Carrier Dynamics in Nanocrystalline Lead Salts and Non-Adiabatic Dynamics in Near-Degenerate States of Molecules

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CARRIER DYNAMICS IN NANOCRYSTALLINE LEAD SALTS AND NON-ADIABATIC DYNAMICS IN NEAR-DEGENERATE STATES OF MOLECULES

by

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A thesis submitted to the
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This thesis entitled:
Carrier Dynamics in Nanocrystalline Lead Salts and Non-Adiabatic Dynamics in Near-Degenerate States of Molecules
written by William Kenneth Peters
has been approved for the Department of Chemistry and Biochemistry

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G. Barney Ellison

Date_____________________

The final copy of this thesis has been examined by the signatories, and we
Find that both the content and the form meet acceptable presentation standards
Of scholarly work in the above mentioned discipline.
Degenerate femtosecond pump-probe transient absorption measurements are presented of hot carrier dynamics following above band-edge absorption in colloidal lead sulfide quantum dots. A transient bleach is only found when pumping to a satellite valley. When pumping in the main valley no transient bleach is seen with 20-25 fs pulses, indicating hot carrier dephasing occurs in 5 fs or less. The signal at long times is \(~300\) times smaller than would be expected from a two level system, indicating systematic excited state absorption. Based on this data, arguments based on bulk band structure and scattering length indicate hot electrons are essentially bulk-like until cooling to quantum confined states.

Femtosecond electronic dynamics are also studied theoretically for model Hamiltonians developed to model near-degenerate states in molecules or molecular dimers. Particular emphasis is placed on the case of weak nonadiabatic coupling when the electronic energy gap is close to one vibrational quantum of energy. A visualization scheme is developed for plotting nonadiabatic wavefunctions with an explicitly shown vibrational wavefunction and coordinate-dependent coloring which indicates both electronic composition and overall wavefunction sign. Nonadiabatic eigenstates are found to display a vibrationally nodeless character, indicating large-amplitude oscillations between zero-order electronic basis states.
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CHAPTER 1
INTRODUCTION

1.1 Femtosecond Electronic-Vibrational Dynamics

In this dissertation we will examine femtosecond electronic and electronic-vibrational dynamics in a variety of systems and will often consider the question of which basis states allow us to most easily understand the system. Pump-probe transient absorption experiments are described which monitor excited electrons in colloidal lead sulfide nanocrystals, in which the exchange of energy between electronic and vibrational degrees of freedom is typically described as “phonon emission” or “carrier cooling.” Polarized transient absorption experiments sensitive to electronic equilibration on the degenerate or near-degenerate lowest excited states of naphthalocyanine dyes are discussed, and simplified versions of the models used to describe\textsuperscript{1,2} these experiments are analyzed to gain insight into the mechanism by which electronic relaxation occurs. A similar model, recently used\textsuperscript{3} to reproduce key experimental signatures\textsuperscript{4} in photosynthetic complexes, is analyzed for signatures of nonadiabatic coupling in the energy transfer process.

Since the full Hamiltonian for molecular problems has no exact analytical solution, zero-order approximate solutions are used as an expansion basis in which numerically exact results can in principle be obtained.\textsuperscript{5,6} For practical purposes, a “good”
basis choice is one which allows accurate results to be easily obtained. This may mean that exact states are linear combinations of only a small number of basis states, that low-order perturbation expansions rapidly converge, or that integrals over the basis functions can be accomplished analytically. From a matrix methods point of view, a “good” basis choice gives a lot of off-diagonal zero elements and allows nonzero elements to be filled in by some rule rather than numerical integration. However, the choice for which zero-order approximation to use as a basis is more than simply a matter of practical convenience. Our approximate solutions often influence our thinking, and lead to certain intuitions about how a system behaves.

1.2 Electronic Dynamics in PbS Nanocrystals

Colloidal semiconductor nanocrystals, or quantum dots, have emerged as exciting new materials and are particularly promising for solar energy applications. These are nanometer-scale semiconductor crystals whose small size allows tuning of their optical properties. In current photovoltaic devices, every absorbed photon, regardless of its intrinsic energy, produces the same amount of electrical power. If a quantum dot device was able to somehow harvest the wavelength-dependent excess energy of an absorbed photon, it would change the fundamental thermodynamic limit of solar cell efficiency from 31% to 44%, or even higher with solar concentration.

After absorbing a photon with energy more than twice the bandgap, there is some chance that the highly excited electron can cool to a lower unoccupied orbital by transferring energy to a second electron, leaving the nanocrystal in a state with two excited electrons (figure 1.1). In quantum dots this process is called multiple exciton
Figure (1.1) Illustration of multiple exciton generation (MEG). A generic quantum dot is pictorially represented by two sets of discrete energy levels: a set of occupied molecular orbitals which arises from confinement of the valence band and a set of unoccupied molecular orbitals which arises from confinement of the conduction band. The HOMO-LUMO gap can also be referred to as the band gap; while the HOMO and LUMO can be referred to as valence and conduction band edges, respectively. Either an electron in a usually-empty orbital or a vacancy in a usually-filled orbital can be referred to as a carrier. In the first step a photon with energy more than twice the band gap promotes an electron from (potentially) well below the HOMO to (potentially) well above the LUMO. In the second step either the “hot” electron cools to the conduction band edge by exciting a second electron across the band gap, or the low-lying vacancy is filled by one valence band electron “dropping” into the vacancy and using its excess energy to excite another valence band electron across the band gap.
generation (MEG), and is related to Auger processes (e.g. Auger ionization) in both molecules and bulk semiconductors.\textsuperscript{12} There is experimental evidence from transient absorption\textsuperscript{11}, electron transfer\textsuperscript{13} and photocurrent\textsuperscript{14} measurements that lead chalcogenide quantum dots may be able to undergo MEG after absorbing visible light, potentially allowing them to harvest some of the energy lost by current solar cells.

Semiconductor electronic structure is generally described by a fully delocalized band theory.\textsuperscript{15,16} In this approach the electronic stationary states are written as linear combinations of atomic or molecular orbitals, with expansion coefficients given by discretizing some envelope function. For bulk systems, the periodicity of the lattice requires the wavefunctions to have translational symmetry, in the sense that translating the wavefunction by any lattice vector can change it by no more than a phase factor. This is accomplished by choosing the envelope function for expansion coefficients to be a plane wave: $\Gamma_{k,c}(r) = \sum_n \exp(\mathbf{k} \cdot \mathbf{r}_n) \gamma_c(\mathbf{r} - \mathbf{r}_n)$ where $\Gamma_{k,c}(r)$ is an eigenfunction of the one-electron Hamiltonian, $\gamma_c(\mathbf{r})$ is the $c^{th}$ atomic or molecular orbital, $\mathbf{r}_n$ is a lattice position and $\mathbf{k}$ is the wavevector for the envelope function, which acts a quantum number. We will refer to this wavefunction, which consists of a discretized plane wave multiplied by a set of molecular wavefunctions, as a Bloch wave.

This procedure is illustrated in figure (1.2). For purposes of constructing the figure, an 8-atom segment of a 1D chain of atoms was treated with simple Hückel theory\textsuperscript{17}, which gives a purely real envelope function $\cos(\mathbf{k} \cdot \mathbf{r}_n)$. Panel (a) shows a few selected molecular orbitals constructed from atomic $s$ orbitals; from the bottom of the panel to the top the number of nodes between atoms increases. The first trace has no
Figure (1.2) Illustration of band theory electronic wavefunctions for a 1D system. Panel (a) shows a cartoon of selection of molecular orbitals constructed from s-orbitals for an 8-atom chain. Panel (b) shows a cartoon of selected molecular orbitals constructed from on-axis p-orbitals for an 8-atom chain. Panel (c) illustrates the discretization of an infinite wave which is used to describe expansion coefficients in an LCAO Bloch wave. Panel (d) illustrates energy of a Bloch wave as a function of its wave vector. The energy of s-based wavefunctions increases as the wave vector gets larger (wavelength gets shorter), as more anti-bonding interactions get included. The energy of p-based wavefunctions decreases the wave vector gets larger, as fewer anti-bonding interactions get included. The curve for the p orbitals has been offset high, to indicate that p orbitals are higher in energy than s orbitals for many electron atoms. The total energy spread across all wave vectors has been drawn larger for p orbitals than for s orbitals to indicate that on-axis p orbitals should have larger orbital overlap with nearest neighbors than s orbitals.
nodes, the second has one node, the third and fourth pictured orbitals (which are the 5th and 8th of the full set) have 4 and 7 nodes, respectively. Using the lowest orbital as a starting point, every time a node is added the number of bonding orbitals decreases by one and the number of antibonding interactions increases by one (unless a node happens to pass through an atomic center). Panel (b) shows the same calculation, but with on-axis p-orbitals instead. The same expansion coefficients are used, since \( \cos(\vec{k} \cdot \vec{r}_n) \) is evaluated at the lattice point. Now however, the fully in-phase combination is composed entirely of antibonding interactions, due to the radial node of the p-orbital. The same four sets of expansion coefficients are shown as in panel (a); here every time a node is added it lowers the energy of the orbital.

Panel (c) shows the expansion coefficients. The envelope functions \( \cos(\vec{k} \cdot \vec{r}) \) for the same molecular orbitals as used in panels (a) and (b) are shown as red lines. The vertical black lines indicate the positions at which the envelope functions are evaluated \( \{\vec{r}_n\} \) in order to find expansion coefficients. In panel (d) we show a plot of wavefunction energy against the wave vector of the envelope function; here the chain has been extended from 8 atoms to \( N=1000 \). As the length of the chain increases, the energy levels form a quasi-continuum. At the simple Hückel level, the \( j \)th energy level is

\[
\alpha + 2\beta \cos \left( j\pi \frac{1}{N+1} \right),
\]

where \( \beta \) is negative if nearest-neighbor interactions are in phase and positive otherwise. The qualitative conclusions from simple Hückel theory and 1D chains carry over to bulk systems.

Electronic dynamics are treated by creating superpositions of Bloch waves; these superpositions produce a localized wavepacket. These wavepackets will travel through
the lattice without scattering so long as the nuclei remain in their assigned positions with respect to the lattice vectors \( \{ \vec{r}_n \} \). Imperfections in the lattice, or even vibrational motions, can cause electronic wavepackets to scatter through vibronic mixing; this acts as the mechanism through which energy transfers between the electronic and vibrational degrees of freedom.\(^{18}\)

To avoid dealing with N electrons, it is imagined that the ground state of the system is a vacuum state,\(^6,^{16}\) and that excited states correspond to creating an electron and a hole, rather than promoting an electron from a filled orbital to an empty orbital. The average influence of all undescribed electrons as well as the lattice is treated by defining “effective masses” for the electron and hole. The one-electron wavefunctions \( \Gamma_{k,e}(r) \), or products of only a few of them, are then used to represent the full system. The hole is positively charged and exerts a Coulombic attraction on the electron; the two carriers may bind each other into a hydrogen-like system known as a Wannier exciton.\(^{18}\) This exciton will have some characteristic size, defined analogously to the Bohr radius in hydrogen atom, but corrected for effective masses and the dielectric constant of the semiconductor.

Colloidal semiconductor quantum dots are nanometer-scale crystals; the nanometer length scale is large compared to lattice constants but smaller than the bulk Bohr exciton radius.\(^8,^{19}\) In this situation the electron (and potentially the hole) is delocalized with respect to its parent atom but confined by the crystal to a space smaller than the characteristic size of the exciton. It is natural to think about the electron (and hole) as something like a particle in a box, although the box has a semiconductor lattice
in it. Using a spherical crystal as an approximation, the Bloch plane wave envelopes are replaced with spherical harmonics.

One may wonder, however, if replacing the plane waves with spherical waves is justified. For example, the ionization potentials of bulk PbS and PbSe are about 5 eV.\textsuperscript{14} Under quantum confinement the optical absorption band edge shifts from about 0.3 eV to about 0.7 eV;\textsuperscript{19} if we split the energy between electron and hole, there is about 0.2 eV per carrier as a confinement effect. We have to conclude that the confinement is a perturbation on a semiconductor system, not that the lattice modifies the results of a particle in a box. If that is so, it may be that there’s still something to be learned from studying quantum dots within a plane wave basis.

### 1.3 Weak Pseudo-Jahn-Teller Interactions

When dealing with the structure of molecules, it is usual to adopt an adiabatic approach.\textsuperscript{20} First the molecular wavefunction is separated as the product of a purely vibrational wavefunction and an electronic wavefunction which depends on vibrational coordinates parametrically, then the nuclear kinetic energy operator is assumed not to operate on the electronic wavefunction. If we take $|k\rangle$ to be an electronic wavefunction, $|v\rangle$ to be a vibrational wavefunction and separate the dimensionless vibrational momentum operator $\omega \hat{p}^2 / 2$ from the full Hamiltonian, using the procedure given,
Here we let $\omega_{kg}$ be the energy of the $k^{th}$ electronic state at the equilibrium nuclear position, $\omega$ is the vibrational frequency and $\hat{H}_e |k\rangle = (\omega_{kg} + U_k) |k\rangle$ is the electronic Schrödinger equation which produces the potential energy curve $U_k$. This allows the Hamiltonian to be separated into an electronic Hamiltonian and a vibrational Hamiltonian that depends on the results of the electronic problem. The $\approx$ sign on the third line is the key approximation: $|k\rangle$ was moved to the left of the derivative operator $\frac{\omega}{2} \hat{p}^2$.

Even for a zero-order approximation, the details of how one handles the electronic Hamiltonian are critical. In an adiabatic molecular calculation, the molecular orbitals are calculated over again for each atomic configuration; this gives electronic wavefunctions which are parametrically dependent on atomic coordinates. In contrast, a “crude adiabatic” calculation is done once at a favorite set of atomic positions, often the equilibrium structure of the ground electronic state of a molecule.\textsuperscript{21,22} The solid state band structure described in the previous section is an example of the crude adiabatic approach.

