Studies of Highly Polar Atomic and Molecular Systems: Quantum Dynamics and the Route to Experimental Investigations

by

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Theoretical investigation of the dynamics of adiabatic quantum mechanics in two different, highly polar systems has been made. The systems were chosen for their fundamental scientific interest, as they represent atoms and molecules with exaggerated properties, as well as ease of experimental study as such highly polar systems are easier to manipulate using readily-available electric fields. A model two-level system is used to derive one approach for maximizing the probability of adiabatic passage through an avoided crossing and this is compared with the classic Landau-Zener result, and the commonly encountered spin-flip problem of a particle with spin located in a rotating magnetic field. This approach is applied to the avoided crossing between the $n = 13, n_1 - n_2 = 11$ (dipole moment of 532 D) and the $n = 14, n_1 - n_2 = -12$ (dipole moment of -657 D) highly polar Stark states of the lithium atom at 447 kV/m.

Ion-pair formation from two neutral lithium atoms, one in the 2s ground state and the other in an excited state, is also investigated. The cross section $\sigma(v)$ for free ion-pairs is calculated for the initial colliding pairs of atomic states located below the ion-pair threshold. Li(2s) + Li(3d) is seen to possess the largest cross section ($\sigma(v_0) = 569.2$ a.u.) at its threshold velocity. The implications of this for bound ion-pair, i.e. heavy Rydberg system, production are briefly discussed. Furthermore, experimental progress towards the production of these atomic and molecular systems from a beam of lithium is presented.
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Dedicated to Carl and Sharon,

the best parents a son could ask for.
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List of Acronyms

CPT – Coherent population transfer
EA – Electron affinity
IP – Ionization potential
MATI – Mass analyzed threshold ionization
PD – Photodiode
PMT – Photomultiplier tube
SHG – Second harmonic generation
STIRAP – Stimulated Raman adiabatic passage
TIPPS – Threshold ion-pair production spectroscopy
VUV – Vacuum ultraviolet
ZEKE – Zero kinetic energy
Chapter 1

Introduction

The early twentieth century saw a divide in the natural world between the macroscopic (classical) and microscopic (quantum). The microscopic scale, governed by quantum mechanics, gives rise to interesting and often counterintuitive results. The boundary between these two regimes remains poorly understood. The emergence of mesoscopic systems such as Bose-Einstein condensates provides experimental testing grounds to probe this boundary. Another possible system is a weakly bound anion-cation pair, known as a heavy Rydberg system, or a heavy Bohr system. These highly polar molecules constitute a large quantum system with bond lengths of approximately 0.5 \( \mu \)m for binding energies from 10 to 20 \( \text{cm}^{-1} \), corresponding to a dipole moment of 28,000 D in the molecular frame, orders of magnitude higher than a HF molecule’s 1.826 D dipole moment. The production of heavy Rydberg systems also provides a test of quantum dynamics, examining how the ion-pairs and their atomic or molecular precursors navigate the many narrowly avoided crossings between state energies relevant to the ion-pair formation. An avoided crossing is an avoided degeneracy in the energies of two states where some coupling prevents the eigenenergies from crossing. The energies approach, avoid crossing then veer away from one another. The functional forms of the two states are exchanged as the avoided crossing
The goal of the Trent Optical Physics Laboratory is the investigation of quantum dynamics and the production and manipulation of heavy Rydberg systems composed of lithium ions. This requires devising the theoretical framework for understanding two-level quantum dynamics, covered in Chapter 3 and applying this to two highly polar lithium systems to be produced in the laboratory. We are looking to devise a theoretical framework for adiabatic quantum mechanics studies, covered in chapter 3 in two highly polar lithium systems and subsequently produce these systems in the laboratory for measurement.

The first system, Stark states of the lithium atom discussed in chapter 4, possesses many avoided crossings between states of adjacent manifolds, characterized by principal quantum number $n$. Navigating these avoided crossings by controlling the applied electric field determines the final quantum state of the atom, which can be detected by selective field ionization. The second system is an ion-pair formed from collisions between neutral lithium atoms and is discussed in chapter 5. Here, one atom is excited into a Rydberg state and collides with a ground state atom. The Rydberg electron is transferred between atoms, producing the ion-pair. A free or unbound ion-pair is formed if the ion possess enough kinetic energy to overcome their coulomb attraction. Alternatively, a bound ion-pair, or heavy Rydberg system, may form if their kinetic energy is insufficient. The mechanisms for this process involve selectively adiabatic and nonadiabatic traversals of avoided crossings between the neutral and ion-pair states, again emphasizing the importance of quantum dynamics.

Both of these systems can be produced and explored within a beam of lithium atoms. To this end, an atomic beam apparatus is under construction in the laboratory,
1.2 Structure of the thesis

Chapter 2 provides a review of the literature concerning electronic and heavy Rydberg systems as well as the quantum dynamics relevant to many parts of this thesis.

The next chapter outlines the adiabatic quantum mechanics we will be investigating. The classic Landau-Zener class of systems is presented as well as numerical work which allows us to move beyond the approximations necessary for their analytic solutions. The familiar problem of a particle with a magnetic moment in a rotating magnetic field is presented with the same formalism.

The following two chapters provide in-depth analysis of the two highly polar atomic and molecular systems we examine in our studies of quantum dynamics and the quantum-classical boundary. Chapter 4 introduces the Stark states of the lithium atom with its many avoided crossings between adjacent states. Next, in chapter 5, we investigate ion-pair formation beginning with two neutral lithium atoms. Different species of ion-pairs have been experimentally observed; table 1.1 provides a chronological list of the relevant studies. Bound ion-pairs constitute the heavy Rydberg systems which we are ultimately aiming to produce and study. The progress towards this experimental goal is presented in the final chapter.

<table>
<thead>
<tr>
<th>Ion-pairs</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb$^+$ + Rb$^-$</td>
<td>1</td>
</tr>
<tr>
<td>K$^+$ + K$^-$</td>
<td>2</td>
</tr>
<tr>
<td>Na$^+$ + Na$^-$</td>
<td>3</td>
</tr>
<tr>
<td>H$^+$ + F$^-$</td>
<td>4</td>
</tr>
<tr>
<td>O$^+$ + O$^-$</td>
<td>5</td>
</tr>
<tr>
<td>H$^+$ + Cl$^-$</td>
<td>6</td>
</tr>
<tr>
<td>H$^+$ + H$^-$</td>
<td>7</td>
</tr>
<tr>
<td>H$^+$ + SH$^-$</td>
<td>8</td>
</tr>
<tr>
<td>H$^+$ + CN$^-$</td>
<td>9</td>
</tr>
<tr>
<td>K$^+$ + Cl$^-$ + CCl$_3$</td>
<td>10</td>
</tr>
</tbody>
</table>
Chapter 2

Literature Review

This thesis explores the role of quantum dynamics in Rydberg systems. The ultimate goal of the Trent Optical Physics Laboratory is to produce and control heavy Rydberg systems. The following literature review covers the study of various Rydberg states and systems and the investigation of their quantum dynamics.

2.1 Electronic Rydberg States

Electronic Rydberg states of atoms and molecules possess an electron with high principle quantum number $n$. These states are spatially large and the excited electron spends a large fraction of its time far away from the nucleus and inner electrons. As such, for all atoms other than H, it experiences a nearly hydrogenic potential $V \propto \frac{1}{r}$. The nucleus (or nuclei) and inner electrons make up the ion core which can be polarized and penetrated by the excited electron, slightly modifying this potential. This is addressed by the inclusion of an angular momentum dependent quantum defect $\delta_\ell$. 
into the state energy:

\[ E_n = - \frac{Ry}{(n - \delta\ell)^2} \]  \hspace{1cm} (2.1)

resulting from a deepening of the potential well at short distances, where \( Ry \) is the Rydberg constant for the atom or molecule. This thesis is concerned with alkali atoms with a single excited electron; atoms with multiple excitations are not considered.

Rydberg states were first experimentally observed over a century ago in spectroscopic experiments.\(^{[11]}\) Early works produced these excited states by inelastic collisions with ions or electrons. Two such excitation techniques are electron impact excitation\(^{[12]}\):

\[ e^- + A \rightarrow A(n\ell) + e^-, \]  \hspace{1cm} (2.2)

and the closely related ion impact excitation with charge transfer\(^{[13]}\):

\[ A^+ + B \rightarrow A(n\ell) + B^+, \]  \hspace{1cm} (2.3)

or without charge transfer:

\[ A + B^+ \rightarrow A(n\ell) + B^+. \]  \hspace{1cm} (2.4)

These production schemes were limiting to subsequent studies in that they produced a broad range of final Rydberg states. It was not until lasers capable of the UV wavelengths required for the excitations in alkali atoms became available that selective control was realized with single photon techniques.

A comprehensive source on Rydberg atoms is the book by Gallagher\(^{[14]}\) which serves as an excellent introduction to the subject. It covers the theory behind Rydberg states and provides many important experimental considerations for working with them.

5
The possibility of excitation to Rydberg states allows the slowing and cooling of atoms and molecules using inhomogeneous electric fields\textsuperscript{[15]}. The large, induced dipole moments of many Rydberg states allow a non-uniform electric field to exert sufficient force upon the atom to be useful without requiring a field capable of inducing ionization, even though Rydberg states ionize at lower field strengths than ground states. Such manipulation is often used to decelerate or cool a thermal beam of atoms for many purposes, such as for spectroscopy or loading an atom trap. In addition, it can be used to deflect and focus beams of atoms and molecules\textsuperscript{[16]}. Cooling methods using time-varying electric field gradients have also been proposed\textsuperscript{[17]}. 

Electronic Rydberg states have been increasingly important tools in molecular spectroscopy. One technique, zero kinetic energy (ZEKE) photoelectron spectroscopy\textsuperscript{[18]}, uses pulsed field ionization of long lived, very high-$n$ Rydberg states and detects the emitted electrons to investigate the ionization potentials and spectroscopy of molecules and molecular ions. A similar method, mass analyzed threshold ionization (MATI) spectroscopy \textsuperscript{[19]}, detects the ions and is mass selective, making it useful for experiments where species identification and ionic state preparation is required.

### 2.2 Heavy Rydberg Systems

Heavy Rydberg systems are similar to electronic Rydberg systems with the excited electron replaced by an anion. They are necessarily weakly bound molecules with a bound pair reduced mass which scales greatly with the constituents’ masses:

$$
\mu = \frac{m_1 m_2}{m_1 + m_2},
$$

(2.5)
unlike with electronic Rydberg systems, where $\mu \approx m_e$ regardless of the mass of the ionic core. The Rydberg constant is dependent on the reduced mass of the system:

$$Ry = \frac{\mu}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 = \frac{\mu}{m_e} R_\infty,$$

resulting in a significant decrease of the spacing between energy levels for heavy Rydberg systems compared to electronic states of the same binding energy, allowing a level of temporal control unobtainable in electronic Rydberg systems. The framework for a mass scaling law allowing $\frac{1}{r}$-potential physics to be applied to these systems is developed in one of the most comprehensive papers on the subject.\[^{[20]}\]

Despite their advantages in quantum control experiments, the literature on heavy Rydberg systems remains limited due in part to the difficulty of their creation. Heavy Rydberg systems, or bound ion-pairs, were first experimentally observed\[^{[21]}\] in electron transfer collisions between electronic Rydberg states of K atoms and CF$_3$I molecules in which the velocities and angular distribution of the I$^-$ ions produced from the dissociation of CF$_3$I$^-$ were investigated. The production of ion-pairs was noted as a mechanism responsible for the decrease in anions detected for the lower $n$ states of the K Rydberg atom downstream of the interaction volume. Some anions travelling in the same direction and with similar velocities to the cations in the beam were not able to overcome their mutual attraction, resulting in bound $K^+ \cdots I^-$ ion-pairs that were not explicitly detected. Since then, this electron transfer technique has been used to conduct further studies of heavy Rydberg systems, such as lifetime measurements of bound ion-pairs for many species.\[^{[22]}\]

The other method used to produce heavy Rydberg systems is by laser excitation of a molecule into the near threshold region for ion-pair production.\[^{[23]}\] When followed by a dissociating electric field pulse, this is the threshold-ion-pair-production spectroscopy (TIPPS) technique\[^{[5]}\], where a VUV (vacuum ultraviolet) laser excites the
molecule to an energy just below the dissociation threshold and a pulsed electric field is used to split apart the molecule, similar to MATI with an electronic Rydberg system. A review of TIPPS and other ion-pair spectroscopic techniques is given by Suits and Hepburn.[24] Omitting the pulsed electric fields from TIPPS leaves the bound ion-pair available for further study as a heavy Rydberg system. This technique has been further refined using a high resolution UV light source to enable the production of clearly-resolved heavy Rydberg states of a so-called heavy Bohr atom, \( H^+ \cdots H^- \).[25]

### 2.3 Quantum dynamics

Many areas of physics are concerned with the control of quantum mechanical systems with a time-dependent interaction such as electric or magnetic fields, light pulses or collisions. The final state from such processes depends not only on the initial and final values of the interaction variable, but also depends critically on its temporal profile. This has become an increasingly important topic of research with the advent of tools such as sub-Doppler cooling in magnetic traps and the absolute phase control of ultrafast lasers that allow scientists unprecedented control of matter. Some classic examples of such precise control include inelastic collisions between atoms and molecules[26] and exposing atomic systems to specific external electric[27] or magnetic fields[28] in order to select the final state of the involved atoms.

The basic theory of quantum dynamics and its history is reviewed by Nikitin.[29] The results of these studies have produced simple models with accompanying formulae that can be used to predict final states for a wide range of two-level systems experiencing time-dependent interactions; from electrons transferring between sites in proteins[30] to the fusion of nuclei[31]. However, some theoretical work has determined that these simple models are not valid for a wide range of coupling strengths and rates of change of the interaction variable[32], requiring caution when using them.
for quantitative results. Strong couplings and fast rates of change allow significant population transfer between states outside of the point-of-closest-approach in the avoided crossing, where the coupling may not be constant. One experiment, exploring avoided crossings between almost degenerate energy levels through the Stark effect in lithium\(^2\), shows that under carefully controlled conditions, the simple models do agree with experiment.

