads, when averaged over realizations, to stationary eigenstates of the Hamiltonian that do not evolve in time. Relaxation in open systems also leads to mixtures of stationary states [100].

5.1.4 Conclusions

This study has shown that the nature of the light-induced wave function of molecular vibration, as well as the resultant electronic (de)coherence in the molecule, is strongly tied to the coherence properties of the incident radiation. Coherent light pulses produce well localized wave packets, whereas incoherent pulses produce irregularly structured coordinate space densities. In addition, the electronic coherence is quantified in the photoexcitation of a molecule into a superposition of two uncoupled electronic states, using the two types of light pulses with different degrees of coherence. The results show decreased electronic coherence values and much faster decoherence rates when the excitation is conducted with pulsed incoherent light than
5.2 Vibrational resonances excited by incoherent light

with coherent pulses of the same central frequency and spectral bandwidth. We would also expect that additional coupling between the excited electronic states, which makes the wave packet dynamics non-adiabatic, could not improve the electronic coherence. This is because we can either switch to the adiabatic potentials and arrive at similar results, or consider that the phases of the wave packet in each diabatic channel would be only randomized even more through the coupling between the electronic manifolds.

Thus, even in the absence of external environmental effects, the random character of the incoherent light is imparted directly into the molecular vibration, and enhances electronic decoherence. This study adds considerable support to the conclusion [98, 100, 110] that excitation with coherent vs incoherent light results in substantially different dynamical behaviour. As such, modern coherent pulsed laser experiments on biological molecules do give insight into the nature of the system and its coupling to the surrounding environment, but do not necessarily imply that similar dynamical behaviour will be observed under natural illumination with incoherent light of the same spectral profiles.

5.2 Vibrational resonances excited by incoherent light

5.2.1 Motivation

As the previous study has shown, the quantum states created by pulsed coherent vs. incoherent photoexcitation are drastically different, in terms of the spatio-temporal dynamics of the wave functions. The resultant electronic coherence determined by the vibration would then be destroyed on a much faster pace and to a much lower level. This study continues on the theme of contrasting coherent vs. incoherent molecular vibration, and stresses some important aspects not yet covered: (1) the statistically averaged spatio-temporal dynamics of vibration, and (2) vibrations of coupled bound-continuum nature, and the accompanying dynamics of energy eigenstates following coherent and incoherent photoexcitation. This study then
5.2. Vibrational resonances excited by incoherent light

serves both as a detailed extension and support for the previous study, where also a different type of optical incoherent light is used, and as a stepping stone to future research on more elaborate analysis of quantum state dynamics under realistic solar radiation.

5.2.2 Excited-state dynamics of IBr

In the previous study, we looked at various model potential energy surfaces (PES), for the energy-degenerate electronic manifolds, into which the molecule is excited by coherent and incoherent light. These pairs of PES’s, without any electronic coupling, support vibrations of either bound or continuum nature. However, more interesting and not previously discussed is a combination of coupled bound and continuum PES’s. The bound manifold supports localized coherent quantum wave packet oscillation (the “closed channel”), whereas the continuum manifold allows only dissociation (the “open channel”). Due to the coupling, population in the closed channel can spontaneously flow to the continuum, and the vibrational eigenstate to the bound manifold effectively acquires a finite lifetime due to the interaction with the open channel. The mixed manifold, viewed as a whole, can then host total vibrational eigenstates as superpositions of bound and continuum states from each individual manifold. Consequently, the optical transition into such total vibrational eigenstates can exhibit sharp peaks as a function of energy, and the original bound eigenstates become so-called vibrational resonances.