Nonadiabatic effects can be considered by allowing nonadiabatic coupling between either diabatic or adiabatic states.\textsuperscript{23} In Figure (1.3) we show two different sets
Figure (1.3) Potential energy curves. Panel (a) shows diabatic curves and adiabatic curves for Hamiltonian (1.1) with parameters $\omega = 176 \text{cm}^{-1}$, $\delta = 150 \text{cm}^{-1}$ and $d = 0.75$. Panel (b) shows site curves and adiabatic curves for Hamiltonian (1.2) with $J = 66.14 \text{cm}^{-1}$ and other parameters the same as panel (a).
of potential curves, generated from different basis functions, for each of two generic Hamiltonians. In panel (a) we show diabatic and adiabatic curves for a 2-state linear pseudo-Jahn-Teller\textsuperscript{24} Hamiltonian:

\[
\begin{pmatrix}
-\frac{\delta}{2} + \frac{\omega}{2} (\hat{p}^2 + \hat{q}^2) & \omega \hat{d} \hat{q} \\
\omega \hat{d} \hat{q} & \frac{\delta}{2} + \frac{\omega}{2} (\hat{p}^2 + \hat{q}^2)
\end{pmatrix}
\] (1.1)

where \(\delta\) is the vertical energy difference between two electronic states, \(\hat{q}\) is the dimensionless coordinate operator, \(d\) parameterizes the strength of the coupling, and other symbols are as above. Purple and orange dashed lines show the potential curves of the diabatic basis (diagonal elements in Hamiltonian (1.1), if \(\hat{p}\) is neglected). Solid lines show adiabatic potential curves; the \(q\)-dependence of the wave function is indicated by color, which maps the two-state mixing angle\textsuperscript{25} for the adiabatic electronic Hamiltonian onto a color wheel shown at the bottom of panel (b). It is the derivative of this \(q\)-dependence which is neglected when making the adiabatic approximation. The plot is generated with \(\omega = 176 \text{cm}^{-1}, \delta = 150 \text{cm}^{-1}\) and \(d = 0.75\). The coupling parameter \(d\) in figure (1.2) is much larger than that used in subsequent chapters, in order to make the nonadiabatic effects more apparent.

Panel (b) shows site and adiabatic curves for a Coulombically coupled dimer model. The Hamiltonian used is

\[
\begin{pmatrix}
\frac{\omega}{2} (\hat{p}^2 + \hat{q}^2) + \omega \hat{d} \hat{q} - \frac{\delta}{2} & J \\
J & \frac{\omega}{2} (\hat{p}^2 + \hat{q}^2) - \omega \hat{d} \hat{q} + \frac{\delta}{2}
\end{pmatrix}
\] (1.2)
where $J = 66.14 \text{cm}^{-1}$ couples the two monomers and other parameters have the same values as for Hamiltonian (1.1). Again, the coupling parameter $d$ in figure (1.2) is much larger than that used in subsequent chapters, in order to make the nonadiabatic effects more apparent. In both panels the adiabatic curves show color variations strongest in regions where the basis functions are closest; in panel (b) the adiabatic curves display an avoided crossing.

The adiabatic and related approximations are known to fail when two electronic states are degenerate, or are separated by much less than a vibrational quantum.\textsuperscript{21,26} We will study the above two cases in which two electronic states are separated by about one vibrational quantum in a coordinate of appropriate symmetry to couple the electronic states.

### 1.4 Organization of this thesis

In chapter 2 we describe femtosecond pump-probe transient absorption measurements on lead sulfide semiconductor nanocrystals, with 20-25 fs pulses tuned through the visible. We argue that the initial dynamics of hot carriers are best thought of as bulk-like, and present arguments based on Bloch plane wave electronic states.\textsuperscript{27} These arguments are based on the hypothesis that a carrier may inelastically scatter before reaching the edge of the nanocrystal; if so it is the local lattice (which is translationally invariant as far as the carrier knows) which determines the electronic properties rather than the confinement. Alternatively a carrier may elastically reflect off the edge of the crystal, so the reflected wave interferes with the incident wave; for valid stationary states this produces standing waves adapted to the entire crystal and we must speak of quantum
size effects. After the carriers cool to the band edge they occupy states which should be considered from a quantum confinement point of view.

In Chapter 3 we discuss prior femtosecond pump-probe polarization anisotropy experiments\textsuperscript{1,2,28} and develop arguments based on Redfield theory\textsuperscript{29} that the measured anisotropy provides experimental signatures for the dynamics occurring at conical intersections. In the case that the femtosecond laser spectrum covers the vibrational envelope of the electronic absorption and emission spectra of a degenerate or near-degenerate state, femtosecond polarization anisotropy measures electronic relaxation processes of dephasing between the excited states and population transfer between them. Conical intersections can be characterized by two special vibrational coordinates: the $g$ coordinate which “tunes” the energy gap and the $h$ coordinate which controls the coupling between two electronic states.\textsuperscript{30} We argue that dephasing between excited states is the signature of dynamical processes driven by the tuning ($g$) coordinate and population transfer is the signature of the coupling ($h$) coordinate. Although the measurement cannot distinguish the two (they are interchanged by a basis transformation), we argue that it can measure the extent to which the electronic relaxation occurs, and whether or not both processes are present.

In chapter 4 we study a two-state pseudo-Jahn-Teller Hamiltonian\textsuperscript{24} which we have used to model femtosecond pump-probe polarization anisotropy experiments in a free-base naphthalocyanine.\textsuperscript{2,31} Exact nonadiabatic wavefunctions and dynamics are considered using both diabatic and adiabatic basis states; we find that the adiabatic approximation fails qualitatively within 50 fs and quantitatively immediately, indicating that the initial forces on an excited state wavepacket are poorly represented by the
adiabatic approximation. Although the stationary states are easiest to understand as nonadiabatic coupling from the adiabatic point of view, the dynamics are easier to follow by considering coordinate-dependent coupling from a diabatic basis. That the diabatic basis is useful for dynamics stems from the initial conditions produced by femtosecond laser pulses.

In chapter 5 we turn our attention to a coupled dimer system in which each pigment has a Franck-Condon active vibration and the pigment’s electronic states are separated by about one vibrational quantum. Pigment-to-pigment energy transfer requires understanding the system from a site basis, but much can be gained from transforming the Hamiltonian to an excitonic basis; after the transformation the system can be considered as a two-state pseudo-Jahn-Teller problem, with the excitonic wavefunctions acting as a diabatic basis. Although the excitonic basis and the adiabatic basis agree very nearly on energy levels and wavefunctions, the exact nonadiabatic states are strongly perturbed. We analyze the nonadiabatic dynamics from an energy transfer point of view and find that, when the electronic energy difference between pigments is close to one vibrational quantum of energy, the nonadiabatic coupling cannot be ignored even when the coupling is weak; indeed, as long as the coupling term remains weak, nonadiabatic effects allow an ultrafast transfer of energy to the lower electronic state.

1.5 Notation Conventions Used in this Thesis

The theory developed when handling nonadiabatic wavefunctions and wavepackets compels us to use several variations of usual quantum chemical notations.
We hope a brief description of our conventions will avoid letting mathematical notations cast too dense a fog on the material presented.

For electronic-vibrational wavefunctions we use the Greek letter psi. \( |\psi_n\rangle \) is a product, or linear combination of products, of electronic and vibrational states. \( |\Psi(T)\rangle \) is used for a time-dependent vibronic wavefunctions.

We use \( k \) as electronic state labels, which come in pairs as we restrict our attention to 2-state systems. We will not need explicit functions of electronic coordinates, but we will need the vibrational coordinate dependence of electronic wavefunctions. We use the Greek letter theta for this function.

\( |k\rangle \) is an electronic state; examples are \( \{|x\rangle,|y\rangle,\{|\alpha\rangle,|\beta\rangle\},\{|-\rangle,|+\rangle\}\}. \)

\( \theta^a(q) \) gives the \( q \)-dependent mixing angle of adiabatic electronic wavefunctions.

\( \theta^d(q) \) gives the mixing angle used to transform from some initial basis to a diabatic basis.

\( \Theta_n(q) \) gives the \( q \)-dependence of the \( n^{th} \) nonadiabatic electronic wavefunction.

\( \Theta(q,T) \) gives \( q \)-dependence of electronic component of a nonadiabatic vibronic wavepacket.

\( |K_n\rangle \) is the electronic component of the \( n^{th} \) nonadiabatic wavefunction.

We use \( v \) as a vibrational quantum number and the Greek letter phi for vibrational wavefunctions. In one situation where a vibrational wavefunction is invalid due to a discontinuity, but useful nonetheless, we use the Icelandic rune thorn, which resembles the right half of phi in appearance.

\( |v\rangle \) is an adiabatic vibrational eigenstate of the ground electronic state.
\[ \langle q|\nu \rangle = \phi_v(q) \] is the corresponding vibrational wavefunction.

\[ |\nu^k \rangle \] is an adiabatic vibrational eigenstate of the electronic state \(|k\rangle\).

\[ \Phi_{n,k}(q) \] is the \(q\)-dependence of the projection of the \(n\)th nonadiabatic eigenstate \(|\psi_n\rangle\) onto the \(k\)th electronic state: \[ \Phi_{n,k}(q) = \langle q|\langle k|\psi_n\rangle \rangle \, . \]

\[ \Phi_k(q, T) \] is the \(q\)-dependence of the projection of a nonadiabatic vibronic wavepacket onto the \(k\)th electronic state.

\[ \langle q|\mathbf{p}_n \rangle = \mathbf{p}_n(q) = \sqrt{(\Phi_{n,k}(q))^2 + (\Phi_{n,k}^*(q))^2} \] is the vibrational wavefunction of the \(n\)th nonadiabatic eigenstate.

\[ \langle q|\mathbf{p}(T) \rangle = \mathbf{p}_n(q, T) = \sqrt{[\Phi_{x}(q, T)]^2 + [\Phi_{y}(q, T)]^2} \] is the vibrational component of a nonadiabatic vibronic wavepacket.

Superscripts indicate approximations: e.g. \(E^a_{kv}\) is the energy of the adiabatic product state \(|\psi^a_{kv}\rangle = |k\rangle|\nu\rangle\) while \(E_n\) is the energy of the exact nonadiabatic wavefunction \(|\psi_n\rangle\).

When the Hamiltonian is written as a matrix, it is indicated by boldface. A tilde or bar above the matrix indicates that adiabatic or excitonic basis functions were used in evaluating matrix elements. For example \(\hat{H}\) indicates a diabatic basis, meaning matrix elements \(H_{ij} = \langle i|\hat{H}|j\rangle\) were evaluated with \(i, j \in \{|x\rangle, |y\rangle\}\); \(\tilde{\hat{H}}\) indicates an adiabatic basis, meaning matrix elements \(\tilde{H}_{ij}\) were evaluated with \(i, j \in \{ |-\rangle, |+\rangle\}\); \(\hat{\hat{H}}\) indicates an excitonic basis, used in chapter 5.
1.5 References


CHAPTER 2
BULKLIKE HOT CARRIER DYNAMICS IN LEAD SULFIDE QUANTUM DOTS

2.0 Abstract

Hot electronic dynamics in lead sulfide nanocrystals is interrogated by transient absorption spectroscopy, using identical 20-25 fs pump and probe pulses (degenerate pump-probe spectroscopy), over a broad frequency range around three times the short-wave infrared nanocrystal band gap. For each nanocrystal diameter, an initial reduction in absorption is seen only at the peak of the quantum confined E1 transition, while increased absorption is seen at all other wavelengths. The signals from the nanocrystals are about 300 times weaker than expected for a two-level system with the same absorbance and molar extinction coefficient and are weaker near time zero. These results appear to be inconsistent with quantum confinement of the initially excited high energy states. Arguments based on carrier scattering length, the wave packet size supported by the band structure, and effective mass are advanced to support the hypothesis that, for many direct-gap semiconductor quantum dots, the carrier dynamics at three times the band gap is localized on the 1–2 nm length scale and essentially bulklike except for frequent collisions with the surface.
2.1 Introduction

The nature and behavior of high energy electronic excitations in semiconductor nanocrystals are important for understanding carrier multiplication, which has possible applications in high efficiency solar cells,1 photodetectors,2 photocatalysts, and optical amplifiers.3 Direct photoexcitation,4 coherent multiple exciton generation,5 and incoherent impact ionization6 have been proposed to explain the reported production of multiple electron–hole pairs from a single photon in nanocrystals.7,8 In bulk semiconductors, a Rydberg series of bound electron–hole pair states (Wannier excitons) starts below the band gap.9 These states have energies and eigenfunctions like a one electron atom with a Bohr exciton radius $a_0 = \frac{4\pi e \hbar^2}{\mu e^2}$, where $\varepsilon$ is the bulk dielectric constant, $\mu$ is the reduced mass calculated from the effective masses of the electron and hole, and $e$ is the electron charge. Above the band gap, electrons and holes are excited to states analogous to the atomic ionization continuum and separate as free carriers. High-energy photons can excite nonequilibrium carriers with group velocities exceeding the saturation velocity (about $10^5$ m/s in bulk semiconductors10). Near the saturation velocity, the rate of energy loss greatly exceeds the Ohm’s law scattering rate (which is usually dominated by acoustic phonons).11

Following the treatment by Éfros and Éfros,12 semiconductor nanocrystals with bulk crystalline lattices but diameters smaller than the Bohr exciton radius have been called quantum dots because their absorption and emission spectra near the band gap display quantum confinement blue-shifts with decreasing size. This confinement forces
electrons and holes closer together, increasing the Coulomb interaction involved in Auger recombination and its inverse, impact ionization.\textsuperscript{13} For strong quantum confinement, the oscillator strength per dot at the band gap is predicted to be independent of size.\textsuperscript{14} Although the growth of band gap absorption relative to the higher energy spectrum has abundant experimental support,\textsuperscript{15} a size-independent oscillator strength is not always observed.\textsuperscript{16}

Because the dense manifold of hot quantum-confined states is predicted to replicate the bulk absorption spectrum,\textsuperscript{12} it has been conventionally thought\textsuperscript{17} that highly excited states of quantum dots also have a quantum confined character (see chapter 18 of Kittel\textsuperscript{18}). However, in an early paper,\textsuperscript{19} Brus made a brief suggestion that a rigorous distinction between quantum dots and small pieces of bulk semiconductor might be made on the basis of carrier scattering length. Because the high energy spectrum can be accounted for with either quantum confined or bulklike states, it is important to experimentally characterize the states in this energy range. According to theory,\textsuperscript{20,21} quantum confined systems absorb light as a single unit, so that their absorption readily saturates to yield pump–probe signals scaling as $\varepsilon A$, where $\varepsilon$ is the molar decadic extinction coefficient and $A$ is the absorbance. Indeed, near the band gap, quantum dots have been used as long-lived saturable absorbers.\textsuperscript{22} In contrast, the weak field saturated absorption of bulk semiconductors is proportional to $\chi^{(3)} l$, where $\chi^{(3)}$ is the nonlinear susceptibility and $l$ is the sample length.\textsuperscript{23} That $\chi^{(3)}$ does not depend on the number of unit cells ($N$) in the bulk crystal can be understood in two equivalent ways: (1) the absorbing unit is smaller than the crystal so that $\varepsilon$ is smaller for each absorbing unit but the number of absorbing units increases so that $A$ remains constant; (2) when the
crystal is excited, the saturated absorption (positive signal proportional to $N^2$) is mostly canceled by systematic excited state absorption (negative signal proportional to $N(N-1)$). When $\varepsilon$ is proportional to $N$, $\varepsilon A$ is proportional to $N^2$, so the resulting pump–probe signal at zero delay is roughly $(1/N)$ weaker in a bulklike system than in a quantum confined system. In molecular aggregates, this reduction in the size of the absorbing unit arises from disorder and coupling to phonons, both of which cause carrier scattering in bulk semiconductors. Excitation by a coherent pulse will prepare a coherent superposition of excited states that both maximizes stimulated emission and minimizes absorption for an identical probe, these positive contributions to the signal scale as $\varepsilon A$. The dephasing and lifetime decay that reduce the signal from this coherent superposition of excited electronic states can occur through both production of multiexciton states and competing carrier scattering; carrier scattering has been estimated to take place on time scales ranging from $50 \text{ fs}^4$ to $3 \text{ ps}^26$ with most estimates ranging from $100 \text{ fs}$ to $1 \text{ ps}^6,27$