Other applications of quantum dynamics include population transfer; coherent population transfer (CPT) is a method for efficiently transferring population from one quantum state to another in atoms or molecules. One technique, stimulated Raman adiabatic passage (STIRAP) uses overlapping laser beams to make use of the CPT phenomenon.\(^3\) The first beam creates a coherent, population-trapping state and subsequent adiabatic evolution using the second beam can produce almost complete transference of the entire population from the initial to a chosen final state. This is often used to prepare selected states for further study. Other techniques use chirped laser pulses\(^4\) or multiphoton absorption\(^5\) to accomplish the same end result.

Bose-Einstein condensates are ensembles of ultracold bosons that all populate the same quantum state. The wavefunctions of the constituent atoms overlap and quantum behaviour is exhibited on a macroscopic scale. This novel state of matter is currently a fertile testing ground with which to test and expand our understanding of quantum mechanics. One experiment involved dynamically splitting the condensate in two by raising a potential barrier in the center of the trap.\(^6\) The purpose was to examine phase coherence between the two resulting condensates, an area where adiabaticity is critically important in their creation and subsequent recombination. This work is important for its application to the reverse problem: merging two condensates. This allows a condensate to be refilled and has applications in interferometry. Furthermore, it may eventually lead to a continuous coherent source of propagating atoms, a continuous atom laser.
Adiabatic quantum mechanics has been applied to quantum computation. A new kind of quantum algorithm\cite{37} has been developed where the computer evolves adiabatically to the solution of the final state. Quantum computers of this type have the additional advantage of being able to observe the role of entanglement in the algorithms since its evolution can be tracked as a continuous function of time.\cite{38}
Chapter 3

Quantum dynamics

Many areas of physics are concerned with the control of quantum mechanical systems under the influence of a time-dependent interaction. The end state of a system relies critically on the temporal profile of the interaction as well as the initial and final conditions. This dependence on the temporal profile has become more important to understand as scientists are increasingly interested in controlling matter, and doing so with unprecedented precision.

The terms *diabatic* and *adiabatic* often arise in the description of the dynamics of quantum mechanical systems under the influence of these time-dependent interactions. A two-level system can be described using two alternative pairs of basis states. Diabatic states are those that retain their properties as the interaction proceeds while conversely adiabatic refers to those states that adapt and change their functional forms, exchanging many properties. The system evolves along the diabatic states when the interaction variable is rapidly changed. We have chosen two examples of physically realistic, isolated and easily envisioned two-level systems which illustrate these concepts. These cases are a two-level system under the influence of an electric field, i.e. linear Stark states, and a spin–$\frac{1}{2}$ particle in a rotating magnetic field. We also introduce a clearly defined approach for determining a good temporal profile to
ensure the system will evolve as adiabatically as possible, as is often the desired case experimentally. This technique will then be applied to two particular, highly polar Stark states of the lithium atom in the next chapter.

3.1 Two-level systems

We first examine the general case of a time-dependent Hamiltonian arising from an interaction parameter, such as a changing electric field, magnetic field or bond length. We limit ourselves to a pure two-level system with explicit time dependence, following a well-established treatment outlined by Stenholm[39] and summarized below. It is worthwhile to take a moment to consider possible basis states at this time. The diabatic basis \{\text{\mathit{\phi}}_n\} represents states that retain their functional forms while the adiabatic basis \{\text{\mathit{\xi}}_n(t)\} represents states that adapt their functional forms as the crossing is traversed. The Hamiltonian for our two-level system is written in the diabatic basis as:

\[
H_{\text{dia}} = \hbar \begin{bmatrix}
\alpha(t) & V(t) \\
V(t) & -\alpha(t)
\end{bmatrix},
\]  

(3.1)

where the diabatic energy \(\alpha(t)\) and coupling \(V(t)\) are assumed to be real. The diabatic energies, \(\pm \alpha(t)\), will cross at some value of the interaction variable at some time as the crossing is traversed. We start by assuming a state vector of the form:

\[
|\psi(t)\rangle = c_1(t)|\phi_1\rangle + c_2(t)|\phi_2\rangle,
\]  

(3.2)
where we have used the Schrödinger picture with the diabatic basis vectors having spatial but no time dependence. From the Schrödinger equation for this system, we obtain the following equations of motion:

\[ i\hbar \dot{c}_1 = \alpha(t)c_1(t) + V(t)c_2(t) \]  
\[ i\hbar \dot{c}_2 = -\alpha(t)c_2(t) + V(t)c_1(t). \]

The state vector can alternatively be described in the adiabatic basis,

\[ |\psi(t)\rangle = a_1(t)|\xi_1(t)\rangle + a_2(t)|\xi_2(t)\rangle, \]

which is accomplished through the unitary transformation:

\[ U(t) = \begin{bmatrix} 
\cos(\theta/2) & -\sin(\theta/2) \\
\sin(\theta/2) & \cos(\theta/2) 
\end{bmatrix}, \]

where

\[ \tan(\theta) = -\frac{V(t)}{\alpha(t)}, \]

resulting in a diagonalized Hamiltonian:

\[ U H_{\text{dia}} U^\dagger = \begin{bmatrix} 
-\epsilon(t) & 0 \\
0 & \epsilon(t) 
\end{bmatrix}, \]
where the adiabatic energy is:

\[ \epsilon(t) \equiv \sqrt{\alpha^2(t) + V^2(t)}. \]  

(3.9)

The time dependence of the system in the adiabatic basis is dictated by the dynamical Hamiltonian (see A.1):

\[ H_{ad} = U H_{dia} U^\dagger - i\hbar U \frac{\partial U^\dagger}{\partial t} = \begin{bmatrix} -\epsilon(t) & -i\gamma(t) \\ i\gamma(t) & \epsilon(t) \end{bmatrix}, \]  

(3.10)

where the off-diagonal matrix elements \( \pm i\gamma(t) \) represent the dynamical coupling between the adiabatic states associated with changing the interaction variable:

\[ \gamma(t) = \frac{\hbar \dot{\theta}(t)}{2} = \hbar \frac{V(t)\dot{\alpha}(t) - \alpha(t)V(t)}{2(\alpha(t)^2 + V(t)^2)}. \]  

(3.11)

The equations of motion in the adiabatic basis are:

\[ \dot{a}_1 = \frac{i\epsilon(t)}{\hbar}a_1(t) - \frac{\gamma(t)}{\hbar}a_2(t) \]  

(3.12)

\[ \dot{a}_2 = \frac{\gamma(t)}{\hbar}a_1(t) - \frac{i\epsilon(t)}{\hbar}a_2(t). \]  

(3.13)

We can directly obtain the composition of the state vector, \( |\psi(t)\rangle \) as the crossing is traversed by solving either system of equations, given the initial conditions.
3.2 Methods for solving the equations of motion

Equations 3.12 and 3.13 can not be solved analytically in general. Instead, there exist classes of systems where specific approximations can be made to achieve a solution by contour integration into the upper complex plane. The Landau-Zener class of systems are those where the energies of the diabatic state $s$ are linear in time and the coupling between them is constant in time in the vicinity of the crossing. Rosen and Zener examined and solved a system where the energy levels were constant but the coupling was a bell-shaped interaction $V(t) \propto 1/\cosh(t/t_0)$. These are the two simplest systems to visualize when studying quantum dynamics. The Landau-Zener system is the basis of our investigation.

3.2.1 The Landau-Zener approximation

The set of approximations made by Landau and Zener allow the equations of motion to be solved analytically. These approximations are:

1. The diabatic energies are linear in time:

\[ \alpha(t) = \kappa t. \]  \hspace{1cm} (3.14)

When applied to crossings between linear Stark states, this requires that the electric field strength varies linearly in time.

2. The coupling $V$ between diabatic states is constant:

\[ V(t) = V_0. \]  \hspace{1cm} (3.15)

The solution of the equations of motion in the adiabatic basis then gives a simple formula for $a_2$ at $t = \infty$, assuming $a_1 = 1$ at a time significantly before the crossing,
i.e. we start purely in one adiabatic state. This allows us to calculate the probability of remaining in that initial state after the crossing is traversed. We shall refer to this probability as the final adiabaticity:

\[ P_A = 1 - |a_2(\infty)|^2 = 1 - e^{-2\pi \Lambda}, \]  

(3.16)

where we define the adiabaticity parameter to be:

\[ \Lambda = \frac{V_0^2}{2\hbar\kappa}. \]  

(3.17)

This is the result reported by Zener, and previously by Landau missing a factor of $2\pi$ in the exponent, and is an indication of how adiabatically the crossing is traversed. When $\Lambda$ is large (corresponding to, in some sense, a slow crossing), there is a high chance of adiabatic evolution.

### 3.2.2 Numerical solution of a Landau-Zener system

We now examine a numerical solution for a system compliant with the Landau-Zener approximations. Our goal is to accurately reproduce the analytic result so that we can move beyond their limiting approximations and investigate other, more general field profiles.

We employ the two-level system from the previous section with the diabatic energies to change between $\pm 100$ and $\mp 100$ over a period of $2\tau = 40$, crossing at the origin. We set $V(t) = V_0 = 1$, and numerically integrate the equations of motion from $-\tau$ to $\tau$, with an initial state $|\xi_1\rangle$ corresponding to $a_1(t = -\tau) = 1$ and set $\hbar = 1$.

For avoided crossings between linear Stark or Zeeman states, the diabatic energies, $\alpha(t)$, are directly proportional to that of the electric or magnetic field: $\alpha(t) = gF(t)$,
where \( F(t) \) is the time varying field and \( g \) is a constant of proportionality, such as the electric or magnetic dipole moment. We have set \( g = 1 \) for our simulation of the two-level system. Figure 3.1(c) shows the final adiabaticity (i.e. \( P_A \)) for a linear electric field as a function of \( \kappa \) and, as expected, it is seen to be acutely dependent on rate of change of the field. At low slew rates the crossing is primarily adiabatic while high slew rates tend to more diabatic behaviour. Figure 3.1(c) shows good agreement between the analytical solution and our numerical solution for a Landau-Zener system. Thus we are ready to go beyond the approximations inherent in the purely analytical model.

Figure 3.1(a) shows plots of the state populations, given an initial state of \( |\psi(-\tau)\rangle = |\xi_1(-\tau)\rangle \), in the adiabatic basis as a function of time for the Landau-Zener compliant linear energy profile of figure 3.1(b). The population oscillations lead us to note that there are different ways to determine the adiabaticity of a particular traversal. One option is \( P_A \), defined in Eq. 3.16, indicating the final probability of ending in the initial adiabatic state once the crossing is completely traversed. A second option is the minimum population in state \( |\xi_1\rangle \) at any time during the passage of the crossing; we shall denote this as \( P_{\xi_1,\text{min}} \) which reflects the probability of remaining in \( |\xi_1\rangle \) throughout the entire traversal. The former is most useful during an interaction where there is very little decay out of the other adiabatic state, i.e. \( |\xi_2(t)\rangle \), such as in atomic collisions. The latter takes into account the possibility of large population oscillations and is useful where decay from the other state may be problematic, such as in adiabatic rapid passage, or when the details of the dynamics are to be investigated. We shall adopt \( P_{\xi_1,\text{min}} \) in what follows as our adiabatic figure of merit, which for the case depicted in figures 3.1(a) and 3.1(b) takes the value of 0.4077.
Figure 3.1: (a) Plots of the state populations in the adiabatic basis as a function of time for a Landau-Zener compliant linear energy profile, in which the system starts in the lower adiabatic state, $|\xi_1\rangle$, at $t = -20$. (b) The corresponding time-dependent eigenenergies of this system. (c) The 'final adiabaticity', $P_A$, for a range of electric field slew rates corresponding to $\kappa = 1, \ldots, 40$, with $g = 1$, across corresponding time periods of $2\tau = 80, \ldots, 2$. The solid curve is derived from the Landau-Zener analytic expression for $P_A$ and the points are determined from a numerical solution of Equations 3.12 and 3.13.
3.2.3 Beyond the Landau-Zener approximations

We now examine a range of different field profiles that produce large probabilities of an adiabatic transition between two model linear Stark states for given initial and final values of the field in a fixed time duration \(2\tau\). The non-linear (in time) fields break approximation 1 for a Landau-Zener system. The case discussed in the previous section, with a field that linearly increased from -100 to 100 in a time of \(2\tau = 40\) (and \(V_0 = 1, g = 1\)) resulted in an adiabatic figure of merit \(P_{\xi_1,\min} \approx 0.4077\). The behaviour of the system depends critically on rate of change of the field and the energy separation of the two states. Figure 3.1(a) suggests that a rapid variation in the field is unlikely to induce a transition between \(|\xi_1\rangle\) and \(|\xi_2\rangle\) when their energy separation is large as population transfer only occurs when the energies are very close together.

This last statement must be quantified. The *global* adiabaticity condition, obtained from the adiabatic theorem\(^{[43]}\) does exactly this (see appendix A.2 for a derivation):

\[
\max \left| \frac{\langle \xi_1 | \frac{dH}{dt} | \xi_2 \rangle}{(\epsilon_2(F) - \epsilon_1(F))} \right| \ll \min |(\epsilon_2(F) - \epsilon_1(F))|. \tag{3.18}
\]

This inequality can also be applied *locally*, with inequality 3.18 being satisfied independently at each value of the field \(F\). This results in:

\[
\langle \xi_1 | \frac{dH}{dt} | \xi_2 \rangle = \rho(\epsilon_2(F) - \epsilon_1(F))^2, \tag{3.19}
\]

where \(\rho\) is a constant indicating how well Eq. 3.18 is locally satisfied. We use \(P_{\xi_1,\min}\) to investigate the adiabaticity of our system under the influence of a field governed...
by Eq. 3.19 with particular values of $\rho$:

$$\frac{dF}{dt} = \rho \frac{(\epsilon_2(F) - \epsilon_1(F))^2}{\langle \xi_1| \frac{dH}{dt} |\xi_2 \rangle} = \rho \frac{(\epsilon_2(F) - \epsilon_1(F))^2}{2gV_0^2}.$$  

(3.20)

In the last step we have assumed linear diabatic energy dependence on the field and constant coupling, $V_0$, between the diabatic states. An approach similar to this is taken for the case of adiabatic searches using quantum computers$^{[44]}$.