The iodine bromide (IBr) molecule has a pair of well-understood electronic excited states that serve exactly as the ideal setup for such photoexcitation dynamics of vibrational resonances. The two excited electronic manifolds are known in the diabatic representation as the $Y(O^+)$ and $B(^3\Pi_{O^+})$ states, which we will simply refer to as $Y$ and $B$. At appropriate excitation energies, the $B$ state is bounded and supports localized vibrational states, while the $Y$ state is purely repulsive and hosts only continuum states. Their potential energy surfaces in the iodine-bromine bond length degree of freedom, as shown in Figure 5.6, overlap in energy, and interact with inter-
5.2. Vibrational resonances excited by incoherent light

Figure 5.6: The potential energy surfaces for the ground, $Y$ and $B$ states of IBr. Shown in the $R = 23 - 25$ Bohr range are the magnitudes of negative imaginary potentials, artificially added as numerical absorbing boundaries, of functional form $V_{\text{absorb}}(R) = -i(0.075 \text{a.u.})(R - 23 \text{Bohr})^2$.

mediate strength [111], enabling the molecule pre-excited in the bounded $B$ state to transition into the open $Y$ state under time evolution, upon which the bond length diverges, and the molecule dissociates.

For the dynamics analysis, we represent the total molecular quantum state by three time-dependent vibrational wave packets in the basis of the three relevant electronic states. The molecule resides completely in the ground vibrational eigenstate $\phi_0(R)$ of the $J = 0$ ground electronic state before the onset of any light field ($t = 0$),

$$
\Psi(t, R) = \frac{1}{R} \begin{pmatrix}
\psi_g(t, R) \\
\psi_Y(t, R) \\
\psi_B(t, R)
\end{pmatrix}, \quad \Psi(t = 0, R) = \frac{1}{R} \begin{pmatrix}
\phi_0(R) \\
0 \\
0
\end{pmatrix}. \quad (5.22)
$$

The photoexcitation is assumed to be a first-order perturbation, and any higher-order electronic or rotational ($J > 1$) excitations are ignored. The optical energies needed to reach resonances in the $Y/B$ mixed manifold from $\phi_0(R)$, the approximate ($R$-independent) coupling between the two manifolds, as well as the resonance line-shapes, are taken from Ref. [111].

The total quantum state of the molecule then evolves in time according
5.2. Vibrational resonances excited by incoherent light

to the Schrödinger’s equation,

\[ i\hbar \frac{d}{dt}\Psi(t, R) = \hat{H}(t, R)\Psi(t, R), \]

where the full Hamiltonian matrix is (although it can be simplified in the perturbative limit [112])

\[ \hat{H} = \begin{pmatrix} \hat{T}_N + W_g(R) & -V_{Y,g}(R)E(t) & -V_{B,g}(R)E(t) \\ -V_{Y,g}^*(R)E(t) & \hat{T}_N + W_Y(R) & V_{B,Y}(R) \\ -V_{B,g}^*(R)E(t) & V_{B,Y}^*(R) & \hat{T}_N + W_B(R) \end{pmatrix}, \]

with the usual kinetic energy operator in 3D (\( m \) being the reduced mass of iodine and bromine atom)

\[ \hat{T}_N = -\frac{\hbar^2}{2m} \left( \frac{d^2}{dR^2} + \frac{2}{R} \frac{d}{dR} \right). \]

This then sets up the necessary formulation for the wave packet dynamics, where the electric field \( E(t) \) can again be random.

5.2.3 Spectral incoherence

There are many physical mechanisms which produce incoherent light. In the previous study, we modelled the field, in the time domain, as if it comes from a single atomic emitter, which has a finite total duration, rather flat intensity profile (see Figure 5.1), but suffers sudden jumps in phase and frequency, with random amount, at random time intervals. The largest magnitude of the jumps and the total duration determine the field’s autocorrelation, and hence its spectral properties [103]. Here, on the other hand, we model the incoherent light in the spectral domain. Such field can be thought of as coming from a purely coherent source, but having spectral phases randomized at each frequency in its spectrum. Assuming the source has a unique linear polarization (e.g. having passed through a polarizer), we can write
the scalar electric field, following above description, as

\[ E_0(t) = \int_{-\infty}^{\infty} s_0(\omega) e^{i\Phi(\omega)} e^{-i\omega t} d\omega \]  