In this letter, we report experiments that suggest quantum dots act as small pieces of bulk semiconductor for hot carriers. Importantly, we show these results on the relaxation of hot carriers over the first 2 ps are insensitive to the apparent multiexciton yield, multiphoton excitation, and other difficulties$^{28-33}$ involved in studying multiple exciton generation. Therefore, this letter concentrates on robust conclusions about relaxation during the first 2 ps after photoexcitation. We then discuss the scattering length using the bulk band structure; this discussion shows that quantum-confined states (with properties different from the photoexcited states in the bulk) should not be expected for the high energy excitations that produce hot carriers in the bulk.
Bulk PbS has a rock salt structure, a small direct band gap (0.42 eV at 300 K), small electron and hole effective masses \( m_e^* = m_h^* = 0.105 m_e \), where \( m_e \) is the rest electron mass, and a large high frequency dielectric constant \( \varepsilon_\infty = 17 \). With \( a_0 \geq 17 \text{nm} \), PbS nanocrystals show strong quantum confinement. Reported multiexciton yields vary significantly between experiments, possibly due to differences between probe methods, sample synthesis and handling, pulse fluence, or sample refreshing. We measure degenerate pump–probe signals for nanocrystals relative to the signals for “slow” saturable absorber dyes, which act as electronic two-level systems with known signal strengths scaling as \( \varepsilon A \). The measurements employ low fluence pulses of 20–25 fs duration and a rapidly spinning, vacuum-tight sample cell to completely refresh the sample after every laser shot.

2.2 Experimental Methods

PbS nanocrystals capped with oleate ligands and dispersed in toluene were purchased from Evident Technologies because production of multiexciton states has been reported in samples synthesized by Evident. The first batch of 8 nm diameter nanocrystals was custom synthesized, shipped in a colored glass bottle without an airtight seal, kept in a refrigerator, and put into airtight sample cells under open air for measurements completed within 10 weeks of the order; it showed signatures conventionally attributed to production of multiexciton states (see below). A second batch of 8 nm nanocrystals, synthesized the same week as the first, was purchased 9 months later and split into two sets: one was handled as above; the other was freeze-pump thawed to remove oxygen, kept in a nitrogen-purged glovebox, and put into airtight
sample cells inside the glovebox. The 5 and 4 nm diameter PbS nanocrystal samples were purchased as stock sizes and also divided into two sets. These smaller nanocrystals and the second 8 nm batch showed greatly reduced, if any, signatures of production of multiexciton states.

The molar decadic extinction coefficient per PbS nanocrystal volume is shown for 8, 5, and 4 nm diameters in Figure 1. The quantum confined first exciton peaks at 0.68, 0.86, and 1.03 eV, respectively, derive from the bulk band gap at the $L$ point of the first Brillouin zone.\textsuperscript{18} It is known that the extinction coefficient becomes proportional to the nanocrystal volume at high photon energy,\textsuperscript{12,16,38,39} and this is noticeable for the rising absorption background in Figure 1. The weak shoulders at 2.14, 2.21, and 2.30 eV, respectively, on top of the rising background derive from the E1 transition of bulk PbS (assigned as either a valence to conduction band transition at the $\Sigma_5$ point\textsuperscript{40} or as the same transition overlapping with a valence to second conduction band transition at the $L$ point\textsuperscript{41}). By analogy to PbSe,\textsuperscript{42} these shoulders represent the first exciton peak of the PbS E1 transition. Compared to the bandgap, they show a smaller quantum confinement blue shift with decreasing nanocrystal size,\textsuperscript{39} which should be expected from the larger effective masses (hence smaller Bohr exciton radii).\textsuperscript{42,43}

The femtosecond pump/probe pulses were generated from a home-built noncollinear optical parametric amplifier (NOPA),\textsuperscript{44} pumped by a 50 fs, 800 nm, 6 μJ regenerative amplifier running at 10 kHz repetition rate (Coherent RegA 9060). NOPA output of up to 150 nJ was generated with bandwidths ranging from 25–40 nm in the 500–700 nm wavelength range. The NOPA pulses were compressed with a pair of fused-silica prisms and were characterized by second harmonic generation frequency resolved
Figure (2.1) Volume normalized molar decadic extinction coefficients of oleate capped PbS nanocrystals in toluene for three nanocrystal diameters: 8 nm (red curve), 5 nm (green curve), and 4 nm (blue curve).
optical gating\textsuperscript{45} in a 100 \(\mu\)m thick Type I KDP crystal. The pulse durations recovered were \(\sim 20-25\) fs. A dielectric beamsplitter divided the NOPA pulses into pump and probe pulses. The probe passed through a compensating block of the same material as the beamsplitter before a variable delay set by a computer-controlled translation stage. The pump and probe propagated on parallel paths into a reflective Cassegrain telescope, after which they crossed in the sample with a 200 \(\mu\)m diameter (as measured by 50% transmission through a pinhole). Pump excitation probabilities were varied from 1 to 40\% (0.5–20 nJ for 8 nm diameter PbS at 610 nm wavelength). The probe energy was fixed at 0.5 nJ. The pump was chopped at 500 Hz and the pump–probe signal, defined as the pump-induced increase in probe transmission, \(\Delta T\), was measured with a Si photodiode and lock-in detector referenced to the pump chopping frequency. The vacuum-tight sample cell was spun at 1800 rpm and probed about 1 cm off-axis, ensuring a fresh sample for each laser shot, but probing the same volume again after a 33 ms delay. This is much longer than the 4 \(\mu\)s excited state lifetime,\textsuperscript{46} but (unfortunately) shorter than the dark state off times observed in single dot spectroscopy.\textsuperscript{47}

2.3 Results

The pump–probe signal from 8 nm diameter PbS nanocrystals is shown in Figure 2 as the negative-going black line (negative signals indicate the pump reduces probe transmission). On the same graph, the pump–probe signal, measured with identical pulses (25 fs duration at 610 nm), for a solution of the saturable absorber dye DQOCI (an electronic two-level system) with the same absorbance \((A = \log_{10}(T) = 0.4)\) is shown as the positive-going gray line. Since the first excited electronic state of a saturable absorber
Figure (2.2) Pump-probe signal $\Delta T$ for 8 nm diameter PbS nanocrystals (black) compared to $\Delta T$ for the saturable absorber DQOCI (grey) under the same conditions. 610 nm excitation/probe wavelength; 10 nJ pump and 0.5 nJ probe pulse energies; 25 fs pulse duration; 200 $\mu$m beam diameter; 10 kHz laser repetition rate; 1800 rpm sample spin rate; absorbance $A = 0.4$ (PbS); $A = 0.4$ (DQOCI). For DQOCI, Beer’s law estimates indicate about 1% of the molecules are excited (implying $\Delta T_{\text{max}} \sim +0.004$ at $\sim 15$ on the vertical scale).
does not absorb light at wavelengths within the first electronic absorption band, the absorbance change upon excitation of a fraction of molecules $f$ is proportional to $-f\Delta A$ ($f$ is proportional to $\varepsilon$). Although the 8 nm nanocrystal’s molar extinction coefficient is 20 times larger than that of DQOCI, so that $\Delta T$ should be $20\times$ larger for the nanocrystals, the initial pump–probe signal from the PbS nanocrystals is nearly zero. At one wavelength, signal could vanish through accidental cancellation of positive (excited state emission plus reduced ground state absorption) and negative (excited state absorption) contributions, but a near zero signal was measured for 7 pump–probe wavelengths between 507 and 670 nm.

A nanocrystal absorbing as one unit is inconsistent with this result; the absorbing unit must be much smaller. When the maximum absorption increase is reached at 2 ps delay, the signal is about 1/15 of that from DQOCI. The small increase in absorption (negative signal) at 2 ps delay is consistent with the excited state having an absorption spectrum that is a red-shifted (by about 1 meV) replica of the ground-state absorption spectrum. Because the steady-state change in the spectrum caused by photoexcitation resembles that caused by a static electric field, it has been attributed to an internal Stark effect caused by charge redistribution in the nanocrystal.

Figure 3 shows the wavelength dependent early time dynamics. An initial positive signal occurs only for 610 nm excitation, which maximally excites the weak shoulder arising from the first exciton peak of the bulk E1 transition. For excitation pulse spectra partially overlapping the E1 transition, E1 excitation adds a short-lived ($\sim$100 fs) positive (two-level like) signal of the kind previously discussed to the negative excited state absorption signal. Our interpretation is that the signals at 550 and 670 nm essentially
Figure (2.3) The degenerate pump-probe signal for 8 nm diameter PbS nanocrystals as a function of pump-probe wavelength. Experimental parameters are the same as Figure 2. The signals are normalized at 2 ps to highlight differences in the fast relaxation, which are dominated by excitation of the E1 transition centered at 610 nm.
represent the dynamics of the hot states excited via the smooth background underneath the E1 shoulder. These hot states show an initial increase in absorption at time zero, which further increases by about a factor of 2 with a 240 fs time constant until the full Stark red shift is developed.\textsuperscript{48} Other experiments\textsuperscript{5,50} and theory\textsuperscript{51} suggest that carrier cooling to the band gap is completed during this time. As the wavelength is tuned toward the peak of the E1 transition, a positive signal from nanocrystals excited via the E1 shoulder is added to the negative signal from nanocrystals excited via the smooth background. Nanocrystals excited to the quantum confined E1 state decay with a roughly 100 fs lifetime via intervalley scattering into high energy states similar to those excited directly via the smooth background; these hot states then relax with about the same time constant as the directly excited high energy states. Before this relaxation, the magnitude of the signal from direct photoexcitation of the hot states is thus about 600 times smaller \([(1/2)(1/15)(1/20)]\) than expected for quantum confinement; except for the sign, this is in reasonable agreement with the bulk prediction (1200 times smaller).\textsuperscript{31}

Figure 4 shows the 8 nm diameter PbS nanocrystal pump–probe signals at different excitation pulse energies. When the signals are divided by the respective pump pulse energies, the traces overlap, so the early time dynamics is independent of the excitation probability up to 40% excitation, when the Poisson distribution predicts 23% of the signal comes from nanocrystals with two or more excitations. Within the precision of the data, the relaxation of one hot electron–hole pair is unaffected by another until at least 2 ps delay (barring filling of the 8-fold degenerate conduction band, which occurs at much higher pulse fluences); the hot carriers thus behave as if uncoupled to one another, as in the bulk.
Figure (2.4) The pump-probe signal divided by the pump pulse energy at constant 0.5 pJ probe pulse energy. 630 nm pump and probe wavelength; 25 fs pulse duration; 200 μm beam diameter; 10 kHz laser repetition rate; 1800 rpm sample spin rate; absorbance $A = 0.4$ at 610 nm. The pump pulse energies were 1 nJ (2%), 2 nJ (4%), 5 nJ (10%), 10 nJ (20%), 15 nJ (30%) and 20 nJ (40%) [numbers in parentheses indicate the corresponding excitation probabilities].
Figure 5 compares the pump–probe signals from the first 8 nm batch to signals from the second 8 nm batch (handled in the same way, not deoxygenated) at three different excitation wavelengths. For PbSe nanocrystals, photo-oxidation causes a blue shift of the first exciton peak.\textsuperscript{52} Approximately 1 meV blue shifts were observed here in PbS nanocrystals after two weeks exposure to dissolved oxygen and the laser beam. Deoxygenation by freeze–pump–thawing inhibited the blue shift, but had no significant effect on the signal (data not shown). However, for higher photon energies, the signal from the first 8 nm diameter batch decayed for delays longer than 2 ps (not shown): the signals measured at 610, 550, and 537 nm decay to half of their 2 ps amplitude with time constants of 100–180 ps, roughly matching the biexciton lifetime of \~120 ps (determined by using a model\textsuperscript{53} to fit the pulse energy dependent signals after multiphoton excitation of the first 8 nm batch at 800 nm). The conventional interpretation\textsuperscript{8} would be 70–100\% yield of the biexciton above three times the nanocrystal band gap; however, yield determination is controversial.\textsuperscript{29,31-33,54} For the smaller nanocrystals and the second 8 nm batch, the data are consistent with 0\% yield and inconsistent with any yield above 10\% (except at 610 nm for the second 8 nm batch, where low signal-to-noise longer scans are compatible with up to 30\% yield). This variation in dynamics for 8 nm diameter nanocrystals on 100 ps time scales may be related to nanocrystal synthesis, storage, or handling. Figure 5 shows that the relaxation of hot carriers over the first 2 ps is not sensitive to nanocrystal handling or biexciton signatures.

Figure 6 shows the initial positive signal observed when pumping and probing at the quantum confined E1 transition in the 4 and 5 nm diameter nanocrystals. As for the 8 nm diameter (Figure 3), the degenerate pump–probe signal is small compared to that
Figure (2.5) Initial dynamics for two batches with different dynamics on 100 ps timescales: The first batch showed long-time decay roughly matching the bi-exciton lifetime, and the second batch did not. Experimental parameters for the first batch are: 2.5 nJ pump and probe pulse energies, 25 fs pulse duration; 100 μm beam diameter; 20 kHz laser repetition rate; 1800 rpm sample spin rate; and absorbance $A=0.6$ (at 610 nm). Experimental parameters for the second batch are the same as in Figure 2.
Figure (2.6) Comparison between degenerate pump-probe signals for 4 nm (black) and 5 nm (gray) diameter PbS nanocrystals at 550 nm (solid) and 570 nm (dotted) wavelengths. All signals are normalized at 2 ps pump-probe delay. 550 nm (570 nm) excites the peak of the E1 transition for 4 nm (5 nm) diameter nanocrystals. The pump pulse energy at 550 nm was 20 nJ, yielding excitation probabilities of 17% (5 nm) and 6% (4 nm). The pump pulse energies at 570 nm were 15 nJ (4% excitation probability for 4 nm diameter) and 17 nJ (14% excitation probability for 5 nm diameter). (The weakness of these signals is illustrated by the negative spikes at T=0, which are observed for neat toluene and might arise from probe focusing changes caused by the instantaneous pump-induced change in solvent refractive index.) Sample absorbance at 610 nm: $A = 0.4$ (5 nm) and $A = 0.6$ (4 nm). All signals used 0.5 nJ probe pulse energy, 25 fs pulse duration, 200 μm beam diameter, 10 kHz laser repetition rate, and 1800 rpm sample spin rate.
from saturable absorbers with the same absorbance and negative at all wavelengths measured between 507 and 670 nm other than the E1 maximum. Given the weakness of the E1 shoulder, it is surprising that the positive signal from E1 excitation is strong enough to cancel the negative signal from the larger smooth background. Quantum-confined states produce more signal for a given extinction coefficient than the hot states.