We now examine the results of a field profile generated using a more general exponent than a quadratic dependence and compare with those obtained using Eq. 3.20:

$$\frac{dF}{dt} = k(\epsilon_2(F) - \epsilon_1(F))^x,$$  

(3.21)

where $k$ is a scaling factor set to meet the desired boundary conditions and the exponent $(x \in \mathbb{R})$ is varied to determine the optimal value which returns the maximum value of $P_{\xi_1,\text{min}}$ for given initial and final conditions.

We increase the field from $-100$ to $100$ in a period of $2\tau$ and calculate the minimum population in $|\xi_1\rangle$, $P_{\xi_1,\text{min}}$, for varying values of $\tau$. Figure 3.2 displays the result of our comparison. The solid line shows $P_{\xi_1,\text{min}}$ for the general exponent case over a range of $\tau$ with the inset showing the corresponding optimized exponent $x$. The dashed-dotted curve is obtained by the application of Eq. 3.20 over the same time intervals and the values of $\rho$ are uniquely determined by $\tau$, as all other parameters are held constant:

$$\rho = \frac{F_{\text{max}}}{2\tau g} + \frac{2g\tau}{3V_0^2}.$$  

(3.22)

In figure 3.2, the value of $\rho$ ranges from $0.001$ at large $\tau$ to $1$ at small $\tau$ and the dashed
region of the dashed-dotted curve corresponds to a value of $\rho < 0.1$, satisfying the local adiabaticity condition.

![Figure 3.2: A comparison of the minimum population found in state $|\xi_1\rangle$, $P_{\xi_1,min}$, for fixed initial and final values of field and different traversal times, $\tau$. The solid line is obtained from a set of solutions of Eq. 3.21 with exponents that maximize $P_{\xi_1,min}$, and these exponents are shown in the inset. The dashed/dotted curve is obtained from Eq. 3.20, and is dashed where $\rho < 0.1$, indicating compliance with the local adiabaticity condition.](image)

The optimized exponent method, governed by Eq. 3.21, produces a greater probability of an adiabatic transition than by application of the local adiabatic condition of Eq. 3.20 at shorter time intervals. At large traversal times, $\tau$, the two methods converge and tend to unity, as is expected when the duration of the traversal approaches infinity.

We now return to the model two-level atom previously discussed and apply the optimized exponent method. In figure 3.3, the adiabatic figure of merit $P_{\xi_1,min}$ is seen to be 0.994, which is substantially greater than the 0.4077 obtained with a Landau-Zener compliant field profile.
3.2.4 The spin-flip problem as an example of quantum dynamics

Another type of system where adiabatic quantum dynamics is important is a particle with a magnetic moment $\mu$ in a rotating magnetic field. The magnetic moment is related to the particle’s angular momentum $j$ by:

$$\mu = -\frac{g_j \mu B j}{\hbar}. \tag{3.23}$$

This system has constant eigenenergies ($\propto$ field strength) as the magnetic field rotates with constant coupling ($\propto$ angular frequency) between eigenstates.

This classic spin-flip problem\textsuperscript{45} is often used to introduce the concept of adiabaticity. The energy eigenstates are labelled by $|m\rangle$, where $m$ is the projection of the angular momentum on the instantaneous magnetic field direction, and their functional form depend on the orientation of the field. The adiabatic basis $\{\xi_m\}$ is made up of these $2j+1$ states and the particle will maintain its initial adiabatic amplitudes, $a_m(\tau)$ defined in Eq. 3.5, if the field is rotated slowly enough. The initial orientation of the field, along direction $\hat{\zeta}$, determines the diabatic basis $\{\phi_m\}$ composed of energy eigenstates along this fixed direction. If the field is rotated rapidly enough, the particle will retain its initial diabatic amplitudes, $c_m(\tau)$, defined by Eq. 3.2.

Generalized angular momentum eigenstates can be difficult to visualize. The classical vector model\textsuperscript{46} can help to illustrate the quantum dynamics of such systems. The simplest and most intuitive physical system is that of a spin-$\frac{1}{2}$ particle in a magnetic field $B(t)$ of constant magnitude $B_0$, rotating in a plane. The equations of motion are simplified if the field is restricted to the $x-y$ plane with $\dot{\phi} = \omega = constant$, where we use the standard $(\theta, \phi)$ spherical coordinates to describe the orientation of $B(t)$. 
A useful parameter is the Larmor frequency:

\[ \omega_L = \frac{|\mu| B_0}{\hbar}, \]  

(3.24)

which is the angular frequency at which \( J(t) \) precesses about \( B \) in the vector model.

If we set the initial direction of the field to be along \( \hat{x} \), then the diabatic Hamiltonian for the system is:

\[
H_{\text{dia}} = \hbar \omega_L \begin{bmatrix}
\cos(\phi) & \sin(\phi) \\
-\sin(\phi) & \cos(\phi)
\end{bmatrix}.
\]  

(3.25)

The coupling between states is \( \phi \)-dependent. The diagonalized Hamiltonian gives the well-known energy eigenvalues:

\[
U H_{\text{dia}} U^\dagger = \hbar \omega_L \begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix}.
\]  

(3.26)

The resulting dynamical Hamiltonian:

\[
H_{\text{ad}} = \hbar \begin{bmatrix}
\omega_L & \frac{i\omega}{2} \\
-\frac{i\omega}{2} & -\omega_L
\end{bmatrix},
\]  

(3.27)

gives the equations of motion for the adiabatic state amplitudes, \( a_\pm \). The probability of no spin-flip, i.e. remaining in the initial adiabatic state \( |\xi_-\rangle \) is given by an oscillatory
function of the subtended angle:

$$P_A = |a_-(t)|^2 = 1 - \frac{\omega^2}{4\omega_L^2 + \omega^2} \sin^2 \left( \frac{\omega t}{2} \sqrt{4(\omega_L/\omega)^2 + 1} \right).$$

There is no explicit dependence on the initial and final values of the interaction parameter $\phi$ since the energy eigenvalues are constant for all $\phi$. This is different than the Stark states previously investigated where the eigenenergies are time dependent.

Figure 3.4 depicts the dynamics of a lithium atom ($g_j \approx 2$) placed in a magnetic field of 1 mT rotating in the $x - y$ plane with $\omega_L = 88.04 \times 10^6$ rad s$^{-1}$. The adiabatic figure of merit, $P_{\xi_{-,\text{min}}}$, is given by the amplitude of Eq. 3.28 and is plotted for a range of values of $\omega$. A 'slow' field rotation, $\omega \ll \omega_L$ allows predominantly adiabatic evolution and a 'fast' field, $\omega \gg \omega_L$ results in diabatic evolution. The insets at high and low $\omega$ show 'before' and 'after' vector model pictures for principally adiabatic and diabatic evolution, respectively, for the particular case when $\mathbf{B}(t)$ rotates from $\phi = 0 \rightarrow \phi = \pi$ and the lithium atom system starts in $|\xi_-\rangle$. The inset graph corresponding to $\omega = 79.24 \times 10^6$ rad s$^{-1} = 0.9 \omega_L$ shows the state populations as a function of time for this system as $\phi$ continually rotates.

We have introduced the fundamental concepts of quantum dynamics and will now move on to more complex, realistic systems of atoms and molecules where we will apply our model.
Figure 3.3: (a) The $|\xi_1\rangle$ state probability as a function of time for a system initially in state $|\xi_1\rangle$, field increased from -100 to 100 and a traversal time of $2\tau = 40$ for the optimized-exponent field profile shown in (b), with optimal exponent of 4.1. The resulting adiabatic figure of merit, $P_{\xi_1 min}$, is 0.994.

Figure 3.4: Plot of the adiabatic figure of merit, $P_{\xi_- min}$, for a lithium atom experiencing a range of magnetic field rotation rates, $\omega$, and starting in $|\xi_-\rangle$. The insets at low and high $\omega$ show 'before' and 'after' vector model pictures for principally adiabatic ($\omega \ll \omega_L$) and diabatic ($\omega \gg \omega_L$) evolution, respectively, for the particular case when $B(t)$ rotates from $\phi = 0 \rightarrow \phi = \pi$ and the atom starts in $|\xi_-\rangle$. The graph corresponding to $\omega = 79.24 \times 10^6$ rad s$^{-1}$ = 0.9 $\omega_L$ (the point on the curve indicated by the arrow) shows the state populations as a function of time for this system as $\phi$ continually rotates.
Chapter 4

Applications of quantum dynamics to a polar atomic system

The first system we will use to study adiabatic quantum dynamics is the lithium atom and its Stark manifolds of Ryberg states. The detection mechanism will be field ionization, which involves applying an electric field to the atom in order to strip away an electron. The precise time when an atom is ionized depends upon the initial state of the atom and the time-dependent properties of the field. A Stark map has been generated for lithium in order to show the possible paths the atom can take until the electron is stripped away. A thorough understanding of the energy levels is required in order to control how adiabatically or otherwise the atom traverses the many avoided crossings on the route to ionization.

4.1 Interactions with electric fields

Atoms and molecules under the influence of an electric or magnetic field typically exhibit many crossings between the energies of adjacent eigenstates. The Stark effect is the result of an interaction between the electric dipole moment, represented by
the dipole moment operator, $\mathbf{d} = \sum_\alpha Z_\alpha \mathbf{r}_\alpha + \sum_i e \mathbf{r}_i$ with $\alpha$ denoting nuclei and $i$ denoting electrons, and an applied electric field, $\mathbf{F}(t)$, which modifies the Hamiltonian by including an additional term:

$$\hat{H}_E(t) = -\mathbf{d} \cdot \mathbf{F}(t).$$

Diagonal matrix elements of $\hat{H}_E$ calculated for $|\eta jm\rangle$ states of definite parity (where $j$ represents the total angular momentum quantum number, $m$ is the projection of this angular momentum, usually taken along the field direction, and $\eta$ represents all other relevant quantum numbers) are identically zero due to the odd parity of $\mathbf{d}$.\[48\] Thus space-fixed electric dipole moments, as measured in the laboratory frame, are zero for atoms and molecules in these states. Electric dipoles in atoms and molecules generally appear in the presence of an external electric field. The field mixes the angular momentum $|\eta jm\rangle$ states of a given $m$, causing many energy eigenstates to have a permanent electric dipole moment, i.e. a dipole moment in the space-fixed laboratory frame, corresponding to a polarized atom or molecule.\[14\] States of the same $n$, referred to as a manifold, will ‘fan out’ as the electric field strength increases. At sufficiently large electric fields, eigenstates from two adjacent manifolds may approach degeneracy and, depending upon the system, subsequently cross or narrowly avoid crossing and repel each other. The avoided crossing provides rich quantum structure and enables an insightful, qualitative and quantitative study of quantum dynamics due to time-dependent interactions, which has been introduced in chapter 3.

### 4.2 Stark map for Rydberg states of alkali atoms

The eigenenergies for the hydrogen atom in an electric field can be obtained precisely, and a Stark map obtained by solving the Schrödinger equation in parabolic...
coordinates. The resulting structure is due to the distortion polarizability of the atom, i.e., the electric field causes different atomic orbitals to be mixed with each other. The outermost states from adjacent $n$ manifolds with $m = 0$ become degenerate at the Inglis-Teller limit, which is, in S.I. units:

$$F = \frac{2Ry}{3ea_0n^5}.$$  \hspace{1cm} (4.2)

Thus hydrogen atoms experience real, rather than avoided, crossings. Rydberg states of alkali atoms in an electric field, however, possess an ionic core that can be polarized and penetrated by the outer electron. To address core polarization, a term is typically included within the one-electron Hamiltonian, corresponding to a deepening of the potential well at short radial distances. This results in two important differences from the hydrogen atom. The first is a quantum defect, $\delta$, within the energy expression for the unperturbed (zero field) Rydberg states:

$$E_n = -\frac{Ry}{(n-\delta)^2}. \hspace{1cm} (4.3)$$

The second difference is that adjacent $n$ states experience avoided, rather than real, crossings. The first-order correction to the Hamiltonian is a $-\frac{1}{r^4}$ term, representing the dipolar contribution to the polarization energy. In S.I. units, the Hamiltonian for the Rydberg electron takes the form:

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0r} - \frac{e^2\alpha_d}{(4\pi\epsilon_0)^2r^3} - \hat{d} \cdot \vec{F}. \hspace{1cm} (4.4)$$
The polarization term in Eq. 4.4 is derived using the long-range expression for the potential due to an electric dipole, and is most valid for those Rydberg states with a low probability of finding the electron at small $r$, i.e. not $s$-states. This is due to our neglect of ionic core penetration effects, such as reduced screening of the nucleus by core electrons when the Rydberg electron is at very small radius. In the numerical work for lithium presented here, the particular Stark states we consider have a probability of less than $1.7 \times 10^{-9}$ of the electron being inside the lithium ionic core\(^1\), with radius 30.2 pm.\(^{[49]}\) In Fig. 4.1, we show the Stark map for the $n = 13, 14, 15$ $m_\ell = \pm 1$ Rydberg manifolds of lithium, obtained by finding the eigenvalues of Eq. 4.4 using $\alpha_d = 3.10 \times 10^{-42}$ m\(^2\)F\(^{[14]}\) and a $|n = 11 \ldots 17, \ell, m_\ell = 1\rangle$ basis. Below each zero-field\(^2\) $n\ell$ manifold can be seen the corresponding $np$ states with $\delta_\ell \approx 0.08$, calculated from our Stark energies; this is relatively close to the experimental value of 0.047\(^{[14]}\) and suspect the error may be due to not including core penetration. The bold circle centred at $F = 447$ kV/m indicates one of several avoided crossings between the energies of two eigenstates and can provide a particularly insightful example of quantum dynamics, as discussed below.