(5.25)

where \( s_0(\omega) \) is a real, deterministic function, but the phase angles \( \Phi(\omega) \) are random variables at each frequency \( \omega \), uniformly distributed across \([-\pi, \pi]\), with delta-function cross-correlation \( \langle e^{i[\Phi(\omega)-\Phi(\omega')]\rangle} = \delta(\omega - \omega'). \)

Due to the randomness in its spectral phases, this incoherent field can in fact stretch indefinitely in time. Its power spectrum can then be calculated using the Wiener-Khinchin Theorem [103], as the Fourier transform \( \mathcal{F}[\Gamma(\tau)](\omega) \) of the field autocorrelation function

\[
\Gamma(\tau) = \langle E_0(t) E_0(t+\tau) \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |s_0(\omega')||s_0(\omega)| \langle e^{i[\Phi(\omega')-\Phi(\omega)]}\rangle \langle e^{i(\omega'-\omega)t} \rangle e^{-i\omega\tau} d\omega' d\omega
\]

\[= \int_{-\infty}^{\infty} |s_0(\omega)|^2 e^{-i\omega\tau} d\omega = \mathcal{F}^{-1} \langle |s_0(\omega)|^2 \rangle. \]  

(5.26)

We then simply have \( \mathcal{F}[\Gamma(\tau)](\omega) = |s_0(\omega)|^2 \).

However, such spectral power is not injected, in full, into the molecular excitation, if only a finite duration of the incoherent field is to be used in conducting a finite-time wave packet simulation. We therefore pre-emptively take a “sample” of this source field by modulating \( E_0(t) \) with a well-behaved, long-duration function \( \epsilon(t) \). The resulting field used for molecular excitation is then \( E(t) = \epsilon(t) E_0(t) \). Since now the duration of \( E(t) \) is finite, we can Fourier transform the field in time [95] to calculate its power spectrum, which, when averaged over many field realizations, converges to a constant fraction of \( |s_0(\omega)|^2 \). In turn, we can use it to construct a coherent pulse by carefully choosing appropriate spectral phases. This way, any further comparison between coherent and incoherent dynamics will be on equal footing in terms of total optical energy input.

Figure 5.7 demonstrates the numerical implementation of such consideration, where \( s_0(\omega) \) and \( \epsilon(t) \) are both assumed to be Gaussian. The modulation \( \epsilon(t) \) has negligible effects on changing the shape of the ensemble-averaged
5.2. Vibrational resonances excited by incoherent light

Figure 5.7: Plotted in the top panel are the coherent (blue) and incoherent (orange) electric fields in time, and the modulation $\epsilon(t)$ (red, scaled). A pair of resonances, indicated by the peaks in the $\phi_0 \rightarrow Y/B$ optical transition matrix element as a function of energy, in the 17900-18000 cm$^{-1}$ range, is plotted in the bottom panel (red). The power spectrum of the incoherent field (orange) is obtained from averaging over 100 field realizations, whereas that of the coherent field (blue), approximately $0.01614|s_0(\omega)|^2$, is simply scaled down from the power spectrum of the incoherent source.
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Power spectrum from $|s_0(\omega)|^2$, since its large width in the time domain results in an essentially $\delta$-like spectrum comparing with $|s_0(\omega)|^2$, thereby making their convolution identical to $|s_0(\omega)|^2$.

5.2.4 Stationary wave packet and flux dynamics

As described above, the vibrational wave packet dynamics can be propagated using equations (5.23) and (5.24), with the electric field having the form of equation (5.25). For the molecular wave packets, the kinetic energy operator is implemented using mid-point numerical differentiation (of second order accuracy). Transition dipole moments $V_{Y,g}(R)$ and $V_{B,g}(R)$, non-adiabatic coupling $V_{B,Y}(R)$, along with $J=1$ effective potentials $W_{g,Y,B}(R)$, are taken from ref. [111]. The effective potentials are further modified artificially to have negative imaginary potentials at $R = 23-25$ Bohr as absorbing boundaries (Fig. 5.6). This makes the numerical propagation of wave functions feasible over very long timescales. The vibrational wave packets, belonging to the three relevant electronic channels, are represented on a spatial grid with 2100 points in steps of 0.01Bohr, in the $R = 4-25$Bohr range. The wave functions are then propagated in time with standard RK4 method, in steps of 0.01fs, according to the Schrödinger’s equation.