2.4 Discussion

A priori, three conclusions seem possible: (1) Some nanocrystals, including those studied here, have surfaces that do not support hot quantum-confined states; (2) hot states of nanocrystals are quantum confined but systematically different from the lowest quantum-confined state in always having excited state absorption that almost perfectly cancels the reduced absorption and emission contributions; or (3) the hot states are bulklike, not quantum confined, and relax independently of one another for the first 2 ps. Under hypothesis 1 or 3, the absence of positive signal during the pump pulse would require destruction of the coherently excited hot state on a time scale much shorter than the pulse duration, perhaps 5 fs. Noting that the convergence of quantum dot absorption spectra to that of the bulk at photon energies around three times the nanocrystal band gap is consistent with all three hypotheses, we now turn to theoretical arguments, based on bulk properties, that support the bulklike hypothesis. Suggestions that the bulk band structure cannot be used because the envelope functions for a nanocrystal are entirely different from Bloch waves and lack translational symmetry are not useful because they prove too much: the same argument applies to any finite bulk solid. Effective masses from the bulk band structure develop at a very short length scale, justifying their use at the core of
quantum confinement theory.\textsuperscript{12,19} Differences in quantum confinement blue shifts for different features of the bulk spectrum have long been explained as arising from differences in effective mass at different critical points in the band structure.\textsuperscript{42,43} The view delineated here is that if the electronic state and its interactions in the bulk can be localized on length scales smaller than the nanocrystal dimensions, then these spatially localized properties and interactions will persist in the nanocrystal.

Such localization criteria can be valid independently of the surface and nonlinear optical properties involved in the first two hypotheses mentioned above. Accordingly, we use the bulk band structure of PbS\textsuperscript{41} and the pulse spectrum to estimate carrier wave packet properties. We first find the vertical excitation wave-vector along $\Gamma$ [the line between the $\Gamma$ point at $k = (0,0,0)$ and the $L$ points\textsuperscript{18} at $k = (\pm \pi / a, \pm \pi / a, \pm \pi / a)$] where $a = 5.94$ Å is the lattice constant\textsuperscript{34} at which the gap $\Delta E_g = E_c - E_v$ between the conduction and valence bands matches the energy of a 600 nm photon; this occurs at $k \sim 0.7\pi / a(\pm 1, \pm 1, \pm 1)$. The group velocity for an electron is $v_g^e = (1 / h) dE_c / dk$,\textsuperscript{9} where $dE_c / dk$ is the slope of the conduction band and $h$ is the reduced Planck constant; at the vertical excitation wave-vector, the electron group velocity is $9 \times 10^5$ m/s and the hole group velocity $v_g^h = (1 / h) dE_v / dk$ is $6 \times 10^5$ m/s in the valence band. Near this vertical excitation wave-vector, the curvatures of both the valence band and the conduction band are near vanishing; the effective masses

$[m_{e,h}^* = \pm \hbar^2 / (\partial^2 E_{e,h} / \partial k^2)]^9$ of the electron and hole have gone up by at least a factor of 10 as they diverge to infinity. Such diverging effective masses are expected at some point above the band gap in all direct gap semiconductors.\textsuperscript{9} This divergence sends the Bohr
exciton radius to zero, so quantum confinement effects should not be expected at these points in the band structure. This extension of the effective mass theory for quantum confinement effects from critical points to the entire band structure does not yet establish that the envelope functions of the nanocrystal support the dynamics of the bulk band structure.

The relevance of bulklike dynamics to the nanocrystal can be established from the size of the carrier wave-packets supported by the band structure and the length scale of their interaction with phonons. A Gaussian wavepacket with probability full width at half-maximum $\Delta k$ has a transform-limited spatial probability full width at half-maximum $\Delta r \Delta k = 4 \ln(2)$. Around the vertical excitation point along $\Lambda$, the bulk band structure indicates near constant group velocities (hence near diverging effective masses) from $k \sim (0.2$ to $0.8)(3)^{1/2}(\pi/a)$, supporting carrier wave-packets smaller than 2 unit cells in width (approximately 1 nm). From the group velocities, such electron and hole wavepackets will rapidly (roughly 3 fs) separate into free carriers. The length scale for their interaction with the lattice is given by the size of the polaron (lattice distortions around free carriers). From eq 10.23 from Klingshirn\textsuperscript{9}, the polaron radii are about 3.8 nm at the PbS band gap, drop by at least a factor of 3 at the vertical excitation point, and tend toward zero as the effective masses diverge. In the bulk, carrier interactions with the lattice involve scattering lengths and polaron radii much smaller than the size of the nanocrystals in these experiments. These local interactions should be the same when wave-packets with the same properties are built from the complete set of nanocrystal envelope functions; this indicates the strength of these interactions with the lattice must be, in some average sense, similar for plane-wave and nanocrystal envelope functions.
Group velocities from the bulk band structure can be used to assess the time and length scales for carrier scattering processes. Since the group velocities are much greater than the fastest phonon group velocities (based on published dispersion relations\textsuperscript{55}, these are about 7000 m/s in bulk PbS), the carriers leave optical and acoustic phonon wakes as they propagate. More importantly, these velocities are much greater than the $10^5$ m/s saturation velocity that the field-induced drift velocity cannot exceed in bulk semiconductors.\textsuperscript{10,56} The Ohm’s law scattering length for PbS calculated from the mobility $\mu$\textsuperscript{34} using $l = \left( \frac{3\mu}{4e} \left( \frac{2\pi m^* k_B T}{e} \right) \right)^{1/2}$ [eq 28b in chapter 11 from Shockley\textsuperscript{57}] is 14 nm; $l$ depends on temperature through the phonons that cause scattering, but is independent of electron velocity [see the discussion below eq 30 in chapter 17 of Shockley\textsuperscript{57}]. Therefore, the mean scattering time $\tau = l / \nu$ is inversely proportional to velocity in the Ohm’s law regime.\textsuperscript{11,57} For hot carriers, new scattering channels become accessible and the inelastic scattering length\textsuperscript{58} can be over an order of magnitude shorter than the Ohm’s law scattering length.\textsuperscript{59} At a velocity of 0.9 nm/fs, electron scattering via impact ionization and optical phonons is thus expected to occur perhaps an order of magnitude more often than the Ohm’s law mean scattering time of 16 fs. The above discussion indicates that for hot states in PbS nanocrystals, bulklike electron–phonon inelastic scattering on a time scale of approximately 5 fs or shorter, as inferred from the experiments, is plausible. The electron and hole also collide frequently with the surface; for an 8 nm diameter nanocrystal, an electron unimpeded by scattering would travel from the center to the surface in about 4 fs. This will make surface properties, already crucial for the mobility of hot carriers in bulk semiconductors\textsuperscript{60} and devices,\textsuperscript{61} even more important for nanocrystals.
If the pulse is much shorter than the scattering time, one can use $d\Delta E_p/dk$ from the band structure and the full width at half-maximum energy bandwidth of the pulse, $\Delta E_p$, to calculate the wave-vector spread $\Delta k = \left[1/(d\Delta E_p/dk)\right] \Delta E_p$ and wavepacket width excited by a coherent pulse (a 20 fs pulse at 600 nm would excite a 25 nm wide wavepacket in bulk PbS). As the pulses are longer than the scattering time, the coherence of scattering becomes relevant, especially because phonon deformations of the lattice are almost stationary during the scattering time. Interpreting a 5 fs scattering time as a lifetime, electronic states would be broadened to a full width at half-maximum, $\Delta E = h/\pi \tau$, of 0.25 eV. Such broadening blurs the distinction between bulk and nanocrystals, allows access to a wider range of $k$ than indicated by the pulse spectrum and band structure, and limits the coherence length of optically excited wavepackets (to less than 6 nm for a 5 fs lifetime). In the spatial domain, quantized cyclotron resonances in semiconductors require a total scattering length greater than the retracing path length divided by $2\pi$. For the minimum retracing path (twice the nanocrystal diameter for a 1S state), this is about 2.5 nm for an 8 nm nanocrystal, thus it seems plausible that hot electrons and holes do not support quantum confined electronic states at room temperature.

The above scenario indicates that the high-energy electronic eigenstates of nanocrystals are, like the high-energy bulk band structure, a concept useful only as a basis set. This picture appears to support arguments in favor of a bulklike or surface-mediated impact ionization mechanism in nanocrystals. However, if the states generated immediately after impact ionization are quantum confined, then the impact ionization coupling between bulklike and quantum-confined states will be important for
the yield. This coupling may be most naturally treated in a quantum-confined basis. Such confinement effects at twice the nanocrystal band gap are necessarily important near the minimum energetic threshold. Qualitatively different results have been reported for the effect of quantum confinement on the density of biexciton states, and not all are coupled. Far above threshold, it is not clear what fraction of the states generated immediately after impact ionization (and before subsequent cooling) have a quantum confined character. However, surface-mediated processes, important for hot carriers in the bulk measurements, are likely more important in nanocrystals than in the bulk.

The above scenario justifies a bulklike picture that explains not only the small pump–probe signal, but also the initial negative signal from the smooth background. For bulk semiconductors, absent scattering, the pump–probe signal involves a delicate cancellation between positive and negative signals. Both elastic and inelastic collisions of carriers with phonons will rapidly (within about 5 fs) scatter the hot electrons and holes into different momentum states during the pulse so that Pauli blocking prevents direct emission. The net result is that negative signal from excited state absorption overbalances the positive signal from ground state depopulation. The elastic scattering of carriers by phonons might underlie the 7 fs electronic dephasing reported in calculations on smaller lead salt quantum dots.

The quantum confined E1 state decays with a lifetime of about 100 fs; this is analogous to intervalley scattering in the bulk and internal conversion in molecules, both of which normally occur on a time scale of approximately 100 fs. This intervalley scattering populates hot bulklike states that relax similarly to those excited directly via the underlying smooth absorption background. The relaxation of these
bulklike states can be fit to a 240 fs exponential decay, which is at the slow end of compatibility with the energy relaxation times reported for probing at the band gap and is in reasonable agreement with calculations for electronic energy relaxation in smaller PbSe nanocrystals. While the degenerate pump–probe experiments reported here may not probe the band gap states directly, they should be directly sensitive to the Stark shift of the spectrum that occurs through carrier migration to the nanocrystal surface; this time scale may differ from that of electronic energy relaxation to the band gap.

2.5 Conclusion

In conclusion, we have time-resolved intervalley scattering and the development of the Stark shift in semiconductor nanocrystals. Direct measurements of hot electronic dynamics in PbS nanocrystals with 25 fs time resolution suggest that hot electronic excitations are bulklike, uncoupled, and insensitive to the surface properties that affect slower dynamics (such as Auger recombination of multiexciton states produced by either single or multiphoton excitation). Production of multiexciton states has been reported in PbS, PbSe, PbTe, InAs, CdSe, and Si quantum dots. In all five direct gap semiconductors, the bulk band structures predict diverging effective masses and optically excited carrier group velocities exceeding the saturation velocity below the reported threshold for single photon production of biexciton states. Except for electrons in InAs, the mobilities indicate Ohm’s law scattering lengths no more than 4 times longer than that of PbS. For carriers above the impact ionization threshold in these systems, quantum confinement should not be expected for three reasons: the Bohr exciton radius tends to zero, the carriers are coupled to polarons whose radius tends to zero, and rapid phonon
scattering prevents carriers from retracing their orbits without collisions. The scattering length depends on carrier-phonon coupling not considered in the exciton Bohr radius criterion for distinguishing a quantum dot from a small piece of bulk semiconductor. This suggests bulklike scattering dynamics is important for hot carriers in many nanocrystals conventionally regarded as quantum dots.

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2.7 References


CHAPTER 3

FEMTOSECOND PUMP-PROBE POLARIZATION SPECTROSCOPY OF VIBRONIC DYNAMICS AT CONICAL INTERSECTIONS AND FUNNELS

3.1 Introduction

This chapter reviews use of the polarization dependence of femtosecond pump-probe spectroscopy to probe the coupled electronic and vibrational dynamics at conical intersections and funnels. Typically, femtosecond pump-probe spectroscopy creates and probes wavepackets in Franck-Condon active vibrations which modulate the electronic absorption and emission frequencies; this requires pulses that are both abrupt with respect to the vibrational period and frequency selective with respect to the electronic spectrum. In contrast, the experiments on napthalocyanine dyes discussed here create and probe electronic wavepackets which are a coherent superposition of the vibrational-electronic states involved in a conical intersection. Such electronic wavepackets have much in common with the electronic wavepackets observed in atoms, but are modified by the vibrational-electronic coupling. These interactions provide signatures of a conical funnel which can be detected in what might otherwise be considered separate vibrational and electronic contributions to the pump-probe signal. Because two electronic states with differently oriented transition moments are involved, vibrational-electronic coupling produces signatures in the pump-probe polarization anisotropy.

In contrast to Franck-Condon vibrational wavepacket signatures, these polarization signatures survive under spectrally non-selective impulsive excitation, so electronic motions and
coupled vibrations can be preferentially detected. This approach has provided experimental
determination of vibrational symmetry (from the polarization anisotropy of vibrational quantum
beats), measurement of electronic-vibrational coupling (from the amplitude of vibrational
quantum beats), and independent characterization of the electronic motion at the conical
intersection. The experiments described here probe a symmetry required Jahn-Teller conical
intersection\(^9,10\) in a four-fold symmetric (D\(_{4h}\)) silicon naphthalocyanine and a pseudo Jahn-Teller
effect\(^11\) that can be modeled as a conical funnel where the point of degeneracy is either absent or
energetically inaccessible in a lower symmetry (D\(_{2h}\)) free-base naphthalocyanine. The
naphthalocyanine chromophores (see Figure 1) have weak electronic-vibrational coupling, which
allows vibronic dynamics slow enough to measure with femtosecond spectroscopy.
Interestingly, the timescale for electronic motion at a conical intersection or funnel can be faster
than the coupled vibrational motion, and can be dictated by the strength of the vibrational-
electronic coupling and the width of the vibrational wavepacket. This role of vibrational
wavepacket width is inherently missing in the semiclassical Landau-Zener approach\(^12,13\) to curve

crossing.