### 4.3 Lithium Stark states in time-dependent electric fields

As any crossing is approached, one choice of basis states, the diabatic states $|\phi_n\rangle$ with fixed functional forms converging to those of the energy eigenstates sufficiently far from the crossing, are particular linear combinations of the unperturbed (zero field)\(^{1}\)

\(^{1}\)This value of the radius for the ionic core of Li\(^+\), calculated from the extent of the populated orbitals, is much smaller than the ‘ionic radius’, often encountered in chemistry texts, which is deduced from the nearest-neighbour separation between anions and cations in an ionic matrix.\(^{[50]}\)
Figure 4.1: The Stark map for the lithium atom showing the $n = 13, 14, 15, |m| = 1$ energy eigenstates. The bold line represents the classical ionization threshold where the atom has sufficient energy to ionize. The circle indicates the avoided crossing that is studied in more detail. Many avoided crossings can barely be resolved on this scale.
In this case, the unperturbed states may be the $|n\ell m\rangle$ no-field angular momentum or $|nn_1n_2m\rangle$ field-mixed parabolic eigenstates, where $n_1$ and $n_2$ are the parabolic quantum numbers. The crossing highlighted in Fig. 4.1 is that between the $n = 13$, $n_1 - n_2 = 11$ state, denoted $|\phi_1\rangle$ below, with a dipole moment of 532 D and the $n = 14$, $n_1 - n_2 = -12$ state, denoted $|\phi_2\rangle$, with a dipole moment of -657 D. An alternative basis set with which to analyze the dynamics is that of the energy eigenstates, termed the adiabatic basis, with states denoted $|\xi_1(t)\rangle$ and $|\xi_2(t)\rangle$ for this two-level system.

Each crossing can be characterized in terms of its minimum energy separation, $\Delta E_{\text{min}}$, at the crossing field, $F_c$, and a width, $q_0$, with the latter parameter defined as the ratio of the $\Delta E_{\text{min}}$ to the difference between the gradients of the diabatic states at the crossing.$^{[27]}$ Fig. 4.2 shows an expanded view of the avoided crossing highlighted in Fig. 4.1, for which $\Delta E_{\text{min}} = 0.04$ meV and $q_0 = 1.59$ kV/m, and shows the probability densities of the adiabatic states and the relationships between the adiabatic and diabatic bases, calculated at $F_c$ and $F_c \pm 6q_0$. The states involved in this crossing include very small mixtures of the other Stark eigenstates included in the calculation. However, these contributions are not displayed for clarity due to their almost negligible nature.

From Fig. 4.2, we can visualize the functional forms of the adiabatic and diabatic states and their evolution through the crossing. For the adiabatic states $\{|\xi_i\rangle\}$, these functional forms are interchanged after the crossing, which is consistent with the interpretation of adiabatic passage. Conversely, under diabatic evolution, the system
Figure 4.2: Expanded Stark map of the avoided crossing shown in Fig. 4.1 between the \( n = 13, n_1 - n_2 = 11 \) and \( n = 14, n_1 - n_2 = -12 \) states. The probability densities \( \langle \xi_i(F) | \xi_i(F) \rangle \) for the adiabatic states \( |\xi_1(F)\rangle \) and \( |\xi_2(F)\rangle \), where \( F \) is the time-dependent field in the direction indicated, are shown before, during and after the crossing. The projections of these states onto the diabatic states, \( |\phi_1\rangle \) and \( |\phi_2\rangle \) which are the energies of the diagonal matrix elements, are calculated at \( F_c \) and \( F_c \pm 6q_0 \) and shown on the plot.
moves through the crossing quickly enough that the system does not have time to
adjust to the variation, and if it is initially in $|\xi_1\rangle$ at low fields, it undergoes a transition
to state $|\xi_2\rangle$ (i.e. remains in state $|\phi_1\rangle$ throughout). The state of the system when
described using the adiabatic basis has then changed, but its functional form and
physical properties have not.

4.4 Maximizing adiabatic transition probability in lithium Stark states

Now that we have introduced the Stark map of the lithium atom and a prescribed
treatment for maximizing the adiabatic transition probability through a crossing, it
is time to apply that method to this real system. There are two notable differences
between the atom and the model two-level system introduced in the previous chapter.
Here, the diabatic energies are only approximately linearly dependent on the field
strength, and additionally the coupling varies with the field strength. However, it
is still possible to determine an optimal exponent for the field to maximize $P_{\xi_1,\text{min}}$.
The results from traversing the crossing expanded in Fig. 4.2 are shown in Fig. 4.3
for a total traversal time of 0.2 ns over a field range from 4.2 kV/cm to 4.7 kV/cm.
$P_{\xi_1,\text{min}}$ is seen to be 0.987, with an optimal exponent of 2.2. There is a remarkable
difference between this value and that for a linear in time, Landau-Zener compliant
field profile using the same initial and final conditions and traversal time, resulting in
$P_{\xi_1,\text{min}} = 0.393$. 
Figure 4.3: The state population (a), energy (b) and electric field profile (c) as functions of time for the avoided crossing between the $n = 13, n_1 - n_2 = 11$ state and the $n = 14, n_1 - n_2 = -12$ state. The field is derived from Eq. 3.21 with an optimized exponent of 2.2. The adiabatic figure of merit $P_{\xi_1,\text{min}}$ is 0.987. Plot (d) shows the state population for the Landau-Zener compliant field profile in lithium, for which $P_{\xi_1,\text{min}} = 0.393$. 
Chapter 5

Applications of quantum dynamics to the formation of a highly polar molecular system

5.1 Electric dipole moments of molecules

Analogously to atomic systems, molecules with zero projection of angular momentum along the symmetry axis (i.e. all linear molecules, which includes diatomics, in $^1\Sigma$ states) do not have permanent, space-fixed electric dipole moments. This applies to polar and non-polar molecules alike, where the designation refers to a dipole moment in the molecule-fixed frame, and follows from the treatment below. First, the dipole moment of the molecule, which lies along the molecular axis, must be presented in the coordinates of the laboratory frame, where the electric field is applied:

$$\hat{H}_E = -\hat{d} \cdot \mathbf{F} = -d_0 D^{(1)}_{00}(\omega) F, \quad (5.1)$$
where $D^{(1)}_{00}$ is the Wigner rotation matrix $D^{(J)}_{mm'}$ rotating the molecular coordinates through angle $\omega$ and $d_0$ is the magnitude of dipole moment of the molecule along the internuclear axis, which now interacts with the field in the laboratory frame. The matrix elements of this term in the Hamiltonian are:

$$
\langle \eta \Lambda J M_J | \hat{H}_E | \eta' \Lambda' J' M'_{J'} \rangle = -dF \{(2J + 1)(2J' + 1)\}^{\frac{1}{2}} (-1)^{M - \Lambda} \left( \begin{array}{ccc}
J & 1 & J' \\
-M_J & 0 & M'_{J'} \\
\end{array} \right) \left( \begin{array}{ccc}
J & 1 & J' \\
-\Lambda & 0 & \Lambda' \\
\end{array} \right).
\tag{5.2}
$$

Molecules in $^1\Sigma$ states have no component of their angular momentum along the internuclear axis, i.e. $\Lambda = 0$. The second 3-$j$ symbol in Eq. 5.2 is non-zero only if $J' = J \pm 1$, the same as for an atom. For states where $\Lambda \neq 0$, the situation is more complicated and permanent, space-fixed electric dipole moments are possible provided other conditions, such as pendular states\textsuperscript{[53]} or higher order distortion coupling,\textsuperscript{[54]} are also met but we will not consider them here.

Often polar molecules, such as hydrogen fluoride, are defined as those that “have permanent dipoles” and diagrams depicting a clear separation of constituents into partial charges in the laboratory frame are shown.\textsuperscript{[55]} In the absence of an external electric field, this oriented partial charge picture is in fact only true in the molecular frame, i.e. fixed with reference to the molecule. An external electric field is required to orient such polar molecules in the lab frame, and because the local environment can often provide such a sufficient field, then this simple description is helpful to explain the behaviour of these molecules in chemical reactions.

The precise magnitude of the electric dipole moment in the laboratory frame depends on both the electric field strength experienced by the molecule and the particular Stark eigenstate of the molecule. From the Hellmann-Feynman theorem applied to
Eq. 5.1, the slope of the energy with respect to electric field for each eigenstate is the electric dipole moment of the state at that electric field. For molecules in $^1\Sigma$ states at low fields, the energies are quadratic with field strength and hence the dipole moment is not constant. Here, the angular probability densities of the eigenstates change with increasing electric field due to rotational polarizability (we neglect the distortion polarizability which occurs at much higher fields), and assume a final functional form once their corresponding energies become linear with field. Fig. 5.1(a) and (b) depict the Stark map for a general diatomic molecule with rotational constant $B$ showing states originating from the $J = 0 \ldots 2$ and $|J = 3, M_J = \pm 2, \pm 3\rangle$ field-free states as a function of electric field parameter: $\lambda = d_0 F/\sqrt{B}$, where $d_0$ is the electric dipole moment of the molecule in its ground electronic state in the molecule-fixed frame. States of the same $M_J$ and adjacent $J$ values are mixed by the second-order Stark effect, resulting in a dipole moment that initially varies acutely with electric field, and each eigenstate having a characteristic limiting lab-frame dipole moment at high $\lambda$ (see Fig. 5.1 (c)). To give an indication of the limiting field required for the case of hydrogen fluoride, for which $B = 2.54$ cm$^{-1}$ and $d_0 = 1.826$ D$^{[66]}$, a lab-frame electric dipole moment of $0.9d_0$ is reached at $3.5$ MV/cm, which could be provided from a fully polarized HF molecule located $0.8$ nm (9 bond lengths) away. The angular probability densities of the eigenstates at large electric fields ($\lambda = 200$) are plotted with a consistent aspect ratio in Fig 5.1(d) and greatly differ from the spherical distribution of the $|J = 0, M_J = 0\rangle$ ground state of the molecule in the absence of an electric field. Each plot represents the angular probability density $\vec{R}$, the relative position vector from the fluorine nucleus to that of hydrogen, and similarities between these shapes can be seen for states with the same limiting dipole moment.

The visible crossing displayed in Fig. 5.1(a) at $\lambda \approx 19$ is real, rather than avoided, due to the contributing states having different $M_J$ values and thus the energy eigenstates do not exchange functional forms as the crossing is traversed. Such crossings
Figure 5.1: (a) and (b) Stark maps for a selected set of the lowest eigenstates of a $^1\Sigma$ diatomic molecule for a range of electric field strengths represented by $\lambda$ (see text for details). The eigenstates are labeled A through H. c) The lab-frame electric dipole moment of these eigenstates as a function of $\lambda$. d) The corresponding angular probability densities of $r_{rel}$ at large electric fields; the field is oriented vertically upwards.
do not provide the option for either examining or controlling the ratio of diabatic to adiabatic evolution of this quantum system, and its dependence upon the electric field profile. We therefore do not pursue study of these rotational Stark states of molecules for investigating quantum dynamics.

5.2 Ion-pair systems

An ion-pair system is an associated anion and cation, interacting via the electrostatic force. They are typically studied with a very large separation between the constituent ions. At these distances, the ions predominantly experience the Coloumbic $1/r$ potential and the system can possess an extremely large dipole moment. Free ion-pairs ($A^+ + B^-$) are formed when the constituent cation and anion have sufficient kinetic energy to overcome their mutual attraction while bound ion-pairs ($A^+ \cdot \cdot \cdot B^-$) do not. The theoretical work below is initially concerned with the creation of free ion-pairs by charge exchange during the collision of neutral atoms, where the interest lies in the avoided crossing between a covalent and ionic potential energy curves and the associated dynamics. At some incident relative velocity $v_0$, the neutral atoms will have a sufficient kinetic energy to overcome the Coulomb attraction between the resulting ions. Later, we will examine the velocity dependence of the ion-pair formation cross sections in order to provide insight into bound ion-pair generation.

5.3 Colliding atoms and charge exchange

The ion-pair and covalent potential energy curves (i.e. the diabatic curves) of molecules can both cross and couple, resulting in avoided crossings between the adiabatic energy curves. Charge transfer during a collision between atoms, with their separation being the interaction variable, is responsible for dictating the outcome of many chemical reactions and collisional processes. Other processes such as predissociation, collisional
excitation and dissociation, quenching, neutralization and ion-pair production can all be influenced by this interaction. The experimental studies performed to date on ion-pair formation by colliding atoms or molecules is summarized in table 5.1, including the species involved in the collision.

Table 5.1: Experimental studies of ion-pair formation through colliding atoms or molecules

<table>
<thead>
<tr>
<th>reaction</th>
<th>product</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb + Rb* → Rb⁺ + Rb⁻</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>K + K* → K⁺ + K⁻</td>
<td>[2]</td>
<td></td>
</tr>
<tr>
<td>Na + Na* → Na⁺ + Na⁻</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>CCl₄ + K* → K⁺ + Cl⁻ + CCl₃</td>
<td>[10]</td>
<td></td>
</tr>
</tbody>
</table>

The formation of an ion-pair from colliding atoms is a rich system for the study of quantum dynamics. Landau and Zener began this field of study by examining this very process. The specific molecule we are interested in is diatomic lithium.

Figure 5.2: Some of the potential curves for the covalent (neutral) state of the lithium dimer. Each state is formed from a combination of the atomic states of the constituent atoms; the atomic states to which each molecular state asymptotes are indicated above each curve. The ion-pair Li⁺ + Li⁻ state is indicated by the dotted curve.

Suppose one atom is excited to a Rydberg state (nℓ) at a large separation from
another ground state atom. As the atoms approach one another, the collective system will traverse the avoided crossing with the ion-pair state at a large separation $R_c$.