The electric field of the light is assumed to be linearly polarized, with the time-dependent part $E(t)$ represented as an array with half the step size of the propagation (i.e. 0.005fs) due to the RK4 method. At each time point, the field is

$$E(t) = \epsilon(t) \sum_j [s_0(\omega_j) \Delta \omega] e^{-i[\omega_j(t-10ps)+\Phi_j]} + c.c.$$

$$\epsilon(t) = \exp[-(t-10ps)^2/2(3ps)^2]$$

$$s_0(\omega_j) = s_0 \exp[-(\omega_j-17950cm^{-1})^2/(30cm^{-1})^2]$$

$$s_0 \Delta \omega = [(10^3W/cm^2)/\epsilon_0 c]^{1/2}$$

Where 2000 frequency components are taken from $17850cm^{-1}$ to $18050cm^{-1}$ in $\Delta \omega = 0.1cm^{-1}$ intervals. The phase angles $\Phi_j$ are independent random variables uniformly distributed in $[-\pi, \pi]$. The Fourier transform of the
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Gaussian envelope function \( \epsilon(t) \) has a spectral width about 1.756\,cm\(^{-1}\).

The spatio-temporal plots for the magnitude-squared wave functions are produced according to above numerical specifications in Fig. 5.8. There is a clear, visual evidence of the presence and absence of vibrational coherence. Under coherent excitation, the motion of the wave packet is oscillatory. The initial excited state wave function is localized due to the very short coherent excitation of the localized ground state \( \phi_0 \). Then after the pulse, it moves outward due to the repulsive forces from both channels, and bifurcates into a dissociative portion into the open channel and a localized portion that bounces back. It then completes another period of oscillation, determined by the energy separation between the resonances, before again transitioning partly into the open channel.

Seen in drastic contrast is the wave packet evolution for the incoherent field, averaged over 100 field realizations. The incoherent wave packet has a much more stationary form that, in time, only scales uniformly in magnitude, but exhibiting no oscillatory motion. This is a clear sign that vibrational eigenstates are excited, with no correlation between relative phases. To confirm this claim, also considered is the photoexcitation by near-monochromatic fields (Figure 5.8), simulating each individual frequency components of the incoherent field. Its spatio-temporal plot, as a sum over squared-magnitudes of individual component field excitations, bears extreme resemblance to the incoherent case.

It’s then clear that, under such spectrally incoherent photoexcitation, no quantum phase correlation exists between eigenstates of the system, thereby eliminating any vibrational or electronic quantum coherence, as supported also by our previous study. However, this does not mean that there are no quantum dynamics under incoherent excitation. One particular time-dependent quantity that still reflects the photoexcitation dynamics is the long-range vibrational flux for the wave packet in the open channel. It represents in general the rate of probability, and in our case the relative amount of molecules photo-dissociated, flowing across the area of the spherical shell with radius \( R \) along the radial direction. It is defined in quantum
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Figure 5.8: Sum of the magnitude-squared wave functions in the $Y$ and $B$ states, i.e. $|\psi_Y(t, R)|^2 + |\psi_B(t, R)|^2$, are plotted in the top three panels for the relevant fields. They are plotted in the same spatial and temporal range, and the same colour scale. Vaguely shown is the extended portion for $R > 8$ Bohr. But they are clearly reflected in the plot for the flux in the lower right panel. Middle panel is the flux as functions of time, created by component fields of the form $s_0(\omega)\Delta \omega \epsilon(t)e^{-i\omega t}$, spaced by $\Delta \omega = 0.1\text{cm}^{-1}$. The sum of the flux across the Excitation frequency axis produces the total flux (red curve) in the panel below it.
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mechanics as

\[ F_\alpha(t, R) = \frac{\hbar}{m} \text{Im}[\psi_\alpha^*(t, R) \frac{d}{dR} \psi_\alpha(t, R)]. \]  