3.1.1) The Polarization Anisotropy

Time-resolved spectroscopy with polarized light can reveal the dynamics of molecular
rotation.\(^14-16\) The principle of the measurement is that a weak, linearly polarized, pump pulse,
resonant with a single vibronic transition, excites an aligned \(\cos^2(\theta)\) angular distribution of
molecules, where \(\theta\) is the angle between the vibronic transition dipole moment and the optical
electric field of the pulse.\(^15,16\) A probe pulse resonant with the vibronic transition excited by the
pump will stimulate emission (Excited State Emission – ESE) from a \(\cos^2(\theta)\) distribution of
excited molecules and not be absorbed by the \(\cos^2(\theta)\) distribution of molecules missing from the
Figure (3.1) Structures for a) silicon 2,3-naphthalocyanine bis(trihexylsilyloxide) (SiNc) and b) 2,11,20,29-tetra-tert-butyl-2,3-naphthalocyanine (H2Nc). R = -O-Si-((CH2)5CH3)3. t-Bu = -C(CH3)3. Each tert-butyl group is likely attached with equal probability to either available naphthalene β position on its given “arm” of the molecule. Lines between the central pyrrole nitrogen atoms (bound to silicon in SiNc) define the x-y axes (with x along NH bonds in H2Nc) in the molecular frame. Neglecting the “R” groups on SiNc, the molecule has D4h symmetry. The t-butyl groups on H2Nc do not significantly perturb the π system; the molecule has D2h symmetry if those groups are neglected.
ground state (Ground State Bleach – GSB). Initially, stimulated emission and reduced absorption contribute equally to increasing probe transmission. If changes in transmission are measured with probe pulses polarized parallel and perpendicular to the pump, the parallel signal is initially 3 times greater than the perpendicular signal.

Experimentally, rotational alignment is quantified using the anisotropy,

$$ r \equiv (S_\| - S_\perp)/(S_\| + 2S_\perp), \quad (3.1.1) $$

where $S_\|$ is the signal for parallel pulses and $S_\perp$ is the signal for perpendicular pulses.\textsuperscript{15} The division by $S_\| + 2S_\perp \equiv 3S_{\text{iso}}$ ($S_{\text{iso}}$ is the isotropic signal, averaged over all laser polarizations and laser beam directions) removes isotropic dynamics, such as decay of excited state population.

For a single dipolar vibronic transition, a 3:1 signal ratio leads to $r = 2/5$. If a signal arises from several sources with non-zero isotropic strength, the total signal has the average anisotropy\textsuperscript{17}

$$ \langle r \rangle = \frac{\sum_i r^i S^i_{\text{iso}}}{\sum_i S^i_{\text{iso}}}. \quad (3.1.2) $$

For a change in transition dipole angle of $\theta'$,

$$ r(\theta') = (1/5)[3 \cos^2(\theta') - 1]. \quad (3.1.3) $$

After rotation and collisions destroy the alignment created by the pump, the distribution of $\theta'$ becomes isotropic in three dimensions, so that the ensemble average $\langle \cos^2(\theta') \rangle = 1/3$ yields $r = 0$. Equation (3.1.3) can also be applied to changes in transition dipole within the molecular frame; for example, a change in state with $\theta' = \pi/2$ yields $r = -1/5$. Different distributions of $\theta'$ can produce the same anisotropy; for example, the distribution $p = 1/2$ for $\theta' = 0$ and $p = 1/2$ for $\theta' = \pi/2$ has the same anisotropy ($r = 1/10$) as the two-dimensionally isotropic distribution of $\theta'$ with $\langle \cos^2(\theta') \rangle = 1/2$ arising from randomized rotation in a plane.

For a single transition between non-degenerate vibronic states, the transition dipole direction is fixed in the molecular frame and has the same direction regardless of the transition
probability. This is not the case when more states are involved. Consider a hydrogen atom coherently excited from the 1s state to the 2p level by a pulse linearly polarized along Z; the excited state will always be a 2p_z state. This should enhance the initial emission anisotropy, yielding \( r_{ESE} = 1 \). Similarly, a doubly degenerate excited state (or a dimer with perpendicular chromophores) should lead to greater alignment than a single dipole; for this case, calculations by the groups of Knox\(^{18}\) and Hochstrasser\(^{19}\) predicted \( r_{ESE} = 7/10 \) (anisotropy of the ESE component of the signal) for an initially isotropic sample in 1993. These emission anisotropies are sensitive to coherent motion of the excited state superposition (which can change the direction of the emission dipole), transfer of population between the degenerate excited states, and loss of coherence between them.

Conflicting reports about pump-probe anisotropies greater than 0.4 in experiments involving coherent excitation of several transitions caused confusion about the above theory for some time.\(^{17,20,21}\) Then, in 2001, Albrecht, Ferro, and Jonas showed that the emission anisotropy is not the same as the pump-probe anisotropy when coherent excitation of more than one transition is involved.\(^1\) The emission result does not apply to the pump-probe anisotropy because, relative to a single non-degenerate transition, the anisotropy of the transmission increase from depopulation of the ground state (GSB) is not more aligned, but less.\(^{1,2}\) For example, in the hydrogen atom, a depletion of the 1s state population causes equal transmission increases for pulses polarized along the laboratory X, Y, and Z axes, so that the anisotropy of the GSB contribution to the signal is \( r_{GSB} = 0 \). Furthermore, the strength of the emission and bleach signals are no longer equal; in hydrogen, the transitions to 2p_x, 2p_y, and 2p_z are all bleached while only one emits (yielding a transmission increase equal to one of the three bleached transitions). The result is that the initial pump-probe polarization anisotropy should be reduced to \( r = 1/4 \). Similarly, for a doubly degenerate transition, both orthogonal transitions to the excited
state are bleached, so that $r_{GSB} = 1/10$. In the absence of molecular rotation, the ground state bleach anisotropy is not time-dependent.

Absorption transitions starting from the initially excited states and terminating on highly excited states (Excited State Absorption: ESA) can also contribute to pump-probe signals (they cause a transmission decrease) and the time-dependence of the pump-probe anisotropy. Indeed, such transitions must be included to recover the known experimental results for isolated chromophores as a limiting case of the theory for coherent excitation of coupled chromophores.\textsuperscript{1,2} When excited state absorption transitions to states with two excited chromophores are included, the initial anisotropy for an aggregate is also $2/5$, consistent with most experiments.\textsuperscript{1,17,22}

Clearly, changes in electronic state character caused by non-adiabatic transitions between electronic states are reflected in the anisotropy whenever there is a change in transition dipole direction. In the vicinity of a conical intersection, the adiabatic electronic states have a strong variation in electronic character as a function of the vibrational coordinates. As a result, adiabatic changes in electronic state character during vibrational motion can also alter the polarization anisotropy.\textsuperscript{1} However, these effects occur against a backdrop of anisotropic “quantum beats” in coherent experiments. Before discussing these, we remark that, if a vibrational wavepacket on one adiabatic electronic state reaches the vicinity of a conical intersection, the non-adiabatic coupling will turn it into a coherent superposition state with amplitude on both adiabatic surfaces. This coherent superposition state will have “quantum beat” dynamics similar to those discussed here.

These quantum beat phenomena can be illuminated by first order time-dependent perturbation theory. In an initially isotropic sample, the pump pulse excites molecules from state $|g\rangle$ to the coherent superposition state
\[ |\psi(t)\rangle = |g\rangle + \sum_e \left( i/\hbar \right) e^{-i\omega_{eg}t} [\vec{\mu}_{eg} \cdot \hat{\mathcal{E}}(\omega_{eg})]|e\rangle \]  

(3.1.4)

where \( g \) is the ground state, the states \( e \) are excited, \( \vec{\mu}_{eg} = \langle e | \hat{\mu} | g \rangle \) is the vibronic transition dipole moment, \( \hat{\mathcal{E}}(\omega) \) is the inverse Fourier transform of the time domain electric field, and \( \omega_{eg} = (E_e - E_g)/\hbar \) is the Bohr frequency.\(^{23} \) The expectation value of the dipole moment in the molecular frame is

\[
\langle \hat{\mu}(t) \rangle = \langle \psi(t) | \hat{\mu} | \psi(t) \rangle = \sum_e \left( i/\hbar \right) e^{-i\omega_{eg}t} [\vec{\mu}_{eg} \cdot \hat{\mathcal{E}}(\omega_{eg})] \vec{\mu}_{ge} + c.c. \]  

(3.1.5)

If the basis is chosen so the transition dipoles are real-valued, and the pulses have real-valued transforms (e.g. cosinusoidal fields), Eq. (3.1.5) simplifies so that, in the case of two states with equal magnitude transition dipoles along \( x \) and \( y \) in the molecular frame,

\[
\langle \hat{\mu}(t) \rangle = (2\mu^2/\hbar)[(\hat{\mathcal{E}} \cdot \hat{x}) \sin(\omega_{eg}t)\hat{x} + (\hat{\mathcal{E}} \cdot \hat{y}) \sin(\omega_{yg}t)\hat{y}] .
\]

The initial dipole has a \( \pi/2 \) phase lag behind the excitation field, and has an initial direction given by the projection of the field onto the \( xy \) plane, but the direction in the molecular frame is a function of time. Substituting \( \omega_{eg} = \omega_0 + \delta / 2 \) and \( \omega_{yg} = \omega_0 - \delta / 2 \) leads to

\[
\langle \hat{\mu}(t) \rangle = (2\mu^2/\hbar) \sin(\omega_{eg}t) \cos(\delta t/2)[(\hat{\mathcal{E}} \cdot \hat{y})\hat{y} + (\hat{\mathcal{E}} \cdot \hat{x})\hat{x}] + (2\mu^2/\hbar) \cos(\omega_{eg}t) \sin(\delta t/2)[(\hat{\mathcal{E}} \cdot \hat{x})\hat{x} - (\hat{\mathcal{E}} \cdot \hat{y})\hat{y}] .
\]

(3.1.6)

Ignoring the optical-frequency oscillations at \( \omega_0 \), the dipole rotates with frequency \( \delta / 2 \) around an ellipse in the molecular frame. This rotation, for a static energy gap \( \delta \), leads to\(^2\)

\[
\mathcal{R}_{ESE}(t) = \left[ 4 + 3\cos(\delta t) \right] / 10 .
\]

(3.1.7)

The factor of 2 frequency difference between equations (3.1.6) and (3.1.7) arises because the anisotropy is sensitive only to alignment (up/down or left/right), and cannot distinguish between up and down at the half periods in equation (3.1.6).
If there is an inhomogeneous distribution of energy gaps, the anisotropy decays as the Fourier cosine transform of the energy gap distribution from $r_{\text{ESE}}(t = 0) = 7/10$ to $r_{\text{ESE}}(t = \infty) = 4/10$ and does not fully equilibrate (in the absence of molecular rotation). The anisotropy does not reach the equilibrium appropriate to delocalization in a plane ($r = 1/10$) because, for some molecular orientations (those with either $\hat{\mathbf{E}} \cdot \hat{x} = 0$ or $\hat{\mathbf{E}} \cdot \hat{y} = 0$) the dipole does not reorient at all through coherent beating without changes in the magnitude of the excited state coefficients. Similarly, off-diagonal couplings that cause change in the coefficients are not, by themselves, sufficient to equilibrate the anisotropy. Knox and Gülen\cite{knock1991} and Wynne and Hochstrasser\cite{wynne1994} showed that “electronic dephasing” caused by stochastic fluctuations in the energy gap, in combination with population transfer caused by stochastic fluctuations in the off-diagonal coupling, would ultimately lead to electronic equilibration and $r_{\text{ESE}}(t = \infty) = 1/10$.

3.1.2) Tuning and Coupling Coordinates

All conical intersections and conical funnels involve two special vibrational coordinates:\cite{24-27} the $g$ coordinate “tunes” the energy gap between two electronic states and the $h$ coordinate controls the coupling between two electronic states. Both energy gap and coupling are zero at a conical intersection. A “conical funnel” is a conical intersection or weakly avoided conical intersection characterized by passage between electronic states “so fast that there is no time for vibrational equilibration before the jump.”\cite{28} Just as a conical funnel can exist without a true conical intersection, a conical intersection may not act as an effective funnel if $g$ or $h$ lifts the degeneracy too weakly. Signatures of both $g$ and $h$, or the electronic processes they drive, are required to prove that measured electronic dynamics arise from a conical funnel. Due to degeneracy at the intersection, the distinction between $g$ and $h$ is dependent on the electronic basis chosen: a $\pi/4$ rotation of the electronic basis vectors interchanges the role of these two
vibrational coordinates. Although $g$ and $h$ are individually dependent on the basis set, the “branching space” containing both coordinates that lift the degeneracy is not. Other directions of motion leave the degeneracy at the conical intersection intact, forming the “seam space”.27

In time-domain spectroscopy, rate theories of electronic relaxation (which we will see can be driven by conical funnels) may invoke three processes: population relaxation, coherence dephasing, and coherence transfer. When a system is perturbed by an optical field, these processes restore thermal equilibrium. Population transfer restores the Boltzmann population distribution, while coherence dephasing destroys coherent phase relationships between states. For a two level system, population transfer and coherence dephasing are often characterized with the optical Bloch $T_1$ and $T_2$ time constants, respectively.30 For larger systems, the density matrix element $\rho_{mm}$ for a coherent superposition of states $m$ and $n$ may evolve into density matrix element $\rho_{kl}$ for coherence between states $k$ and $l$, a step usually described with a Redfield rate constant, $R_{kllm}$.31,32 Redfield rate constants can also be used to describe population transfer ($R_{kkmm}$) and coherence dephasing ($R_{kldl}$). Although rate theories are not applicable to vibrationally correlated dynamics, as at conical intersections and funnels,33 they connect terms in the Hamiltonian to relaxation processes and provide convenient labels for the non-exponential relaxation processes measured with femtosecond spectroscopy.

In quantum mechanics, the probability amplitudes for each basis state are constant unless there is an off-diagonal coupling in the Hamiltonian, therefore we identify population transfer between states in a conical intersection as the electronic process driven by the $h$ coordinate.34 Similarly, the relative phase between states in a coherent superposition evolves as $\delta t / \hbar$, where $\delta$ is the energy gap; the $g$ coordinate will cause a randomization of this phase, known as dephasing, that damps oscillations of observables such as the dipole moment direction in Eq.
Both dephasing and population transfer must occur at a conical funnel and will be defined more precisely in section 2.