Figure 5.3: The model potential curves for the $\text{Li}^+ + \text{Li}^-$ ionic (ion-pair) state and $\text{Li}(3d) + \text{Li}(2s)$ covalent (neutral) state of a lithium dimer at large $R$. The avoided crossings, such as the one at $R_c$, between the neutral states and the ionic state are of interest as the quantum dynamics associated with this crossing dictates the probability of charge exchange. The diabatic covalent and ionic potentials are indicated by the dashed curves. The energy and separation are given in atomic units with zero energy being at the Li(2s) + Li(2s) asymptote.

A bound ion-pair state can possess a very large dipole moment due to its large separation (for example, $A^+ \cdots B^-$ bound by 20 meV has a maximum dipole moment of 3455 D). These highly polar systems provide a great tool for studying the quantum mechanics and control of exotic, large molecules.
5.4 Dynamics of ion-pair formation from colliding atoms

We now examine the transitions through these avoided crossings in a molecular system. We restrict ourselves to using the Landau-Zener model as this is the best initial approach to the problem since we cannot control the relative velocity like we can an applied field and the coupling between the ionic and covalent states varies very slowly over the width of the crossing \( q_0 = \frac{2H_{12}}{\Delta F} \). Time did not permit us to revisit this system using a numerical integration routine where we could account for this slowly varying coupling. The probability of a diabatic crossing, i.e. following the covalent or ion-pair state and jumping from one energy eigenstate to another is given as:

\[
P_{12} = e^{-\frac{2\pi H_{12}^2}{v_c \Delta F}},
\]

where \( H_{12} \) is the coupling between the ionic state and the covalent state involved in the avoided crossing, taking the role of \( V_0 \) in equation 3.17, \( \Delta F \) is the difference between the slopes of the ionic and covalent states at \( R_c \) and \( v_c = \frac{dR}{dt} \) is the relative velocity of the two atoms at \( R_c \), the crossing separation. If we assume that all subsequent crossings are followed diabatically, the total probability of an ion-pair being formed during a collision between neutral atoms is given by:

\[
P = 2P_{12}(1 - P_{12}),
\]
taking into account the two possible mechanisms displayed in figure 5.4. For each incoming channel with relative velocity $v$, the cross section $\sigma(v)$ can then be calculated by integrating the total probability over the impact parameter $b$ from zero to its maximum value of $R_c$.

Figure 5.4: The two possible formation paths for ion-pair formation following Landau-Zener dynamics at avoided crossings. The particular crossing shown is with the Li(3d) + Li state from figure 5.3.

Now the parameters $H_{12}$, $\Delta F$ and $v_c$ from equation 5.3, as well as $R_c$, must be determined. For simplicity, all quantities will henceforth be given in atomic units ($a_0 = 0.529 \times 10^{-10}$ m for distance, $m_e = 9.109 \times 10^{-31}$ kg for mass and $Ry = 27.212$ eV for energy). $R_c$ is calculated by equating the ion-pair and covalent potential energies. The energy of the covalent state at large $R$ is, to a good level of approximation, simply the energy of the excited atom and its ground state partner, taking the ground state of two atoms as zero potential energy; $E_{\text{covalent}} = E_{n\ell}$. The ionic state’s potential energy is the energy required to make the ion-pair at separation $R_c$, that is the energy to remove an electron from one atom (its ionization potential $IP$) and attach it to the other atom (its electron affinity $EA$), added to the (negative) potential energy of the
separated pair. To find the crossing separation, we solve, in atomic units, for \( R_c \):

\[
E_{nl} = IP - EA - 1/R_c, \tag{5.5}
\]

At large \( R \), the energy of the covalent state is essentially constant, thus \( \Delta F \) is given by the slope of the ionic state’s energy;

\[
\Delta F = \frac{dE_{ionic}}{dR} = R^{-2}. \tag{5.6}
\]

For initial comparisons with published work\(^{[b]}\) for which only free ion-pair formations has been considered, we choose to calculate the cross section at the threshold velocity, below which the creation of free ion-pairs is energetically impossible. The energy deficit is made up by the kinetic energy of the atoms due to their relative velocity. As an example, for the Li(3d) + Li(2s) state, the threshold speed is 7053 m/s. We can consider the Maxwell-Boltzmann speed distribution of the atoms (valid for a vapour), which tells us the fraction of atoms having a certain speed;

\[
M(v)dv = \left( \frac{\mu}{2\pi k_BT} \right)^{3/2} e^{-\mu v^2/2k_BT} 4\pi v^2 dv. \tag{5.7}
\]

As the most probable speed for lithium at 300°C is approximately 1656 m/s, only a very small fraction of atoms are above the threshold velocity. The fraction of atoms at any given velocity decreases by orders of magnitude for small increases above the threshold velocity. Thus, for collisions involving all but the highest Rydberg levels, most of the contribution to a cross section for free ion-pair production will come from atoms very close to the threshold velocity \( v_c \).
The coupling between ionic and covalent states, \( H_{12} \), is the final and most difficult parameter to determine. Olson’s law\(^{[58]}\), an empirical law determined by studies on alkali-halogens, alkali-oxygen and alkali-hydrogen molecules, does not produce accurate results for alkali-alkali molecules. Instead, the method of Janev and Salin\(^{[59]}\) using asymptotic forms for the radial wavefunctions is employed to determine the strength of the coupling between ionic and covalent states. The coupling is expressed analytically as the relation:

\[
H_{12}(R) = \frac{1}{2} N_1 R^{\frac{1}{\alpha} - 1} e^{-\alpha R (2\ell_1 + 1)^{1/2}} N_2 \left( \frac{C_0}{2\beta} (2\beta - \gamma) + \frac{1}{2} \left( 1 + \frac{\gamma}{\beta} \right) \right).
\]

The values \( \alpha = \sqrt{2IE} \) and \( \gamma = \sqrt{2EAE} \) are state dependent properties of the two atoms that become the cation and anion respectively, where \( IE \) is the ionization energy and \( EAE \) the electron attachment energy (analogous to the ionization potential and electron affinity respectively), and \( \beta = \alpha + 1/R \). \( N_1 \) is the normalization constant of the radial wavefunction of the Rydberg electron in the covalent state. If it is far enough from the ionic core such that it experiences primarily the \( 1/r \) Coulomb potential, \( N_1 \) is very close to:

\[
N_1 = \alpha (2\alpha)^{1/\alpha} (\Gamma[1/\alpha + \ell_1 + 1] \Gamma[1/\alpha - \ell_1])^{-1/2},
\]

referred to as the Coulomb normalization constant.\(^{[59]}\) \( N_2 \) is the normalization constant for the wavefunction of the electron in the negative ion. It is determined by matching
the asymptotic wavefunction:

\[
\chi_2(r) = N_2 e^{-\gamma r} / r, \tag{5.10}
\]

with an exact form, such as a Hartree-Fock wavefunction. It should be noted that fitting this asymptotic wavefunction is not exact; we have done our best in accordance with established methods\[60\] to match the two wavefunctions in the range of the crossing. \(C_0\) is a coefficient related to the low energy scattering of an electron by an atom and is given by:

\[
C_0 = 2\beta \left[ \frac{1}{L} + \frac{\pi \alpha_p \beta}{3L^2} + \frac{4\alpha_p \beta}{3L} \beta^2 \ln \left( \frac{\beta \alpha_p^{1/2}}{4} \right) \right]^{-1}, \tag{5.11}
\]

where \(\alpha_p\) is the dipole polarizability of the atom and \(L\) is the scattering length of the low energy electron.

### 5.4.1 Ion-pair formation in diatomic rubidium

The only published results using this method are for \(\text{Rb}(n\ell) + \text{Rb}(5s) \rightarrow \text{Rb}^+ + \text{Rb}^-\), summarized in Table 5.2, and it proved useful to compare the results of our calculations with these before extending the calculations to lithium.

<table>
<thead>
<tr>
<th>Level</th>
<th>(R_c) (a.u.)</th>
<th>(\Delta F) (a.u.)</th>
<th>(v_0) (a.u.)</th>
<th>(H_{12}) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5d</td>
<td>53.93</td>
<td>3.44 \times 10^{-4}</td>
<td>6.90 \times 10^{-4}</td>
<td>9.38 \times 10^{-5}</td>
</tr>
<tr>
<td>7s</td>
<td>63.43</td>
<td>2.49 \times 10^{-4}</td>
<td>6.36 \times 10^{-4}</td>
<td>2.78 \times 10^{-5}</td>
</tr>
<tr>
<td>7p</td>
<td>114.35</td>
<td>7.65 \times 10^{-5}</td>
<td>4.74 \times 10^{-4}</td>
<td>2.08 \times 10^{-8}</td>
</tr>
<tr>
<td>6d</td>
<td>202.54</td>
<td>2.44 \times 10^{-5}</td>
<td>3.56 \times 10^{-4}</td>
<td>1.38 \times 10^{-14}</td>
</tr>
<tr>
<td>8s</td>
<td>302.68</td>
<td>1.09 \times 10^{-5}</td>
<td>2.91 \times 10^{-4}</td>
<td>3.25 \times 10^{-22}</td>
</tr>
</tbody>
</table>

The ionization potential and electron affinity of ground state rubidium are 0.1535
a.u. and 0.01786 a.u. respectively. Other constants that must be obtained from literature are the polarizability, $\alpha_p = 321$ a.u., and scattering length, $L = 27$ a.u.\cite{62}.

The normalization constant $N_2$ is determined by overlap with a Roothaan-Hartree-Fock atomic wavefunction\cite{63}, giving a value of $N_2 = 2.5$ a.u. With these numbers it is now possible to calculate the total probability of producing an ion-pair from each initial molecular state. The values of all calculated parameters are shown in table 5.3 and generally agree with Barbier, who did not calculate $\sigma(v)$ as he was only interested in the free ion-pairs he could detect in his experiment and assumed the vast majority of ion-pairs formed at the threshold velocity.

<table>
<thead>
<tr>
<th>Level</th>
<th>$R_c$ (a.u.)</th>
<th>$\Delta F$ (a.u.)</th>
<th>$v_0$ (a.u.)</th>
<th>$H_{12}$ (a.u.)</th>
<th>$\sigma(v_0)$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5d</td>
<td>53.92</td>
<td>$3.44 \times 10^{-4}$</td>
<td>$6.90 \times 10^{-4}$</td>
<td>$9.40 \times 10^{-5}$</td>
<td>3680</td>
</tr>
<tr>
<td>7s</td>
<td>63.40</td>
<td>$2.49 \times 10^{-4}$</td>
<td>$6.36 \times 10^{-4}$</td>
<td>$2.79 \times 10^{-5}$</td>
<td>1307</td>
</tr>
<tr>
<td>4f</td>
<td>73.70</td>
<td>$1.84 \times 10^{-4}$</td>
<td>$5.90 \times 10^{-4}$</td>
<td>$2.91 \times 10^{-6}$</td>
<td>33.28</td>
</tr>
<tr>
<td>7p</td>
<td>115.20</td>
<td>$7.53 \times 10^{-5}$</td>
<td>$4.72 \times 10^{-4}$</td>
<td>$1.83 \times 10^{-8}$</td>
<td>$9.817 \times 10^{-3}$</td>
</tr>
<tr>
<td>6d</td>
<td>202.76</td>
<td>$2.43 \times 10^{-5}$</td>
<td>$3.56 \times 10^{-4}$</td>
<td>$1.02 \times 10^{-14}$</td>
<td>0</td>
</tr>
<tr>
<td>8s</td>
<td>301.65</td>
<td>$1.10 \times 10^{-5}$</td>
<td>$2.92 \times 10^{-4}$</td>
<td>$3.88 \times 10^{-22}$</td>
<td>0</td>
</tr>
</tbody>
</table>

Notice that the cross sections for the Rb(6d) + Rb(5s) and Rb(8s) + Rb(5s) states are predicted to be zero according to Landau-Zener theory, due to their extremely small coupling with the ionic state. However, Barbier et al. did observe negative ions produced by collisions in these excited states. They proposed a different mechanism, depicted in figure 5.5, to explain how atoms colliding in these states at the threshold velocity, $v_0$, are able to create free ion-pairs.

In this mechanism, the avoided crossing with the ionic state is crossed diabatically as the nuclei approach one another. Then, at short internuclear distances where the different covalent states cross, covalent couplings allow a collisional transition to a lower energy covalent curve, denoted $n'\ell'$, one with a large coupling to the ionic curve at its $R_c$. Thus, as the separation increases, the molecule will pass through the next avoided crossing adiabatically, followed by diabatic passage through the remaining

47
avoided crossings.

Figure 5.5: The collisional transfer mechanism adapted from Barbier\cite{1} explaining how ion-pairs may be formed for levels with negligible probability of adiabatic transitions following a collision. A short range collisional transition to a lower energy state, with a higher probability of an adiabatic transition at long range, allows the system to separate along the ionic potential curve.

Note that every subsequent avoided crossing between state \(n'\ell'\) and the ion-pair threshold, i.e. up to and including the Rb(8s) + Rb(5s) state, must be traversed diabatically as the ion-pair separates. Thus, the probability of an ion-pair forming after the collisional transition at short range to level \(n'\ell'\) is:

\[
P_{n'\ell'} = (1 - P_{12}(n'\ell')) \prod_{n''\ell'' > n'\ell'} P_{12}(n''\ell''),
\]

and \(P_{12}(n''\ell'')\) values are calculated using the threshold velocity of their respective \(n''\ell''\) levels, consistent with the conservation of energy. \(P_{n'\ell'}\) values are given for the most significant levels in figure 5.6.
Figure 5.6: The $H_{12}$ couplings and probabilities $P_{\ell'\ell}$ for the collisional transfer mechanism $\text{Rb}(n\ell) + \text{Rb}(5s) \rightarrow \text{Rb}^+ + \text{Rb}^-$ of equation 5.12 in rubidium. Most ion-pairs formed from higher levels, which have very low probabilities of directly forming, will have made transitions at short ranges to the states that asymptote to the 6p or 5d atomic levels.
Note that the 6p and 5d levels possess the largest probabilities for ion-pair formations from this half-collision. Thus, most ion-pairs formed from the higher energy states will have transferred to either of these two states and the ion-pair formation cross section will be:

$$\sigma(n\ell) = P_{5d} \sigma_{n\ell \rightarrow 5d} + P_{6p} \sigma_{n\ell \rightarrow 6p},$$  

(5.13)

where $\sigma_{n\ell \rightarrow n'\ell'}$ is the cross section for a collisional transfer from the $n\ell$ state to the $n'\ell'$ state at short range.