(5.28)

with the unit of probability per time, in electronic channel \( \alpha \). Such flux is zero for a bound eigenstate, since the wave function would be real. The continuum nature of the excited state of IBr, in this case, enables eigenstate dynamics under incoherent excitation. In particular, we choose \( R = 15 \) Bohr, because it is much farther away from the bound regions and both the \( Y \) and \( B \) potential curves are flat. In practice, one can measure such defined flux by examining, for example, the rate of photo-ionization signal at a particular solid angle, representing a fractional value of the above flux.

The flux as a function of time for both types of electric fields are then plotted in Figure 5.8 and reflects the corresponding wave packet dynamics exactly. For the coherent case, since the oscillatory wave packet motion leaves a trail of “impressions” of its transition into the open channel, we see a train of periodic bursts of flux. Under spectrally incoherent excitation, the averaged flux follows the shape of the modulated field amplitude \( \epsilon(t) \). When again summed over the near-monochromatic frequency component fields, the total flux is seen to be the converging limit of the incoherent case. Here we emphasize that all component fields contribute to the flux dynamics. Namely, off-resonance frequency components, even though only causing significant flux temporarily, are also an important contributor to the total incoherent dynamics [113]. Furthermore, the flux contribution at each individual excitation frequency, as the middle panel of Figure 5.8 shows, is much higher near-resonance than off-resonance, at long times. The exact value may be determined by actual forms of the vibrational eigenfunctions between the ground and excited states, or their Franck-Condon factors.

5.2.5 Conclusions

In summary, we have considered in this study the photoexcitation of a molecule into a pair of coupled electronic states of mixed bound-continuum nature, supporting both bound and dissociative vibrational motion. The incident light can be a coherent pulse or its incoherent counterpart with
only spectral phases randomized, but sharing the same central frequency, bandwidth and power spectrum.

We numerically computed the exact spatio-temporal evolution of the excited-state quantum wave packet, and demonstrated that, when initiated by the incoherent pulse, the molecule does not sustain the same quantum-coherent behaviours as that from coherent one. This is attributed entirely to the loss of mutual quantum phase correlation, inherited from the incoherent property of the excitation light, between excited vibrational eigenstates. As a result, the incoherent wave packet dynamics coincide with that formed via summing the squared-magnitudes of wave packets, excited separately by near-monochromatic excitations at all relevant frequencies included in the spectrum of the incoherent pulse.

Furthermore, we confirm directly that incoherent light also initiates dynamics, although not of coherent nature, where “movement” of the system is in the incoherent mixture of eigenstates, rather than coherent superposition among them. In the context of dissociating IBr molecule, the incoherent dynamics is simply the flow of probability of finding the bond length at large values. In this case, one would not expect any coherent transfer of molecular population or quantum superposition in general. We’d also like to point out that if the continuum manifold of the Hilbert space considered here is provided by a dissipative environment instead of the dissociative electronic state, the incoherent dynamics will then represent a unidirectional heat flow into the environment. Although without any quantum coherence, one can nevertheless speculate that the efficiency of such unidirectional flow of flux can be controlled, in principle, by incoherent means such as adjusting the “receiver” of the flux in energy so that resonances with greater flux has stronger coupling and are better received. This calls for further research on the resonant intramolecular energy or population transfer, after the incoherent photoexcitation step.
Chapter 6

Final conclusion

In this doctoral dissertation, a number of studies had been presented on the interaction physics between light, from coherent and incoherent sources, and diatomic molecular systems. On a fundamental level, the electric field of the light, interacting with the transition dipole moment of the molecule, can bring the molecule to new quantum states consisting of different combinations of energy eigenstates. Due to the many internal degrees of freedom of even simple diatomic molecules, such transitions can be complex, especially in the cases when the excitation field is strong in intensity and broad in spectral bandwidth. However, numerous mathematical formulations, derivations and approximations can be made for us to gain useful insight into the underlying mechanisms for these light-induced molecular transitions, and how to actively control them via coherence properties such as interferences and resonances. Particular innovative are the theories and practices of coherent control techniques, where tuning only the coherent properties of the excitation field can alter the outcome of the physical process.