As \( g \) and \( h \) are basis-set dependent, so are dephasing and population transfer \(^{20}\) (although the state of complete electronic relaxation is basis set independent). In the \( \{|x\rangle, |y\rangle\} \) basis, a field projecting onto \((\hat{x} + \hat{y})/\sqrt{2}\) in the molecular frame excites \((|x\rangle + |y\rangle)/\sqrt{2}\) so that dephasing caused by the \( g \)-coordinate is needed for equilibration. If, however, the basis set had been chosen as \(|\pm\rangle = (|x\rangle \pm |y\rangle)/\sqrt{2}\rangle\), the excited state would be simply \(|+\rangle\), and population transfer caused by the \( h \)-coordinate would be needed for equilibration. Of course, the \( g \)-coordinate for the \( \{|x\rangle, |y\rangle\} \) basis is the \( h \)-coordinate for the \(|\pm\rangle\rangle \) basis. In an isotropic solution, molecules will be oriented randomly with respect to the light polarization, so that when a single basis set is used for all orientations both population transfer and dephasing are required for complete equilibration.

3.2 Theory

3.2.1) Model System and Hamiltonian

A diabatic electronic basis (which diagonalizes the nuclear kinetic energy but not coordinate dependent coupling \(^{35}\) ) is useful because the vibronic basis states and their linear combinations closely correspond to the states excited by a linearly polarized pulse. We use \( D_{4h} \) point group symmetry labels, but the discussion in this section applies more generally to fourfold symmetry and can be extended to symmetries lower than four-fold by inclusion of static vibrational displacements between potential surfaces (see section 3.2). We choose \(|x\rangle\) and \(|y\rangle\) as doubly degenerate basis states with \( x \) and \( y \) polarized electronic transitions to the ground state in the molecular frame. In the \( \{|x\rangle, |y\rangle\} \) basis, asymmetric vibrations of \( b_{1g} \) symmetry (rectangle
deformations) tune the energy gap so that the \( g \) coordinate is a linear combination of Jahn-Teller active \( b_{1g} \) normal modes. Asymmetric vibrations of \( b_{2g} \) symmetry (diamond deformations) control the off-diagonal coupling so that the \( h \) coordinate is a linear combination of Jahn-Teller active \( b_{2g} \) normal modes. Franck-Condon active \( a_{1g} \) normal modes belong to the seam space.

Because \( b_{1g} \) and \( b_{2g} \) vibrations are nondegenerate,\(^{10,11,36} \) the electronic dephasing and population transfer can occur on different time scales, as in a reactive conical intersection.

For fourfold symmetry, the linear Jahn-Teller Hamiltonian in the diabatic electronic basis \( \{|x\rangle, |y\rangle \} \), divided by \( \hbar \), is\(^{36} \)

\[
\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB},
\]

\[
\hat{H}_S = \omega_{eg} \langle x | x \rangle \langle y | y \rangle = \omega_{eg} \hat{I},
\]

\[
\hat{H}_B = \left( \frac{1}{2} \omega_{1} \left( \hat{p}_1^2 + \hat{q}_1^2 \right) + \frac{1}{2} \omega_{2} \left( \hat{p}_2^2 + \hat{q}_2^2 \right) + \frac{1}{2} \omega_{s} \left( \hat{p}_s^2 + \hat{q}_s^2 \right) \right) \hat{I}, (3.2.1)
\]

\[
\hat{H}_{SB} = \begin{pmatrix}
\omega_{1} d_{1} \hat{q}_{1} & \omega_{2} d_{2} \hat{q}_{2} \\
\omega_{2} d_{1} \hat{q}_{1} & \omega_{1} d_{2} \hat{q}_{2}
\end{pmatrix}.
\]

Here \( \hat{H}_S \), \( \hat{H}_B \), and \( \hat{H}_{SB} \) are the Hamiltonians for the two-state electronic system, the harmonic vibrational bath, and the system-bath interaction, respectively, and \( \omega_{eg} \) is the vertical electronic excitation energy (a constant). \( \hat{p}_i \) and \( \hat{q}_i \) are the momentum and position operators for dimensionless normal coordinates; the subscripts 1, 2, and \( s \) indicate \( b_{1g} \), \( b_{2g} \) and \( a_{1g} \) symmetry vibrations. The coupling terms \( \omega_{i} d_{i} \) in equation (3.2.1) are usually attributed to electrostatic stabilization.\(^{36} \) For a harmonic oscillator with coupling \( \omega d \), the potential well is displaced by a distance \( q = d \) and the bottom of the well is lowered by \( (1/2) \omega d^2 \). For a symmetric mode this stabilization energy of \( (1/2) \omega d^2 \) is commonly referred to as the Marcus\(^{37} \) reorganization energy \( \lambda \), while for an asymmetric mode it is commonly referred to as the Jahn-Teller\(^{11} \) stabilization energy \( (D \omega) \).
The Born-Oppenheimer electronic potential energy surfaces are generated by neglecting the nuclear kinetic energy terms \( \hat{p}_1, \hat{p}_2, \hat{p}_s \) in Hamiltonian (3.2.1), treating the coordinates \( \hat{q}_1, \hat{q}_2, \hat{q}_s \) as parameters, and diagonalizing to find the electronic eigenvalues as a function of the vibrational coordinates \( q_1 \) and \( q_2 \). Figure 2 shows a contour plot of the lower Born-Oppenheimer surface. The adiabatic character of the electronic eigenfunction for the lower surface is indicated by wavefunctions for a particle in a 2D box placed around the outside of the plot (the adiabatic wavefunction depends only on angle in the \( b_1g-b_2g \) coordinate system). One can see that starting at the top of the figure the adiabatic electronic wavefunction is \( y \)-polarized. Moving clockwise, \( x \) character builds until at the bottom of the figure the wavefunction is \( x \)-polarized. Continuing the clockwise motion, the wavefunction mixes in more \( y \) character so that when returning to the top of the figure the wavefunction is \( y \)-polarized again, except that continuity requires a sign change of the electronic wavefunction. This is a manifestation of Berry’s phase. The requirement that the overall vibronic eigenfunction be single-valued imposes a compensating sign change on the vibrational wavefunction.

3.2.2) Reduced Density Matrix and Redfield Equations

In condensed phase dynamics the molecular wavefunction is entangled with its environment and the molecule is only part of a system described by a density matrix

\[
\dot{\rho} = \sum_\psi p_\psi |\psi\rangle\langle\psi| \quad \text{with probabilities } p_\psi \text{ for various wavefunctions } |\psi\rangle.
\]

With \( \dot{\rho} \), one can trace over the degrees of freedom that are not directly measured to obtain a reduced density matrix \( \hat{\sigma} \) from which all measurements can be calculated using \( \langle \hat{O} \rangle = Tr[\hat{O}\hat{\sigma}] \). Impulsive pump-probe measurements in SiNc and HNc can be calculated from the electronic reduced density matrix \( \hat{\sigma} \) obtained from \( \dot{\rho} \) by integration over all vibrational coordinates,

\[
\hat{\sigma} = \int \langle R_{\text{vib}} |\hat{\rho}| R_{\text{vib}} \rangle dR_{\text{vib}}.
\]
Figure (3.2) Contour plot of the lower Born-Oppenheimer potential energy surface as a function of the two vibrational coordinates most active in driving electronic motion via the conical intersection in SiNc. The surface was generated from Hamiltonian (3.2.1) using $\omega_1 / 2\pi c = 140 \text{ cm}^{-1}$, $\omega_d_1 / 2\pi c = 6 \text{ cm}^{-1}$, $\omega_2 / 2\pi c = 138 \text{ cm}^{-1}$, $\omega_d_2 / 2\pi c = 7 \text{ cm}^{-1}$, chosen to reproduce measured dynamics when other Jahn-Teller active vibrations are included. Contours are spaced at 0.5 cm$^{-1}$, with dashed contours below the saddle points along $b_{1g}$ to emphasize the minima along $b_{2g}$. Electronic eigenfunctions for a particle in a 2D box are drawn around the edges to illustrate how their character changes around the singularity at the conical intersection.
Experimentally, this integration is complete when the ultrafast pulse spectrum uniformly covers the molecular absorption, emission, and excited state absorption and the pulse duration is transform limited in the time domain. Therefore, it is useful to view the adiabatic approximation from an electronic viewpoint (in which all vibrational coordinates are hidden but the electrons are fully described) rather than the more common vibrational viewpoint (in which a vibrational wavepacket on one electronic surface can be fully described, but the electronic state is hidden in a surface label). This full description of the electrons is necessary because electronic wavepacket motion, by itself, does not prove a conical intersection, or even vibronic coupling, is present. Indeed, electronic wavepackets can be excited in atoms.\textsuperscript{8}

If two vibrational coordinate independent electronic states form an approximately complete basis for the doubly degenerate excited state over the range of vibrational coordinates accessed in the experiment, four elements of the electronic reduced density matrix are sufficient to describe the experiment: the two “populations” $\sigma_{xx} = \langle x | \hat{\sigma} | x \rangle$ and $\sigma_{yy} = \langle y | \hat{\sigma} | y \rangle$, plus the two “coherences” $\sigma_{xy} = \langle x | \hat{\sigma} | y \rangle$ and $\sigma_{yx} = \langle y | \hat{\sigma} | x \rangle$. After a linearly polarized pump pulse, the initial value of each of these elements is a function of the Euler angles that indicate molecular orientation, and their subsequent evolution is determined by the underlying vibronic dynamics of the density matrix $\hat{\rho}$.\textsuperscript{40} The pump-probe experiments described in this chapter provide information on the orientation dependence of the relaxation dynamics of $\hat{\sigma}$.\textsuperscript{4}

Electronic equilibration is defined by the approach of $\hat{\sigma}$ to equilibrium: it requires both dephasing (to send the off-diagonal elements to zero; this is the signature of the $g$-coordinate) and population transfer (to equilibrate the diagonal elements; this is the signature of the $h$-coordinate). In Redfield’s theory\textsuperscript{31} of density matrix relaxation, the Hamiltonian is separated
into a reference Hamiltonian $\hat{H}_s$ (diagonal in the same basis as the density matrix), a bath Hamiltonian $\hat{H}_b$, and a perturbation $\hat{H}'$,

$$\hat{H}' = \begin{bmatrix} \hat{\Lambda} & \hat{V} \\ \hat{V} & -\hat{\Delta} \end{bmatrix}$$  \hspace{1cm} (3.2.2)

where $\langle \hat{\Lambda} \rangle = \langle \hat{V} \rangle = 0$. This perturbation describes the interaction of the system (the electrons) with the bath (the vibrations). It is this interaction that relaxes a nonequilibrium $\hat{\sigma}$ and leads to equations of motion for reduced density matrix elements.

The experiments are related to linear combinations of density matrix elements such as the population difference $(\sigma_{xx} - \sigma_{yy})$, the real coherence $(\sigma_{xy} + \sigma_{yx})$ and the imaginary coherence $(i\sigma_{xy} - i\sigma_{yx})$. Assuming $|x\rangle$ and $|y\rangle$ to be a degenerate basis set for which $\hat{H}_s$ is diagonal, taking $\hat{V}$ to be real, assuming $[\hat{\Lambda}, \hat{V}] = 0$ and using equation 2.19 in Redfield\textsuperscript{31} yields

$$\frac{d}{dt}(\sigma_{xx} + \sigma_{yy}) = 0$$
$$\frac{d}{dt}(\sigma_{xx} - \sigma_{yy}) = -k_{VV}(\sigma_{xx} - \sigma_{yy}) + k_{DV}(\sigma_{xy} + \sigma_{yx})$$
$$\frac{d}{dt}(\sigma_{xy} + \sigma_{yx}) = -k_{DD}(\sigma_{xy} + \sigma_{yx}) + k_{DV}(\sigma_{xx} - \sigma_{yy}),$$
$$\frac{d}{dt}(i\sigma_{xy} - i\sigma_{yx}) = -(k_{DD} + k_{VV})(i\sigma_{xy} - i\sigma_{yx})$$

with rate constants

$$k_{VV} = 2 \int_{-\infty}^{\infty} \langle \hat{V}(0)\hat{V}(\tau) \rangle d\tau,$$
$$k_{DD} = 2 \int_{-\infty}^{\infty} \langle \hat{\Delta}(0)\hat{\Delta}(\tau) \rangle d\tau,$$
$$k_{DV} = 2 \int_{-\infty}^{\infty} \langle \hat{\Delta}(0)\hat{V}(\tau) \rangle d\tau,$$ \hspace{1cm} (3.2.4)

where $\hat{V}$ and $\hat{\Lambda}$ have dimensions of radians per unit time and the angular brackets indicate ensemble averaging. If $\hat{\Lambda} = 0$ or $k_{DV} = 0$, $k_{VV}$ quantifies the decay of the population difference.
Similarly, if $\hat{V} = 0$ or $k_{PV} = 0$, $k_{DD}$ quantifies decay of the real coherence. $k_{PV}$ couples real coherence with the population difference if $\hat{\Lambda}$ and $\hat{V}$ are correlated. $^41$

To apply Redfield theory to Hamiltonian (3.2.1), we move the symmetric modes from $\hat{H}_{SB}$ to $\hat{H}_S$ (since they do not contribute to the mixing between $|x\rangle$ and $|y\rangle$) and identify what remains in $\hat{H}_{SB}$ with $\hat{H}'$ in equation (3.2.2) yielding

$$
\begin{align*}
    k_{yy} &= (2\omega_d x_2 d_2)^2 \int_0^\infty \langle \hat{q}_2(0)\hat{q}_2(\tau) \rangle d\tau, \\
    k_{DD} &= (2\omega_1 d_1)^2 \int_0^\infty \langle \hat{q}_1(0)\hat{q}_1(\tau) \rangle d\tau, \\
    k_{PV} &= (2\omega_1 d_1)(2\omega_d x_2 d_2) \int_0^\infty \langle \hat{q}_1(0)\hat{q}_2(\tau) \rangle d\tau.
\end{align*}
$$

A key result in equation (3.2.5) is that vibrational motion, which can only decrease a coordinate’s correlation function, decreases the rate of relaxation via the conical intersection. The rate constants in equation (3.2.5) are only applicable after the correlation function has decayed to zero.$^{31,33}$ The femtosecond spectroscopy described here probes the nonexponential dynamics at timescales faster than the vibrational motions which determine these correlation functions.$^{42}$

3.2.3) Effect of Electronic Relaxation on the Anisotropy

The experiments discussed in this chapter measure the polarization anisotropy of femtosecond pump-probe signals. The pump-probe signal $S_{pp}$ is defined as the change in transmitted probe intensity caused by previous interaction with a pump and depends on the delay $T$ between the pump and probe pulses.$^7$ This “transient transmission” pump-probe signal is the net sum of positive GSB, positive ESE, and negative ESA contributions (defined in section 3.1.1; other methods of measuring pump-probe signals combine the three with different signs). As in vibrational spectroscopy, the term “doubly excited” is taken to indicate the level of excitation.
energy for the final states reached by ESA, and does not distinguish between electron configurations with one or two excited electrons, which are strongly mixed by configuration interaction in porphyrins and phthalocyanines.43