### 5.4.2 Ion-pair formation in diatomic lithium

Now that we have been able to replicate the published results from previous calculations for Rb($n\ell$) + Rb(5s) → Rb$^+$ + Rb$^-$, we now apply this method to the lithium dimer that will be the main system of experimental investigation. The parameters that must be obtained from literature are the scattering length, $L = 8$ a.u. calculated from the low energy electron scattering cross section $Q_{Li} = 255$ a.u.$^{[64]}$, and the atomic polarizability, $\alpha_p = 165$ a.u.$^{[61]}$. The normalization constant $N_2 = 2.8$ a.u. is calculated as before using the Roothaan-Hartree-Fock atomic wavefunction.$^{[63]}$ The ionization potential of Li(2s) is 0.1981 a.u. and the electron affinity is 0.02271 a.u.. Now the crossing separations, threshold velocities, level couplings and ion-pair formation cross sections can all be calculated. They are summarized in table 5.4.

Again, we see that direct ion-pair formation requires a balance of coupling $H_{12}$; if it is too strong then every crossing is passed adiabatically, such as the 3p state, and if too weak every crossing is crossed diabatically, such as the 4p and higher states, similarly resulting in no ion-pairs. Now, the collisional transfer method is examined for
Table 5.4: Dynamical properties calculated for Li($n\ell$) + Li(2s) → Li$^+$ + Li$^-$ in this work.

<table>
<thead>
<tr>
<th>Level</th>
<th>$R_c$ (a.u.)</th>
<th>$\Delta F$ (a.u.)</th>
<th>$v_0$ (a.u.)</th>
<th>$H_{12}$ (a.u.)</th>
<th>$\sigma(v_0)$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3p</td>
<td>28.95</td>
<td>$1.19 \times 10^{-3}$</td>
<td>$3.30 \times 10^{-3}$</td>
<td>$1.93 \times 10^{-3}$</td>
<td>3.187</td>
</tr>
<tr>
<td>3d</td>
<td>30.41</td>
<td>$1.08 \times 10^{-3}$</td>
<td>$3.22 \times 10^{-3}$</td>
<td>$9.05 \times 10^{-4}$</td>
<td>569.2</td>
</tr>
<tr>
<td>4s</td>
<td>62.87</td>
<td>$2.53 \times 10^{-4}$</td>
<td>$2.24 \times 10^{-3}$</td>
<td>$7.85 \times 10^{-6}$</td>
<td>33.62</td>
</tr>
<tr>
<td>4p</td>
<td>108.06</td>
<td>$8.56 \times 10^{-5}$</td>
<td>$1.71 \times 10^{-3}$</td>
<td>$1.28 \times 10^{-9}$</td>
<td>$1.035 \times 10^{-5}$</td>
</tr>
<tr>
<td>4d</td>
<td>116.88</td>
<td>$7.32 \times 10^{-5}$</td>
<td>$1.64 \times 10^{-3}$</td>
<td>$7.96 \times 10^{-10}$</td>
<td>$5.667 \times 10^{-6}$</td>
</tr>
<tr>
<td>4f</td>
<td>117.38</td>
<td>$7.26 \times 10^{-5}$</td>
<td>$1.64 \times 10^{-3}$</td>
<td>$5.41 \times 10^{-10}$</td>
<td>$2.671 \times 10^{-6}$</td>
</tr>
<tr>
<td>5s</td>
<td>1096.24</td>
<td>$8.32 \times 10^{-7}$</td>
<td>$5.37 \times 10^{-4}$</td>
<td>$6.79 \times 10^{-97}$</td>
<td>0</td>
</tr>
</tbody>
</table>

lithium following equation 5.12. The results for levels with non-negligible probability are shown in figure 5.7, of which only the 3p and 3d states possess an appreciable probability of producing an ion-pair once populated by short-range collisional transfer. Thus, the cross section for ion-pair production by this mechanism is:

$$\sigma(n\ell) = P_{3p}\sigma_{n\ell \rightarrow 3p} + P_{5d}\sigma_{n\ell \rightarrow 5d}. \quad (5.14)$$

We now have the theoretical framework in place to make comparisons with results from our lithium beam.

Bound ion-pairs are created when the atoms in the collisions do not have sufficient kinetic energy to overcome their mutual attraction. The cross section for ion-pair formation is velocity dependent and examining this dependence will provide insight into the formation of bound ion-pairs.

Figure 5.8 shows the velocity dependent ion-pair formation cross sections for the Li(3d) + Li(2s) state at (a) low velocity and (b) high velocity as well as the Li(4s) + Li(2s) at (c) low velocity and (d) high velocity. The two states exhibit the same general behaviour. At zero velocity, the cross section is also zero due to there being no possibility of a diabatic transition through an avoided crossing which is required for ion-pair production. The location of the maximum is dictated by the coupling
Figure 5.7: The $H_{12}$ couplings and probabilities $P_{\kappa'\ell'}$ from equation 5.12 for $\text{Li}(n\ell) + \text{Li}(2s) \rightarrow \text{Li}^+ + \text{Li}^-$. The most significant levels for ion-pair formation by this method are the 3p and 3d states.

between the neutral and ion-pair state; the 3d state has stronger coupling and thus the peak occurs at a greater crossing velocity than the 4s state with its relatively weaker coupling. Recall that the crossing velocity is given by the relative velocity of the two atoms; thus we do not need to consider the absolute directions of each atom when considering whether a bound ion-pair is likely to form. For example, if the two atoms are moving in the same direction with similar absolute velocities, a bound ion-pair is more likely to form than if they were moving in opposite directions with the same absolute velocities. This would be important in an experimental rate coefficient but not for our theoretical cross section. Next, consider that the discrete bound ion-pair states are very closely spaced in energy. Thus, they can be treated as a pseudocontinuum and we need not impose reductions in the ion-pair formation cross section below the threshold velocity for each state for this reason.
Figure 5.8: The cross section for ion-pair formation for the (a) Li(3d) + Li(2s) at low velocity, (b) Li(3d) + Li(2s) at high velocity, (c) Li(4s) + Li(2s) at low velocity and (d) Li(4s) + Li(2s) at high velocity for the direct formation mechanism. The threshold velocity is to the left of the peak in the cross section for the Li(3d) + Li(2s) while the Li(4s) + Li(2s) state has the threshold velocity to the right of the cross section maximum.
Chapter 6

Experimental Progress

The two systems we have explored, Stark states in Rydberg atoms and colliding atoms, can be created using a beam of lithium atoms. A properly tuned laser incident upon the beam will excite the atoms into the desired Rydberg state. A pair of parallel plates with an applied voltage will produce the environment for investigation of the Stark states considered in Chapter 4. Alternatively, the atoms in the beam will collide on their own; this is the environment under consideration in Chapter 5.

Lasers are used as light sources for atomic and molecular experiments due to the control offered by their narrow linewidths. The selection of an appropriate type of laser is an important step in the design of an experiment. Once chosen, the laser system itself must be characterized and a control scheme developed to operate the laser during data collection. For the production of lithium Rydberg states, we require two lasers at different frequencies. A diode laser will excite the atoms to the $1s^22p^1$ state and a dye laser will perform the excitation to the higher Rydberg state.

6.1 Dye lasers

To access a large number of Rydberg states, a tunable laser with a broad range of wavelengths is required. A dye laser allows selection of the desired wavelength range
with a relatively easy change of the lasing medium, rather than requiring an entirely new laser system. A suitable choice of organic dye and solvent, along with pump laser wavelength and frequency doubling crystal, allows a single laser to produce light at wavelengths from 1 \( \mu \text{m} \) to approximately 200 nm. We will use a Nd:YAG pumped dye laser for excitation of lithium to high lying Rydberg states.

The Quanta Ray Nd:YAG pump laser produces pulses at 1064 nm which are frequency tripled to 355 nm with repetition rates of up to 10 Hz. The pulse shapes have been measured for different intensities and are displayed in figure 6.1. Neutral density filters were used in collecting this data so as not to saturate the photodiode used to measure the pulses. For this reason, the pulse amplitudes should not be quantitatively compared between measurements. This is acceptable as pulse energy needs to be measured constantly during an experiment to normalize the data collected.

![Pulse shapes and arrival times](image-url)

**Figure 6.1**: The pulse shapes and arrival times relative to the Q-switch trigger are recorded for different Q-switch delays, corresponding to increasing energy per pulse. The traces (two datasets for each Q-switch delay) have been scaled to the same height and offset by 1.25 units for clarity with the longer Q-switch delays appearing lower on the plot.
The Sirah Cobra-Stretch pulsed dye laser is a grazing incidence-type laser with two dye cells, shown in figure 6.2. It selects the wavelength of the resonator by shallow incidence upon a diffraction grating and feeds the resulting narrow bandwidth light back into the pre-amplification dye cell. Plane diffraction for light of wavelength $\lambda$ is governed by:

$$m\lambda = d(\cos(\theta_0) - \cos(\theta_m)),$$

(6.1)

where $m$ is the diffraction order, $d$ is the grating spacing and $\theta_0$ and $\theta_m$ the complements of the angles of incidence and diffraction, respectively, as shown in Figure 6.3.

![Figure 6.2: A diagram of the Sirah Cobra-Stretch dye laser](image)

The pump beam is produced by a Specta Physics Quanta Ray Nd:YAG laser. The angle of the grating controls the wavelength selection. Most of the power is generated in the 40 mm dye cell. The output is coupled into a frequency doubling crystal to allow access to shorter wavelengths.

This selects a narrow bandwidth of light to be amplified. The light produced by the resonator is then passed through the amplifier cell. A subsequent frequency doubling crystal placed at the laser output is optionally available to allow access to ultraviolet wavelengths. Tuning the laser wavelength is as simple as adjusting the
angle of the grating in the resonator, along with the angle of the frequency doubling crystal to ensure maximum power output.

6.2 Second harmonic generation

Second harmonic generation, or frequency doubling, is a non-linear optical process by which photons are combined to produce single photons with twice the energy, i.e. double the frequency, of the original photons. It is covered in numerous optics texts and a brief derivation is provided in appendix A.3.

Phase matching in the nonlinear crystal is critical to extracting appreciable power at the doubled frequency from the laser system. A small mismatch causes the output power to oscillate with crystal length. The maximum value of the output greatly decreases with increasing phase mismatch, see figure 6.4.

A physical interpretation of the causes behind this is that the radiating dipoles in the crystal are no longer exhibiting constructive superposition in the beam direction. Thus, the crystal must be rotated as the dye laser wavelength is varied in order
Figure 6.4: The maximum output power as a function of phase mismatch $\Delta s = \Delta k \ell$, where $\ell$ is a characteristic interaction length over which roughly 75% of the power would be converted into the second harmonic at perfect phase matching.

to maintain maximum power output. The software included in the Sirah Control program will use the calibration data collected to adjust the crystal angle with respect to the input beam, shown in figure 6.5.

### 6.3 Optogalvanic spectroscopy

The wavemeter we have available is only suitable for continuous wave light. Thus we need a means to determine exactly what wavelength the dye laser is producing. To this end, we employ optogalvanic spectroscopy using a hollow-cathode, neon-filled lithium optogalvanic lamp.

The optogalvanic effect is observed in gas discharge lamps wherein the atoms in the discharge have been excited by incident radiation. When the radiation is resonant with a transition of the atoms, ions or molecules present in the lamp, there is a change
Figure 6.5: Calibration data for the SHG crystal angle. The motor controlling the position of the crystal stage moves to the predetermined position in order to maximize the power output at a given input wavelength.
in the electric characteristics of the discharge. Thus, a measurable increase or decrease in the current through the lamp, due to a change in conductance of the discharge, can be observed. This is useful as a calibration of laser wavelength as little laser power is required to observe a resonance, leaving the bulk of the light available to be used for the experiments.

The atoms inside the lamp are excited by collisions with electrons or ions accelerated between electrodes. The cross-sections of these collisions are greatly dependent upon the state of the target atom or ion. Thus when the incident radiation is on resonance with a transition, the different cross-section of the excited state causes an increase or decrease in the electron-ion current between electrodes. A comprehensive review of optogalvanic spectroscopy, including the proposed mechanisms for the effect, is given by Barbieri[69].

A program was created in LabView to control the laser scan as well as collect the lithium lamp current. The laser wavelength is calibrated by comparing the position of the motor controlling the grating angle in the resonator with the discharge current. The optogalvanic spectrum we acquired was compared with the known spectrum[70], giving us an absolute wavelength measurement in figure 6.6. There are many more transitions observed in the full spectrum than expected from pure atomic lithium. This is due to the presence of neon atoms in the lamp as well as ionic forms of both gases. The abundance of transitions allows much more accurate calibration of the laser scan.

Using this method allows us to calibrate any future scans. A scan through a lithium Rydberg series in our atomic beam, for example, will be compared to the optogalvanic spectrum of our lamp in the literature and the absolute wavelength will be known.
Figure 6.6: A portion of a scan of a lithium, neon-filled, hollow-cathode optogalvanic lamp. The average pulse energy is 2.8 mJ in order to prevent power broadening. The two peaks have been fitted with Gaussian line shapes (thick lines) and their positions correspond to two known transitions, allowing a calibration of the wavelength of the dye laser.
6.4 Diode lasers

Laser diodes are to be used for the initial excitation to the $^2P$ state. Electron-hole pairs recombine when current is injected into the depletion region of the semiconductor and photons corresponding to the band gap energy are produced. If another photon passes near an electron-hole pair before they recombine (during the so-called recombination time), that photon may induce recombination and stimulated emission, resulting in gain. A general introduction to diode lasers and their use in atomic physics can be found in the review article by Wieman\cite{71}. A diffraction grating in the Littrow configuration, see figure 6.7, is used to produce an external cavity around the diode itself which narrows the bandwidth and allows tuning of the wavelength. The first diffraction order is fed back into the diode while the zeroth order is used as the output of the laser. The wavelength of the emitted photons is influenced by three adjustable parameters: the injection current, the diode temperature and the position of the external grating.