Such coherent control ability goes hand in hand with the coherence of the light source for the molecular excitation. Laser sources are excellent choices by default, in terms of their intrinsic coherent characteristics such as amplitude and carrier-phase stability and spatial and temporal coherence; their bandwidth availabilities, ranging from narrowband CW-excitations, to broadband, ultrafast femtosecond pulses; and also the accompanying technologies that enable active manipulation of the laser pulses, such as chirping and other general spectral shaping.

Invariable to all studies in this thesis, we aim to achieve our research objectives by first presenting a design for the excitation light field. When the field is incident to a model molecular system, the resultant quantum dynam-
ics are analyzed, and would bring us to the confirmation of a hypothesized outcome, such as the high-efficiency transition to a particular target quantum state (e.g. ultracold molecular state), or a specific correlation between properties of the light (e.g. intensity, coherence) and the characteristics of the resulting molecular state (e.g. linear response, stationary wave packets).

Our main methodologies are mathematical analysis and numerical computation and simulation. We base on the quantum mechanical theories to formulate the quantum dynamics problem, provide exact or approximate solutions, physical and analytical insights, or simplified derivations that are suitable for computational analysis. When no simple or direct analytical solution can be derived, or randomness is required as part of the demonstration, we conduct numerical calculations and simulations, to reveal the quantitative evolution and outcome of the molecular system.

In the first study, we extend the general technique of stimulated Raman adiabatic passage (STIRAP) to photoassociation processes, where colliding atoms are combined, under the action of a pair of coherent pulses, into deeply bound ground molecular state, thereby forming an ultracold molecule. Such transfer from atomic to molecular state is especially efficient when the atoms are at ultracold temperatures, where their extremely narrow kinetic energy uncertainty greatly enhances the adiabatic passage. However, the efficiency can be additionally improved using atomic scattering resonances such as a Feshbach resonance. Previous studies have concluded that, based on the increased eigenstate-to-eigenstate coupling (Franck-Condon factor) provided by the resonance, large resonance width is always preferred to increase the efficiency. However, by our computational analysis, we found that when an ensemble of ultracold atoms is considered, the dynamical aspects of the resonance plays a crucial role in determining the best resonance width for highest efficiency. With a narrow resonance, the effective collision rate, i.e. the number of atom pairs still in the collision process, is increased in the time window for photoassociation. This is because the collision duration between any pair of atoms are prolonged by a larger factor than the decrease in the photoassociation probability. The net effect is then the existence of an optimal, narrow resonance width for the best ensemble transfer efficiency.
Next, we apply the coherent control strategy and demonstrate that phase-only manipulation of a broadband, high-intensity, ultrafast laser pulse can give rise to linear molecular response to the field intensity. Although a necessary relation with weak, perturbative fields, it has been assumed, mistakenly in most studies, to be absent in the strong-field domain. Experimental observations where both linear response and coherent control coexist, then, relied on the above false assumption and lead to the conclusion of phase-only coherent control using a perturbative excitation field, an impossibility according to conventional, closed-system coherent control theories. Although open quantum systems, as later studies have shown, can indeed fill in the gap, we resolve this issue by providing pulse shaping scenarios where both essentially linear molecular response to high-intensity light, and coherent control over electronic branching ratio, are present in isolated molecules. Examples using a model three-potential molecular system, and the realistic $\text{H}_2^+$ molecular ion, are provided. As the pulse manipulation is solely coherent, the reason for the existence of linear response in the strong-field domain is then attributed to interference effects. Furthermore, wave packet interferometry analysis in the vibration of $\text{H}_2^+$ also reveals the correlation between the linear response and the wave packet’s concentration outside the Franck-Condon region. Meanwhile, control over branching ratios, and quantum beating in the population among various electronic and rotational channels are also present.