Since the first excited singlet state of SiNc has a symmetry required (Jahn–Teller9-11,36) conical intersection at the fourfold symmetric ($D_{4h}$ point group) equilibrium geometry of the electronic ground state, an electronic wavepacket can be excited directly at the conical intersection. This allows the dynamics occurring at the intersection to be measured without convolution with slower vibrational transport to and from the intersection. In each randomly oriented molecule, the pump laser coherently excites transitions to degenerate electronic states polarized along the two perpendicular axes.2 Upon electronic excitation, asymmetric vibrations lower the total energy by elongating the molecule parallel to the electronic wavepacket momentum.3,9-11,36,44 The asymmetric modes excited depend on the molecular orientation: vibrations that lower the symmetry to that of a rectangle ($b_{1g}$) are excited if the projection of the laser field onto the molecular frame lies along $x$ or $y$; vibrations that lower the symmetry to that of a diamond ($b_{2g}$) are excited if that projection lies halfway between $x$ and $y$. At a general orientation, both $b_{1g}$ and $b_{2g}$ symmetry vibrations are excited.3

Polarized pump-probe experiments depend on the elements of $\hat{\sigma}$ immediately after the pump and at the time of the probe pulse. To incorporate the former effect, we indicate the initially excited element of $\hat{\sigma}$ by a subscript in parentheses to the right of the current element: for example, $\sigma_{x(3y)}$ indicates the current population of state $x$ created by initial excitation of state $y$.4 The evolution of the reduced density matrix for the doubly degenerate state is thus described by $16 = (4 \text{ current}) \times (4 \text{ initial})$ quantities for each fixed molecular orientation. Calculations for an isotropic sample require orientational averaging over all possible angles between
molecular frame transition dipole vectors and laboratory frame electric field vectors of the polarized pulses. Upon angular averaging, the excited state emission signal becomes

\[
S_{\parallel}^{\text{ESE}} = \frac{1}{5}\left(\sigma_{xx} + \sigma_{yy}\right) + \frac{1}{15}\left(\sigma_{xy} + \sigma_{yx}\right) + \frac{1}{15}\left(\sigma_{yx} + \sigma_{xy}\right)
\]

\[
S_{\perp}^{\text{ESE}} = \frac{1}{15}\left(\sigma_{xx} + \sigma_{yy}\right) - \frac{1}{30}\left(\sigma_{xy} + \sigma_{yx}\right) + \frac{2}{15}\left(\sigma_{yy} + \sigma_{xx}\right) - \frac{1}{30}\left(\sigma_{yx} + \sigma_{xy}\right)
\]

The angular brackets indicate ensemble averaging, while orientational averaging gives rise to the constant prefactors on each term. The information content of the experiment can be clarified by introducing four real quantities that survive angular averaging: the excited state population,

\[
p = \left(\sigma_{xx} + \sigma_{yy}\right) + \left(\sigma_{xy} + \sigma_{yx}\right)
\]

the normalized orientational population difference,

\[
d_-(T) = \left[\left(\sigma_{xx} + \sigma_{yy}\right) - \left(\sigma_{xy} + \sigma_{yx}\right)\right] / p
\]

the normalized real coherence,

\[
c_+(T) = \left[\left(\sigma_{xy} + \sigma_{yx}\right) + \left(\sigma_{yx} + \sigma_{xy}\right)\right] / p
\]

and the normalized orientational coherence difference,

\[
c_-(T) = \left[\left(\sigma_{xy} + \sigma_{yx}\right) - \left(\sigma_{yx} + \sigma_{xy}\right)\right] / p
\]

For experiments with linearly polarized light, the signals depend on \(p, d_-,\) and \(c_+\) (experiments with circularly polarized light access \(c_-.\)). \(d_-\) and \(c_+\) are interchanged by a \(\pi / 4\) rotation of the electronic basis, while \(c_-\) is unaffected. Both \(d_-\) (which decays through population transfer) and \(c_-\) (which decays through dephasing) are initially one and decay to zero at equilibrium. However, if \((D \omega)_z = 0\) there is no population transfer and \(d_- = 1\) is constant; similarly, if \((D \omega)_i = 0\), there is no dephasing and \(c_+ = 1\).
Decomposing each pair of parallel and perpendicular signals into a magic angle signal 
\[ S_{MA} = (S_n + 2S_\perp) / 3 \] and an anisotropy leads to simple expressions in terms of these three new variables. For the ESE signal given in equation (3.2.6) we obtain

\[ S_{MA}^{ESE} = (1/9)p \]
\[ r_{ESE}^p(T) = (1/10)[1 + 3d_m(T) + 3c_c(T)]. \]  

(3.2.11)

The magic angle signal depends only on excited state population, and the anisotropy decays with population transfer and dephasing. The ground state bleach has \[ S_{MA}^{GSB} = (2/9)p \] and a constant anisotropy,

\[ r_{GSB}^p(T) = (1/10). \]  

(3.2.12)

As discussed by Qian and Jonas,\(^2\) the anisotropy for the ESA contribution depends on the symmetry of the final state through a cyclic set of 4 transition dipoles of the form

\[ \langle a|\mu|b\rangle \langle b|\mu|c\rangle \langle c|\mu|d\rangle \langle d|\mu|a\rangle \] with an overall sign that is independent of the arbitrary wave function phases and physically significant.\(^2-4\) The transition dipoles and ESA anisotropy for the four symmetry changes with transition dipoles in the \(xy\) plane are shown in Figure 3. This anisotropy also applies to frequency resolved Raman scattering,\(^19\) but not vibronic quantum beats. Vibronic quantum beats either involve a different time-ordering on the ground state or states not degenerate by symmetry on the excited state, aspects treated by Farrow et al.\(^5\) The latter paths provide additional information on electronic relaxation processes.\(^5\) The time-dependence of the anisotropy is entirely contained in signals which evolve on the excited state. The ESA contribution, depending on symmetry, can either reinforce or cancel out the contribution to the signal from either \(d\) or \(c\). A consequence of this is that the possible symmetries of the doubly excited states \textit{must} be considered when interpreting data. These contributions can be averaged once the relative strengths of GSB, ESE and ESA transitions are
Figure (3.3) Cyclic sets of transition dipoles in the $x$-$y$ plane. The cyclic set of directions, relative magnitudes, and overall sign through a degenerate state are dictated by the overall change in symmetry from bottom to top of each diamond, but the individual transition dipoles are basis set dependent. In each diagram, the magnitudes of the two transition dipoles labeled $\mu$ ($\mu'$) are equal by symmetry. The anisotropy $r(T)$ for a time-ordered process in which the pump pulse interacts with the lower two transition dipoles, followed by probe interaction with the upper two transition dipoles is given under each set in terms of the reduced density matrix observables $c_{\gamma}(T)$ and $d_{\gamma}(T)$. This anisotropy applies to excited state absorption and frequency resolved Raman scattering, but not vibronic quantum beats. (Vibronic quantum beats either involve states not degenerate by symmetry on the excited state or a different time-ordering on the ground state.)
known (for example, from a spectrally resolved pump-probe experiment, which contains the linear absorption and emission spectra of the excited state).

To illustrate the critical importance of excited state absorption, and the symmetry of the doubly excited state, we consider three scenarios. For all three, relative signal strengths are approximated by those from a simple model: two non-interacting electrons in a 2D box. Just as in porphyrins and phthalocyanines, there are four doubly excited states in this model, one each with A
_\text{1g}, B
_\text{1g}, \text{ and } B
_\text{2g} symmetries plus one “extra” state of either B
_\text{1g}, or B
_\text{2g} symmetry. The ratio of signal strengths is 4:2:-1:-1:-1:-1 for GSB:ESE:ESA:ESA:ESA:ESA.

If the “extra” state has B
_\text{2g} symmetry,

\[ r_{\text{tot}}(T) = (1/10)[1 + 3d_{-}]. \] \hspace{1cm} (3.2.13)

The anisotropy in this case decays from an initial value of 0.4 to a final value of 0.1. The anisotropy in ESA and ESE coming from coherences cancels out and only population transfer is observable in the electronic anisotropy. If the “extra” state instead had B
_\text{1g} symmetry, we would have found

\[ r_{\text{tot}}(T) = (1/10)[1 + 3c_{+}]. \] \hspace{1cm} (3.2.14)

In this case dephasing dynamics dominates the signal. For the third example, consider the case in which no excited state absorption occurs. In that case we find

\[ r_{\text{tot}}(T) = (1/10)[1 + d_{-} + c_{+}]. \] \hspace{1cm} (3.2.15)

The initial anisotropy is only 0.3, the final value is still 0.1, and both relaxation processes are observable.

If the pulse is shorter than half a vibrational period, molecular vibrations can modulate the pump-probe signal by changing the frequency, strength, or direction of a transition. In the impulsive limit, when the pulse spectrum covers the entire absorption, emission, and excited state absorption spectra, pump-probe should become insensitive to Frank-Condon active
vibrations; however, quantum beats can arise from the breakdown of the adiabatic and Condon approximations. In this way, Jahn-Teller active asymmetric vibrations may be observed indirectly via their effect on the electrons. These quantum beats can arise with different phases and/or different amplitudes in parallel and perpendicular signals, and have an anisotropy. The anisotropy of each vibration is calculated with

\[
r_{\text{vib}}(\omega) = \frac{A_{\|}^v - A_{\perp}^v \cos(\phi_{\|}^v - \phi_{\perp}^v)}{A_{\|}^v + 2A_{\perp}^v \cos(\phi_{\|}^v - \phi_{\perp}^v)},
\]

(3.2.16)

where \( A_{\|}^v \) (\( A_{\perp}^v \)) indicates the amplitude of the oscillation at frequency \( \nu \) in the perpendicular (parallel) signal and \( \phi_{\|}^v \) (\( \phi_{\perp}^v \)) is its phase. Equation (3.2.16) has the same form as equation (3.1.1) except for the cosine, which accounts for the phase difference between the quantum beat in parallel and perpendicular signals. The vibrational quantum beat anisotropy allows determination of the vibrational symmetry (\( b_{1g} \) and \( b_{2g} \) vibrations have \( r_{\text{vib}} = \infty \) vs. \( r_{\text{vib}} = 1/10 \) for \( a_{1g} \)). For vibrations on the excited state, \( r_{\text{vib}} \) probes vibronic relaxation in a different way than the “electronic” anisotropy decay. Because the amplitudes of the vibrational quantum beats depend on the couplings in the Hamiltonian, their measurement links the electronic and vibrational dynamics.

3.3 Experiment

3.3.1) A D_{4h} Silicon Naphthalocyanine (SiNc)

Farrow et al. performed pump-probe measurements using linearly polarized pulses with 25 fs duration that spectrally covered the \( \pi \) to \( \pi^* \) \( Q(0,0) \) transition of SiNc in benzonitrile solution. The \( Q(0,0) \) transition connects the nondegenerate \( ^1A_{1g} \) ground state to the doubly degenerate \( ^1E_u \) symmetry first excited singlet state without any change in high frequency vibrational quantum numbers. Low pulse fluence, low absorption, and a complete sample change
between laser shots were needed to prevent distortion of the fast anisotropy decay, while a high signal-to-noise ratio was required to recover low-amplitude quantum beat modulations. Naphthalocyanine’s size makes diffusive rotation in the benzonitrile solvent slow (450 ps), 1 so that any faster changes in the polarization anisotropy must be attributed to vibronic dynamics without molecular rotation.

The pump-probe anisotropy in Figure 4 decays from \( r(0) \sim 2/5 \) (slightly before time zero) to \( r(\sim 2 \text{ps}) = 0.1005 \pm 0.0008 \), which is characteristic of randomized electronic alignment within the naphthalocyanine plane \( (r = 1/10) \). 4 The vibrational quantum beats can be fit at long times and then subtracted from the measured anisotropy to reveal that the fast dynamics are a complicated monotonic decay, which is mostly complete in about 100 fs. For convenience, this monotonically decaying component will be referred to as the electronic anisotropy and the quantum beats will be referred to as vibrational, without implying a separation of the vibronic dynamics. Subtracting a fit to the electronic anisotropy from the total anisotropy and taking a Fourier transform of the residuals shows the power spectrum of vibrational quantum beats (inset to Figure 4).

Fitting of the parallel, perpendicular, and magic-angle signals recovers two vibrations \((686 \text{ cm}^{-1} \text{ and } 617 \text{ cm}^{-1})\) assigned to Frank-Condon active \( a_{1g} \) modes based on \( r_{vib} = 1/10 \). 4,5 The 686 cm\(^{-1}\) mode dominates the individual pump-probe traces, but is a minor peak in the total anisotropy power spectrum while the 617 cm\(^{-1}\) peak does not appear in the anisotropy power spectrum. Three Jahn-Teller active modes \((535 \text{ cm}^{-1}, 301 \text{ cm}^{-1} \text{ and } 140 \text{ cm}^{-1})\) are assigned based on anisotropies consistent with infinity, due to a vanishing denominator (within error) in equation (3.2.16). 4,5 These three modes are minor components of the individual pump-probe traces, but dominate the power spectrum of the anisotropy. The stabilization energies for each vibration were determined from the amplitude of the vibrational modulation of the signal, the
Figure (3.4) Pump-probe polarization anisotropy in SiNc. The anisotropy is not shown before $T = -16$ fs, when low signal-to-noise in the denominator causes wild oscillations. The earliest reliable anisotropy is $r(-12$ fs) $= 0.395$, and the anisotropy has decayed to $r(0) = 0.380$ at $T = 0$ (maximum pump-probe temporal overlap). Inset) Fourier transform power spectrum of the anisotropy after subtraction of the monotonic anisotropy decay. The peaks at 147, 309 and 538 cm$^{-1}$ and 684 cm$^{-1}$ are reproducible.
pulse duration, the pulse spectrum, and the equilibrium absorption and emission spectra of the sample by extending established procedures\textsuperscript{46} for determination of vibrational reorganization energies for Franck-Condon active modes.