The magnitude of the current dictates the power output of the diode, once past the initial lasing threshold. Furthermore, the injection current heats the junction, affecting the band gap and hence the energy of the emitted photons. Thus, a means of temperature control is important to ensure reliability and reproducibility in the laser diode. This is accomplished with a Peltier cooler block upon which the diode is mounted. In our experience, for the wavelength ranges used, the setting of the cooler does not need to be adjusted to tune the diode to the required wavelength. The angle of the diffraction grating determines what wavelength of photons will be fed back into the diode, selecting the lasing wavelength. In our setup, this angle can be adjusted two ways. Coarse adjustment is accomplished through the means of a mechanically rotated mount. Fine adjustment is achieved by a voltage applied to a stack of piezoelectric disks. Together, these allow precision of 10 MHz over a range of a few tens of GHz.
Figure 6.7: A diode laser in the Littrow configuration\cite{72} provides optical feedback into the diode via the first order diffraction off a diffraction grating while the zeroth order reflection forms the output beam. The wavelength sent back to the diode is determined by the angle of the grating, controlled coarsely by a screw and more finely by a piezoelectric disk.
One problem with diode lasers is their inclination to mode hop and become multimode discontinuously in the adjustment of the aforementioned parameters. Thus, a map of the behaviour of a specific diode in the desired operating region is very helpful for qualitative understanding of its behaviour. The wavelength of the emitted light is measured using a wavemeter and regions of single mode operation, as determined using an optical spectrum analyzer, are mapped by adjusting both the current and piezo stack voltage. Turning their respective potentiometers controls both the current and stack voltage. The current is measured across a sensing resistor and shown on a digital display. The value of the stack voltage is taken from the position of its potentiometer dial. Note that the stability map of figure 6.8 is quantitatively valid only for a particular alignment of a specific external cavity diode laser; other diode lasers or alignments will display quantitatively different mode behaviour.

![Figure 6.8](image)

**Figure 6.8:** This map shows the simultaneous adjustments of the stack voltage and current required to maintain with single mode operation when scanning the frequency of the diode laser during the experiment. The numerical values on the plot are the approximate frequencies above 446800 GHz for that region of single mode operation.

When the injection current is set to 54 mA, the stack voltage potentiometer is
set to 95 arbitrary units and the temperature is 15.40 °C, then the frequency of the emitted light is 446810 GHz, and in the region of the $^7$Li D2 line, as seen below. This initial tuning of the diode laser required before locating the narrow transition of a transversely cooled lithium beam.

### 6.5 Saturated absorption spectroscopy

The dominant form of line broadening at high temperatures and low pressures (such as in our lithium heat pipe) is Doppler broadening. This arises from the thermal motion of the target atoms. Motion in the direction of light propagation causes a shift in the frequency seen by the atom. If the atom is moving parallel to the direction of propagation the apparent frequency is shifted down (red shifted), if moving anti-parallel, the apparent frequency is shifted up (blue shifted). Thus for a wide range of wavelengths, there is a velocity group that will be in resonance with the incident photons. Consider an atom travelling with velocity $v$ along the propagation direction of the laser and a transition energy corresponding to angular frequency $\omega = 2\pi \nu$. The apparent angular frequency of the light is given by:

$$\omega = \omega_0 \left(1 \mp \frac{v}{c}\right). \quad (6.2)$$

for non-relativistic velocities where $\omega_0$ is the transition frequency. In the heat pipe, the atoms follow a Maxwellian velocity distribution at thermal equilibrium. Thus the
number of atoms with velocity between \( v \) and \( v + dv \) is:

\[
n(v)dv = \frac{N}{v_w \sqrt{\pi}} e^{-\left(\frac{v}{v_w}\right)^2} dv.
\]  

(6.3)

where \( N \) is the total number of atoms in the heat pipe and \( v_w = \sqrt{\frac{2kT}{m}} \) is the most probable velocity. Replacing \( v \) with the corresponding \( \omega \) gives:

\[
n(\omega)d\omega = \frac{Nc}{v_w \omega_0 \sqrt{\pi}} e^{-\left(\frac{\omega - \omega_0}{v_w \omega_0}\right)^2} d\omega.
\]  

(6.4)

Combining the Maxwellian distribution with the frequency shift leads to a Doppler broadened spectral line:

\[
I(\omega) = I_0 \left(1 - e^{-\left(\frac{\omega - \omega_0}{v_w \omega_0}\right)^2}\right),
\]  

(6.5)

which has a Gaussian profile whose width is determined by the most probable velocity \( v_w \), which is in turn dependent on the temperature of the atoms being illuminated.

In the atomic beam, the atoms will be transversely cooled by collimation, thus a laser tuned somewhere within the Doppler broadened heat pipe transition may not detect atoms in the beam. Eliminating the Doppler component would produce much better resolution and allow the fine and hyperfine transitions to be individually seen and ensure the tuned laser would scatter off of atoms in the beam. This would require looking at a single velocity group and is also the purpose of saturation absorption spectroscopy, i.e. to observe features at the resolution of their much narrower Lorentzian linewidth (dictated only by collisions and the natural lifetime of the excited state).

A strong laser beam capable of saturating the gas is sent around the heat pipe and then backwards through it. A weaker beam, is sent collinearly through the pipe in the forward direction. These are the pump and probe beams respectively.
Figure 6.9: A diagram of saturated absorption spectroscopy showing the collinear, counter-propagating pump and probe beams passing through the heat pipe. The pump beam, intensity controlled using a half-wave plate, is separated from the probe beam by a beam splitter and sent around the pipe. At resonance, the weaker probe beam then has a higher transmittance due to the transition being saturated by the pump beam.

When the frequency of the laser is not exactly on resonance, the two beams interact with different velocity groups inside the heat pipe; they do not affect one another’s absorption. However, when the laser is tuned exactly on the resonance, they both interact with the zero-velocity group. This refers to zero-velocity in the direction of propagation of the beams, not only those atoms that are at rest. The strong pump beam depletes the ground state population by excitation to the upper state. Additionally, if the nucleus of the atom has non-zero spin, the upper state may decay into a different hyperfine state from where it started, leaving the atom no longer on resonance with either beam. This leaves fewer atoms that are able to interact with the probe beam and thus the absorption of the probe beam is reduced. This dip in the absorption profile is called a Lamb dip, a Doppler-free feature at the centre of the line. The Lamb dip is a Lorentzian with the linewidth of the zero-velocity group.

Additional dips in the absorption profile that are caused by the presence of two transitions are called crossover resonances. These additional features are located halfway between Doppler-free positions of two transitions. They occur when the probe beam is on resonance with one transition and the pump beam is on resonance with a different transition. If the laser is tuned halfway between two resonances, there will be a velocity group in resonance with each beam. Atoms excited by the pump beam deplete the ground state so again there will be a decrease in probe beam absorption.
Figure 6.10: A model saturated absorption spectrum showing absorption as a function of frequency. The Lamb dip occurs when both beams interact with the zero translational velocity group of atoms.

absorption, producing a dip. If the atom has nuclear spin, some crossovers will be peaks, as opposed to dips, between two hyperfine levels. This is due to the pump beam removing atoms from the hyperfine state inaccessible to the probe beam and putting them back into the ground state where they will absorb photons from the probe beam, increasing absorption and a peak will appear in the spectrum.

Lithium has two naturally occurring isotopes, both with hyperfine splitting in the ground state and with unresolved splitting (i.e. 9 MHz on the D2 line). The diode laser is tuned to the D2 line in $^7$Li, thus we expect to observe two absorption dips for the ground state splitting, separated by 803.5 MHz, and a crossover peak between them. Once loaded with lithium and evacuated to approximately $10^{-5}$ mbar, the heat pipe is insulated and heated by current passing through thermocoax wire powered by a variac set to 33 VAC. The temperature is measured using a K-type thermocouple. The spectrum present in figure 6.11 was taken when the pipe reached 324°C immediately after being pumped down. The diode laser is scanned over 1 GHz centered around the crossover peak between the two hyperfine transitions.

The saturated absorption spectrum shows that we have tuned our diode laser correctly onto the D2 transitions in $^7$Li. Thus we will be able to detect any lithium
Figure 6.11: Saturated absorption spectrum from the heat pipe showing photodiode voltage (not absorption) as a function of detuning from the crossover feature. The two peaks (Lamb dips) are separated by 803.5 MHz, the hyperfine splitting of the ground state of $^7$Li.
atoms present in the atomic beam produced by the oven in our vacuum chamber.

6.6 Lithium oven and vacuum chamber

The experimental beam apparatus consists of an oven loaded with lithium in a vacuum chamber evacuated by a diffusion pump. Windows in the chamber provide optical access for laser beams and a photomultiplier tube to detect fluorescence.

![Diagram of the lithium beam apparatus including excitation and detection equipment. Molten lithium is formed in the oven causing atoms or molecules to stream through the nozzle into the vacuum chamber where they are to be detected by fluorescence picked up by the photomultiplier tube.](image)

The diffusion pump, with a mechanical roughing pump inline with it, evacuates the vacuum chamber to approximately $10^{-5}$ mbar, measured using a Penning gauge. The oven is heated by two thermocoax wires (resistive wire insulated from a metal sheath), one around the body and the other around the nozzle. The body heater is 11.5 Ω and will accept current up to 4 A while the nozzle heater is 6 Ω and can operate at up to 2 A. This lower power nozzle heater prevents lithium from depositing on the nozzle walls and plugging the pinhole opening to the vacuum chamber. A K-type thermocouple is attached to the body of the oven to measure its temperature while
a shutter midway down the beam chamber can be open and closed to interrupt any beam as required.

The power supplies built for these two heaters proved to be unsuitable at all ranges of desired currents. The problem is that when the current is at mid ranges, approximately 1 to 3 A, the power being dissipated in the Darlington transistors inside the power supply is too large and destroys them, disabling the power supply. Instead, commercial power supplies were borrowed from neighbouring laboratories to operate our beam apparatus.

Optical access for the laser beam is provided by a pair of windows in the side of the vacuum chamber. Above the laser-lithium intersection point lies a third window over which a photomultiplier tube is placed. At this time, only the diode laser tuned to the $2S \rightarrow 2P$ transition is being sent into the beam apparatus. Detection of fluorescence photons by the PMT will indicate the presence of a beam of lithium atoms in the chamber. Despite our efforts, we have not yet confirmed that the oven is producing a lithium beam. Future work, once a beam is detected, is to insert a pair of field ionizing plates into the beam chamber to conduct the lithium Stark states experiment of the type described in chapter 4. Additionally, the oven can be operated at a higher temperature, increasing the density of atoms in the beam, and allowing the ion-pair production experiment to begin.
Chapter 7

Conclusions and future work

Significant progress has been made in developing theoretical models for the understanding of adiabatic quantum dynamics in two different atomic and molecular systems.

The extension beyond Landau-Zener and other analytical models has successfully shown that it is possible to improve upon the control of state populations throughout the traversal of an avoided crossing, as desired. Our non-analytic treatment maintains more than three times the population in the initial state than the Landau-Zener compliant solution for the same parameters. Future work will involve further exploration of other non-analytic solutions in order to determine the optimal profile for the most adiabatic traversal possible.

The Stark states of the lithium atom are well understood and provide a good, realistic example of the applications of quantum dynamics. The behaviour of the states through an avoided crossing have been determined and provide an excellent tool for intuitive understanding of adiabatic quantum mechanics. The profile of the electric field used to ionize the states can be shaped in order to have the atoms remain in their initial quantum state, which can be determined by the field magnitude at ionization. This will be tested experimentally in the lithium beam.
Ion-pair formation from neutral lithium atoms has been examined and the velocity-dependent cross sections for different initial states of one of the atoms have been calculated. Free ion-pairs, relatively simple to generate and detect compared to bound ion-pairs, will first be created in the laboratory using the lithium beam. Then bound ion-pairs, a heavy Rydberg system, will be produced for future studies.