The last theme of this thesis is concerning the vibration of molecules under incoherence photoexcitation. With weak-intensity excitation light, such as natural sunlight or laser light, a simple stochastic Schrödinger’s equation is derived for the excited vibrational wave packet dynamics. The temporal coherence of the electric field is shown to directly govern the randomness of the excited wave packet. Under the excitation of a field modelled after a single thermal emitter, which suffers phase and frequency interruptions, the resultant vibrational wave packets are calculated for two overlapping electronic potentials. The mutual electronic coherence is shown to be drastically decreased, comparing with the coherent counterpart of the field sharing the same spectral profile. Based on this, we conclude that sunlight,
which consists of a large number of such thermally emitted fields at each frequency, can induce much less, if none, electronic coherence in molecules, as compared with that resulting from laboratory experiments using broadband laser pulses. Therefore, although the long-lived quantum coherence discovered in light-harvesting molecules, under laser excitation, is an interesting phenomena that holds many scientific and technological potentials, its relevance to natural photosynthetic processes is cast into great doubt.

To further study the behaviour of molecular vibration under incoherent photoexcitation, we model another type of incoherent light source by introducing randomness in the spectral domain, where each frequency component of the excitation has statistically random phase angles. When a molecule is excited with such field into a continuum of vibrational eigenstates, all frequencies of the light contribute to the state transition, and as a result, these vibrational eigenstates lose mutual coherence in the phases as well. This causes excited vibrational wave packet that is stationary. To make the comparison clear, the excited region of the vibrational continuum also hosts resonances, i.e. coupling to bound states that support bounded oscillatory motion. This enables oscillation of the wave packet created by the spectrally coherent field, during its dissociation. Despite the lack of oscillatory motion and quantum interference, incoherently excited vibrational resonances nevertheless have a dynamical aspect: the outgoing probability flux at asymptotic distances. In the context of dissociating IBr molecule, such dynamics is the stream of dissociating atomic fragments. The flux values near different vibrational resonances are also different, but always higher than those off-resonance.

The study on the incoherent excitation of vibrational resonances alone, then, calls for further investigations for the possibility of tuning into the structural degrees of freedom of the molecule, in order to improve the efficiency of intra- or intermolecular transfer of population or energy. Specifically, if the properties of the resonance, such as its peak location in energy, can be altered, the incoherent flux at a target energy can in principle be controlled. One would then speculate that if the molecule has the ability to change its own excited state PES, it can, under natural evolution, search
for the best shape of the PES in order to optimize flux or energy transfer via resonances. Such proposed approach can add motivation to improve the understanding and possible manipulation of molecular processes such as intramolecular vibrational redistribution (IVR), intra- and intermolecular energy transfer involved in photosynthesis, and the protein folding problem.

On the more coherent side, the application of the coherent control approach also sees endless possibilities. One particularly fascinating application is on the effects of coherent photoexcitation on mechanical motions of a polyatomic molecule. The optical access to the electronic excitation of a polyatomic molecule might mean, for example, the controlled breaking and re-forming of double bonds on a central part of the molecule. Different bond structures can enable different torsional and other vibrational motions, hence opening up possibilities on controlling the mechanical motion of the molecule as a whole. Targeted and efficient quantum state transfer, coherent manipulation of vibrational wave packets, can all be excellent techniques to achieve such goal. Depending on the environment of the molecule, potential applications can range from molecular propulsion in fluids, to the self-transportation across surfaces.

In all, it is my deepest belief that, since the dynamics of light-induced molecular wave packets is essential to a variety of physical and chemical processes, its control, especially coherent ones utilizing wave phenomena such as interference and resonance, holds endless possibilities, both in terms of our fundamental understanding of the photo-molecular physics, and practical and innovative applications, impossible by conventional means.
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