All of the tools are in place for the operation and detection of a beam of lithium atoms. The dye laser, to be used for excitation to Rydberg states, has been characterized and a calibration approach tested and confirmed viable. The diode laser has been tuned to the lithium D1 line and regions of stable, single-mode operation mapped. The beam detection is ongoing and expected to be completed in the near future, after which the two quantum dynamics experiments will begin.
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Appendix A

Proofs and derivations

A.1 The dynamical Hamiltonian

The evolution of the diabatic states is dictated by the time-dependent Schrödinger equation:

$$H_{dia} |\phi\rangle = i\hbar \frac{\partial}{\partial t} |\phi\rangle,$$  \hspace{1cm} (A.1)

which becomes:

$$\langle \phi | H_{dia} |\phi\rangle = \langle \phi | i\hbar \frac{\partial}{\partial t} |\phi\rangle,$$ \hspace{1cm} (A.2)

The diabatic states are related to the adiabatic states by the unitary transformation of equation 3.6, written as:

$$|\xi\rangle = U |\phi\rangle.$$ \hspace{1cm} (A.3)

Substituting the adiabatic states into equation A.2 produces:

$$\langle \xi | U H_{dia} U^\dagger |\xi\rangle = \langle \xi | U i\hbar \frac{\partial}{\partial t} U^\dagger |\xi\rangle,$$ \hspace{1cm} (A.4)
and applying the chain rule on the RHS results in:

$$\langle \xi | U H_{dia} U^\dagger | \xi \rangle = \langle \xi | U i \hbar \frac{\partial U^\dagger}{\partial t} | \xi \rangle + \langle \xi | U i \hbar U^\dagger \frac{\partial | \xi \rangle}{\partial t} \rangle. \quad (A.5)$$

Now, the time-dependent Schrödinger equation for the adiabatic state is:

$$H_{ad} | \xi \rangle = i \hbar \frac{\partial}{\partial t} | \xi \rangle. \quad (A.6)$$

The RHS of this equation is present in equation A.5 and thus substituting produces:

$$\langle \xi | U H_{dia} U^\dagger | \xi \rangle = \langle \xi | U i \hbar \frac{\partial U^\dagger}{\partial t} | \xi \rangle + \langle \xi | H_{ad} | \xi \rangle. \quad (A.7)$$

Therefore, the adiabatic Hamiltonian is:

$$H_{ad} = U H_{dia} U^\dagger - i \hbar U \frac{\partial U^\dagger}{\partial t}. \quad (A.8)$$

### A.2 The adiabatic approximation

The adiabatic approximation is a condition which determines whether a system will remain in its initial state as it undergoes a variation in some parameter and is the guiding principle behind our local adiabatic approach. Beginning with a general, time-dependent Hamiltonian, the Schrödinger equation with slowly-varying potential $V(r, t)$:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(r, t)\right) | \psi \rangle = i \hbar \frac{\partial | \psi \rangle}{\partial t}, \quad (A.9)$$
has an instantaneous solution \( \Phi_n \) satisfying \( H(t')|\Phi_n(r, t')\rangle = E_n(t')|\Phi_n(r, t')\rangle \). Assuming that this state is constant since \( V(r, t) \) is slowly varying, i.e. \( \frac{\partial \Phi_n}{\partial t} \approx 0 \), the solution to equation A.9 is:

\[
|\psi_n(r, t)\rangle = |\Phi_n(r, t)\rangle e^{-\frac{i}{\hbar} \int_{t_0}^{t} E_n(t') dt'}.
\] (A.10)

Expanding the general solution in the \( \Phi_n \) basis produces:

\[
|\psi(r, t)\rangle = \sum_n a_n(t)|\Phi_n(r, t)\rangle e^{-\frac{i}{\hbar} \int_{t_0}^{t} E_n(t') dt'},
\] (A.11)

and substituting into equation A.9 gives:

\[
i\hbar \sum_n (\dot{a}_n|\Phi_n\rangle + a_n|\dot{\Phi}_n\rangle - \frac{i}{\hbar} E_n a_n|\Phi_n\rangle) e^{-\frac{i}{\hbar} \int_{t_0}^{t} E_n(t') dt'} = \sum_n a_n E_n|\Phi_n\rangle e^{-\frac{i}{\hbar} \int_{t_0}^{t} E_n(t') dt'}.
\] (A.12)

Note that the third term on the LHS cancels with the RHS, resulting in:

\[
\sum_n (\dot{a}_n|\Phi_n\rangle + a_n|\dot{\Phi}_n\rangle) e^{-\frac{i}{\hbar} \int_{t_0}^{t} E_n(t') dt'} = 0.
\] (A.13)

Now, take the inner product with \( \langle \Phi_m|e^{\frac{i}{\hbar} \int_{t_0}^{t} E_m(t') dt'} \), giving:

\[
\sum_n (\dot{a}_n\langle \Phi_m|\Phi_n\rangle + a_n\langle \dot{\Phi}_m|\Phi_n\rangle) e^{-\frac{i}{\hbar} \int_{t_0}^{t} (E_n(t') - E_m(t')) dt'} = 0,
\] (A.14)

rearranging, and applying \( \langle \Phi_m|\Phi_n\rangle = \delta_{mn} \), produces:

\[
\dot{a}_m = -\sum_n a_n\langle \Phi_m|\dot{\Phi}_n\rangle e^{-\frac{i}{\hbar} \int_{t_0}^{t} (E_n(t') - E_m(t')) dt'}.
\] (A.15)
Now, from $\frac{\partial}{\partial t}(\hat{H}|\Phi_n\rangle = E_n|\Phi_n\rangle)$ comes:

$$\frac{\partial \hat{H}}{\partial t}|\Phi_n\rangle + \hat{H}|\dot{\Phi}_n\rangle = \dot{E}_n|\Phi_n\rangle + E_n|\dot{\Phi}_n\rangle, \quad (\text{A.16})$$

and taking the inner product with $\langle \Phi_m |$ gives:

$$\langle \Phi_m | \frac{\partial \hat{H}}{\partial t}|\Phi_n\rangle + \langle \Phi_m | \hat{H}|\dot{\Phi}_n\rangle = \dot{E}_n \langle \Phi_m |\Phi_n\rangle + E_n \langle \Phi_m |\dot{\Phi}_n\rangle. \quad (\text{A.17})$$

For $n \neq m$, equation A.17 becomes:

$$\langle \Phi_m | \hat{\Phi} \rangle = \frac{\langle \Phi_m | \frac{\partial \hat{H}}{\partial t}|\Phi_n\rangle}{E_n - E_m}. \quad (\text{A.18})$$

Now, pulling out the $n = m$ term in equation A.15 and substituting in equation A.18 produces:

$$\dot{a}_m = -a_m \langle \Phi_m |\hat{\Phi} \rangle - \sum_{n \neq m} a_n \frac{\langle \Phi_m | \frac{\partial \hat{H}}{\partial t}|\Phi_n\rangle}{E_n - E_m} e^{-\frac{i}{\hbar} \int_{t_0}^{t} (E_n(t') - E_m(t')) dt'}. \quad (\text{A.19})$$

If the system starts initially in one state, i.e. $a_n(0) = \delta_{nj}$, then, recalling that $n \neq m$ and hence $j \neq m$:

$$\dot{a}_m = -\frac{\langle \Phi_m | \frac{\partial \hat{H}}{\partial t}|\Phi_j \rangle}{E_j - E_m} e^{-\frac{i}{\hbar} \int_{t_0}^{t} (E_j(t') - E_m(t')) dt'}. \quad (\text{A.20})$$
Assuming that $E_j(t)$ and $E_m(t)$ are slowly varying functions of time, equation A.20 integrates to become:

$$a_m \approx -\frac{i}{\hbar(E_j - E_m)^2} \left[ e^{-\frac{i}{\hbar}(E_j-E_m)t} - e^{-\frac{i}{\hbar}(E_j-E_m)t_0} \right]. \quad (A.21)$$

The system evolves adiabatically when $|a_m|^2 \ll 1$ or:

$$|\langle \Phi_m | \frac{\partial \hat{H}}{\partial t} | \Phi_j \rangle| \ll (E_j - E_m)^2, \quad (A.22)$$

which is known as the adiabatic approximation and may also be written as:

$$\frac{|\langle \Phi_m | \frac{\partial \hat{H}}{\partial t} | \Phi_j \rangle|}{(E_j - E_m)} \ll (E_j - E_m). \quad (A.23)$$

This adiabatic condition is *globally* satisfied when:

$$\max \frac{|\langle \Phi_m | \frac{\partial \hat{H}}{\partial t} | \Phi_j \rangle|}{(E_j - E_m)} \ll \min |(E_j - E_m)|. \quad (A.24)$$

### A.3 Second harmonic generation

Second harmonic generation is nonlinear optical technique where the frequency of photons are doubled as they pass through a crystal with nonlinear polarizability. The derivation of the coupled amplitude equations describing this process begins with
Maxwell's equations in matter:

\[ \nabla \cdot D = \rho_f \]
\[ \nabla \times E = -\frac{\partial B}{\partial t} \quad (A.25) \]
\[ \nabla \cdot B = 0 \]
\[ \nabla \times H = J_f + \frac{\partial D}{\partial t}, \]

in a region with no free charge or free current \((\rho_f = 0 \text{ and } \vec{J}_f = 0)\) and nonlinear electric field response \((D = \epsilon_0 E + P, \text{ where } P \text{ depends nonlinearly on } E)\) can be combined to produce the wave equation:

\[ \nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2}. \quad (A.26) \]

If the polarization is split into linear and nonlinear part, the wave equation becomes:

\[ \nabla^2 E - \frac{1}{c^2} \frac{\partial^2 D^{(1)}}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 P^{(NL)}}{\partial t^2}. \quad (A.27) \]

For a dispersive medium, each frequency component needs to be considered separately. The field is represented by a sum of its frequency components:

\[ E(r, t) = \sum_n E_n(r, t), \quad (A.28) \]

where the field frequency components are represented by:

\[ E(r, t) = E(r)e^{-i\omega t} + c.c.. \quad (A.29) \]
The displacement field and nonlinear polarizability are represented in the same way. With dissipation neglected, the electric field and displacement field can be related using a real, frequency dependent dielectric tensor:

\[
\mathbf{D}^{(1)}_n(\mathbf{r}, t) = \epsilon_0 \epsilon^{(1)}(\omega_n) \cdot \mathbf{E}(\mathbf{r}, t). \tag{A.30}
\]

This produces a wave equation analogous to A.27 valid for all frequency components:

\[
\nabla^2 \mathbf{E}_n - \frac{\epsilon^{(1)}(\omega_n)}{c^2} \frac{\partial^2 \mathbf{E}^{(1)}_n}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 P^{(NL)}_n}{\partial t^2}. \tag{A.31}
\]

Now, with the field components represented by:

\[
\mathbf{E}_j(z, t) = A_j(z) e^{ik_j z} e^{-i\omega_j t} + c.c., \tag{A.32}
\]

where \( A_j(z) \) is a slowly varying amplitude, \( k_j = n_j \omega_j / c \) is the propagation constant and \( n_j = \sqrt{\epsilon^{(1)}(\omega_j)} \) is the refractive index. The nonlinear polarization is:

\[
P^{NL}(z, t) = P_1(z, t) + P_2(z, t), \tag{A.33}
\]

with

\[
P_j(z, t) = P_j(z) e^{-i\omega_j t}. \tag{A.34}
\]

The polarization amplitudes are:

\[
P_1(z) = 4\epsilon_0 d_{eff} E_2 E_1^* = 4\epsilon_0 d_{eff} a_2 a_1^* e^{i(k_2-k_1)z}, \tag{A.35}
\]
and
\[
P_2(z) = 2\varepsilon_0 d_{\text{eff}} E_1^2 = 2\varepsilon_0 d_{\text{eff}} A_1^2 e^{2ik_1z}. \tag{A.36}
\]

Substituting equations A.32, A.33, A.35 and A.36 into the driven wave equation A.31 for each field component, considering only the \( \hat{z} \) direction, on which the fields depend, produces:

\[
\left( \frac{d^2 A_1}{dz^2} + 2ik_1 \frac{dA_1}{dz} - k_1^2 A_1 + \frac{\varepsilon^{(1)}(\omega_1)\omega_1^2 A_1}{c^2} \right) e^{i(k_1 z - \omega_1 t)} + \text{c.c.} = \frac{-4d_{\text{eff}}\omega_1^2}{c^2} A_2 A_1^* e^{i(k_2-k_1)z-\omega_1 t} + \text{c.c.}, \tag{A.37}
\]

for the input frequency. Dropping the complex conjugate terms and simplifying results in:

\[
\frac{d^2 A_1}{dz^2} + 2ik_1 \frac{dA_1}{dz} = \frac{-4d_{\text{eff}}\omega_1^2}{c^2} A_2 A_1^* e^{i(k_2-2k_1)z}. \tag{A.38}
\]

The first term can be neglected by invoking the slowly varying amplitude approximation, valid when the change in the amplitude over the distance of a wavelength is very small. This gives the amplitude equation:

\[
\frac{dA_1}{dz} = \frac{2i\omega_1 d_{\text{eff}}}{k_1 c^2} A_2 A_1^* e^{-\Delta kz}, \tag{A.39}
\]

for the input frequency, where quantity \( \Delta k = 2k_1 - k_2 \) is the wavevector or momentum mismatch. The amplitude equation for the doubled frequency can be derived analogously and is:

\[
\frac{dA_2}{dz} = \frac{i\omega_2 d_{\text{eff}}}{k_2 c^2} A_1^2 e^{\Delta kz}. \tag{A.40}
\]
The general solution of this pair of coupled equations is easier in dimensionless form and separating the modulus and phase of the complex field amplitudes. The slowly varying field amplitudes are written:

\[ A_1 = \left( \frac{I}{2n_1 \varepsilon_0 c} \right)^{1/2} u_1 e^{i\phi_1}, \quad (A.41) \]

and

\[ A_2 = \left( \frac{I}{2n_2 \varepsilon_0 c} \right)^{1/2} u_2 e^{i\phi_2}, \quad (A.42) \]

where \( I = I_1 + I_2 \) is the total intensity and \( I_j = 2n_j \varepsilon_0 c |A_j|^2 \). Next, the normalized distance parameter \( \xi = z/l \), where:

\[ l = \left( \frac{2n_1^2 n_2}{\varepsilon_0 c I} \right)^{1/2} \frac{c}{2\omega_1 d_{\text{eff}}}, \quad (A.43) \]

is the characteristic distance over which energy is exchanged between fields. The relative phase of the interacting fields is:

\[ \theta = 2\phi_1 - \phi_2 + k\Delta z. \quad (A.44) \]
The coupled amplitude equations A.41 and A.42, with these quantities, become a new set of coupled equations in \( u_1, u_2 \) and \( \theta \):

\[
\frac{du_1}{d\xi} = u_1 u_2 \sin \theta \quad \text{(A.45)}
\]

\[
\frac{du_2}{d\xi} = -u_2^2 \sin \theta \quad \text{(A.46)}
\]

\[
\frac{d\theta}{d\xi} = \Delta k l + \frac{\cos \theta}{\sin \theta} \frac{d}{d\xi} \ln(u_1^2 u_2), \quad \text{(A.47)}
\]

the solution of which gives the amplitudes of the initial frequency and doubled frequency beams as well as the relative phase between them. The amplitude of the doubled frequency beam is dependent on a number of conditions, such as phase matching and length of the nonlinear crystal, which must be optimized for maximum power output in that beam.