If a single relaxation mechanism dominates the dynamics, the data enable direct calculation of the relevant asymmetric vibrational correlation function, $M(t)$. For harmonic potential surfaces with the same curvature, the Brownian oscillator model uses the vibrational correlation function and displacement between curves for Franck-Condon active vibrational modes to predict signals in linear and nonlinear electronic spectroscopy.\textsuperscript{42} Smith and Jonas exploited symmetry to develop a Brownian oscillator model for Jahn-Teller active vibrational modes that applies whenever a single relaxation process dominates.\textsuperscript{3} This Brownian oscillator model leads to the coherence decay\textsuperscript{3} between components of the $E_u$ state

$$c_x(t) = \exp(-4\text{Re}[g(t)]), \quad (3.3.1)$$

where $g(t)$ is the absorption lineshape function for $b_{1g}$ vibrations. [The factor of 4 arises because the $E_u$ states are displaced twice as far from each other (at $q = \pm d$) as each is from the ground electronic state (at $q = 0$) and the lineshape function is proportional to the square of the displacement.] The lineshape function is zero at $t=0$ and has zero derivative, so the fast dynamics are determined by its second derivative. In the high-temperature limit, this is

$$d^2 \text{Re}[g(t)]/dt^2 = [2(D\omega)/(\hbar\beta)]M(t). \quad (3.3.2)$$

where $\beta$ is the inverse thermal energy and $(D\omega)$ is the Jahn-Teller stabilization energy (for several modes, the right hand side becomes a sum of such terms, one for each mode). $(D\omega)$ calculated from the initial anisotropy decay is 5 cm\textsuperscript{-1}, about that of the asymmetric 140 cm\textsuperscript{-1} and 300 cm\textsuperscript{-1} vibrations. $M(t)$ deduced from the anisotropy is shown in Figure 5; it is initially underdamped, then suddenly settles to near zero by approximately 150 fs, about when such a vibrational wavepacket first begins returning to the conical intersection. The oscillation and
Figure (3.5) Asymmetric vibrational correlation function $M(T)$ calculated from a smoothed fit to the anisotropy using Eqs. (3.2.14), (3.3.1), and (3.3.2). $M(T)$ has its maximum delayed to $T = 15$ fs by finite pulse duration and shows an initial underdamped oscillation (frequency roughly 220 cm$^{-1}$) before suddenly dying away at about 150 fs.
stabilization energy suggest coupling to these low frequency Jahn-Teller vibrations determines the fast electronic dynamics, while the sudden death of \( M(T) \) suggests the single relaxation hypothesis is incorrect.

Model Hamiltonians with the \( 300 \text{ cm}^{-1} \) vibration assigned as \( b_{1g} \) symmetry and the \( 140 \text{ cm}^{-1} \) vibration assigned as \( b_{2g} \) symmetry (or vice versa) could not produce the fast anisotropy decay. Since the vibrations of porphyrins and phthalocyanines often occur in nearly degenerate pairs, a model in which the \( 140 \text{ cm}^{-1} \) vibrations is a near degenerate pair was tried and found sufficient to account for most of the anisotropy decay. This model was used to guide phenomenological inclusion of population relaxation into a Brownian oscillator type model that could be used to calculate finite pulse effects, such as the amplitude of the totally symmetric vibration at \( 686 \text{ cm}^{-1} \). This model fit, to within experimental error, the linear absorption spectrum, the excited state absorption and emission spectra, the electronic anisotropy decay, and the vibrational quantum beat amplitudes and anisotropies. Interestingly, the dominant totally symmetric quantum beat at \( 686 \text{ cm}^{-1} \) (for which the stabilization energy can be determined from the absorption spectrum) cannot be fit without invoking complete electronic relaxation. This suggests that the anisotropy of pump-probe quantum beats will be useful for characterizing general conical intersections where the \( g \) and \( h \) coordinates are not both asymmetric.\(^{27}\)

3.3.2) A D\(_{2h}\) Free-Base Naphthalocyanine (H\(_2\)Nc)

The SiNc experiments showed that low frequency vibrational modes with modest (less than \( 10 \text{ cm}^{-1} \)) Jahn-Teller stabilization energies could drive fast (on the order of 100 fs) equilibration, and that studying the anisotropies of vibrational modes, even totally symmetric ones, could reveal signatures of the intersection. Smith \textit{et al.}\(^6\) studied a system where symmetry alone does not predict a conical intersection. Free-base naphthalocyanine (H\(_2\)Nc ) has D\(_{2h}\) symmetry (ignoring the peripheral R groups which do not join the delocalized \( \pi \) system); the
two central hydrogen atoms in free-base porphyrins and phthalocyanines are fixed in place by barriers of about 10 kcal/mol. Although D$_{2h}$ molecules have no required degenerate electronic states (and therefore no required conical intersection), the LUMO and LUMO+1 in H$_2$Nc are close enough that that the first two excited states are expected to mix though the pseudo Jahn-Teller effect.$^{11,48}$

The relevant electronic and vibrational symmetries can best be discussed by analogy to SiNc. Starting from D$_{4h}$, the hydrogens are a $b_{1g}$ (rectangle) static perturbation, totally symmetric ($a_g$) in D$_{2h}$. The diamond deformation remains asymmetric ($b_{2g}$ in D$_{4h}$, $b_{1g}$ in D$_{2h}$); the electronic ground state remains totally symmetric ($A_{1g}$ in D$_{4h}$, $A_g$ in D$_{2h}$); the degenerate E$_u$ state of D$_{4h}$ splits into B$_{2u}$ and B$_{3u}$ states with $y$ and $x$-polarized transitions from A$_g$ in D$_{2h}$. For many porphyrins and phthalocyanines this splits the $Q$ band into $Q_x$ and $Q_y$, but as the size of the aromatic system increases, the $Q_x$ - $Q_y$ frequency gap decreases and the two transition strengths become equal.$^{50}$ For H$_2$Nc in liquid solutions, the splitting disappears, although splittings can be seen in solid naphthalene (120 cm$^{-1}$)$^{51}$ and low-density polyethylene (243 cm$^{-1}$)$^{52}$.

The experiment was more difficult than for SiNc because the lack of axial ligands (‘R’ in Figure 1) causes increased aggregation, so the concentration was lower and the pathlength longer. The transients were wavelength dependent, so Smith et al. measured once spectrally covering the $Q(0,0)$ absorption (blue tuned 29 fs pulses) and once on the low-energy edge of $Q(0,0)$ (red tuned 38 fs pulses). The red-tuned pulses excited vibronic wavepackets near the classical turning points of the ground state vibrations, allowing for larger quantum beat amplitudes.

Figure 6 shows the measured anisotropies. Both red and blue tuned pulses give an initial anisoptropy near 0.3, which [from equation (3.2.15)] suggested that the experiment did not access any doubly-excited states. The lack of excited state absorption was confirmed by measuring a spectrally resolved pump-probe signal at 100 ps delay. The asymptotic blue-tuned
Figure (3.6) Pump-probe polarization anisotropy in H$_2$Nc from $T = -20$ fs, with the earliest reliable anisotropy $r(-13 \text{ fs}) = 0.34$ for the blue-tuned pulses and $r(-13 \text{ fs}) = 0.31$ for red-tuned pulses [$r(0) = 0.32$ for blue and 0.31 for red-tuning]. The inset shows a power spectrum obtained by subtracting the monotonic anisotropy decay and then taking a Fourier transform of the residuals. Peaks at 163 cm$^{-1}$ (blue) and 174 cm$^{-1}$ (red) match within the discrete frequency resolution of the grid (16 cm$^{-1}$ for blue and 22 cm$^{-1}$ for red).
anisotropy is $0.101 \pm 0.003$, which is 1/10 within error, suggesting the electronic wavepacket is fully delocalized in the plane of the molecule. The red-tuned anisotropy decays to 0.126 $\pm$ 0.003 during the experiment, which indicates incomplete equilibration. For a single relaxation mechanism, in the absence of excited state absorption, the anisotropy decays from 0.3 to 0.2 (equation (3.2.15) with either $c_+$ or $d_-$ fixed to 1). For both “red” and “blue” pulses, the anisotropy decays well below 0.2, which indicates that more than one relaxation mechanism is active, suggesting a conical funnel. For the “blue” pulses, both $c_+$ and $d_-$ fully decay, and the anisotropy reaches 0.1 (within error) by about 300 fs. The anisotropy for the “red” pulses, however, behaves differently. It decays past 0.2, indicating that both relaxation mechanisms are active, but does not reach 0.1, indicating that one or both relaxations are incomplete.

The two excited states accessed by the experiment are nondegenerate and may have a well defined energy gap hidden under the 450 cm$^{-1}$ wide $Q(0,0)$ band and/or unequal transition strengths. As an energy gap is needed to explain the pulse dependent final anisotropy (and transition strengths are almost equalized in H$_2$Nc when splittings can be resolved) Smith et al. focused on characterizing the energy gap while assuming equal transition strengths. This energy gap arises from the $b_{1g}$ (in D$_{4h}$) static perturbation of the hydrogens. The Hamiltonian also includes coupling through a $b_{2g}$ (in D$_{4h}$) vibration analogous to the 140 cm$^{-1}$ vibration of SiNc; the pump-probe transients reveal a vibration at 176 cm$^{-1}$ with $r_{vib}$ roughly equal to 8, indicative of $b_{1g}$ symmetry in D$_{2h}$. The simplest Hamiltonian that can account for the data is

$$
\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB},
\hat{H}_S = \omega_{os} \left( |x\rangle \langle x| + |y\rangle \langle y| \right),
\hat{H}_B = \left( \frac{1}{\omega} \mathbf{q} \cdot \mathbf{p} \right) \left( |x\rangle \langle x| + |y\rangle \langle y| \right),
\hat{H}_{SB} = \left[ \begin{array}{cc}
(-\delta / 2) & (\omega d \tilde{q}) \\
(\omega d \tilde{q}) & (\delta / 2)
\end{array} \right].
$$

(3.3.3)
The best fit to the data indicate an energy gap of $\delta / 2\pi c = 110$ cm$^{-1}$ and a stabilization energy of $(D\omega)/2\pi c = 9$ cm$^{-1}$ for the 176 cm$^{-1}$ asymmetric vibration. The simplest model consistent with this data, therefore, is an avoided crossing that drives fast (< 300 fs) but incomplete equilibration. If the static energy gap arises from the zero-point vibration of the hydrogens, one is led to a picture of a conical funnel, possibly with an energetically inaccessible intersection displaced away from the Franck-Condon region.

Inspection of the vibronic energy levels for the above model in Figure 7 shows that even weak nonadiabatic coupling ($\langle D\omega \rangle / \omega = 0.05$) can have dramatic effects, qualitatively inconsistent with the Born-Oppenheimer approximation, if Born-Oppenheimer vibronic levels associated with different electronic curves are nearly degenerate. The diabatic and Born-Oppenheimer potential curves are shown for the nonadiabatic Hamiltonian (3.3.3). The diabatic potential curves (dashed curves) and basis state energies (dashed lines) were calculated by neglecting the coordinate-dependent terms $\omega dq$ of $\hat{H}_{SB}$. The Born-Oppenheimer potential curves (gray) were calculated by neglecting nuclear momentum, treating nuclear coordinate operators as parameters, and diagonalizing to obtain the coordinate dependent electronic eigenvalues

$$U_{\pm}(q) = \frac{1}{2} \omega q^2 \pm \sqrt{(\delta / 2)^2 + (\omega dq)^2}$$

that make up the upper (+) and lower (-) Born-Oppenheimer potential curves. The adiabatic dimensionless normal coordinates$^{53}$ and harmonic vibrational frequencies are related to the diabatic ones by $q_{\pm} = \gamma_{\pm} q$ and $\omega_{\pm} = \gamma_{\pm}^2 \omega$, respectively, where

$$\gamma_{\pm} = [1 \pm (2\omega d^2 / \delta)]^{1/4}.$$ 

The Born-Oppenheimer vibronic energies (gray lines) in Figure 7 result from numerically diagonalizing to find the anharmonic vibrational energies on each potential energy surface.

The non-adiabatic vibronic eigenstate energy levels were found by numerical diagonalization in the both the diabatic direct product basis (with the off-diagonal vibronic
Figure (3.7) Diabatic (dashed) and Born-Oppenheimer (solid gray) potential energy curves, associated basis state energies (lines attached to each curve), and exact non-adiabatic vibronic energy levels (thick solid black line segments, not attached to any curve) for the vibrational coordinate most active in electronic equilibration for H₄Ne. For each diabatic basis state energy, diabatic basis state quantum numbers are given on the right-hand side. Constructed from Hamiltonian (3.3.3) with \( \delta / 2\pi c = 110 \text{ cm}^{-1} \), \( (D\omega) / 2\pi c = 9 \text{ cm}^{-1} \) and \( \omega / 2\pi c = 176 \text{ cm}^{-1} \).
coupling of Eq. (3.3.3) as the perturbation), and the Born-Oppenheimer vibronic basis (with the non-adiabatic coupling operator given by Eq. (VIII.7) of Born and Huang\textsuperscript{54} as the perturbation). In diabatic dimensionless normal coordinates, the non-adiabatic coupling operator has matrix elements

$$
\hat{A}_{k \nu, k' \nu'} = -\omega \langle \chi_{k \nu} | (\partial / \partial q) | \phi_{k} (q) \rangle \langle \phi_{k} (q) | (\partial / \partial q) | \chi_{k' \nu'} \rangle - \frac{1}{2} \omega \langle \chi_{k \nu} | (\partial^2 / \partial q^2) | \phi_{k} (q) \rangle \langle \phi_{k} (q) | \chi_{k' \nu'} \rangle,
$$

where $| \phi_{k} (q) \rangle$ is a Born-Oppenheimer electronic eigenfunction depending parametrically on the vibrational coordinate $q$ and $| \chi_{k \nu} \rangle$ is a Born-Oppenheimer vibrational eigenfunction with $\nu$ quanta of vibrational energy on electronic state $k$. The diagonal energy correction from the non-adiabatic coupling was included in this perturbation, not as part of the potential energy curves (see appendix VIII of Born and Huang\textsuperscript{54}); for this reason we refer to Born-Oppenheimer curves. This diagonal correction is relatively small and about the same size (ranging from $+5 \text{ cm}^{-1}$ to $+15 \text{ cm}^{-1}$) for the levels shown. The energies of the non-adiabatic vibronic eigenstates are indicated by solid black lines unassociated with any potential energy surface.

With respect to the diabatic curves, the lower Born-Oppenheimer curve is softened and the upper hardened. Therefore, all of the Born-Oppenheimer vibronic energies for the lower curve lie below the corresponding diabatic basis state energies, while all the Born-Oppenheimer vibronic energies for the upper curve lie above the corresponding diabatic basis state energies. However, on the lower diabatic curve, only the lowest non-adiabatic level (nominally $| x \rangle | \nu = 0 \rangle$) is shifted down from the diabatic basis state energy, the two other levels shown have been shifted up. On the upper diabatic curve, the two non-adiabatic level shifts are both downward from the corresponding diabatic basis state energies, qualitatively opposite the Born-Oppenheimer prediction. Even without numerical diagonalization, such failure can be predicted from the
interaction between diabatic states $|y\rangle|v = 0\rangle$ and $|x\rangle|v = 1\rangle$. The Born-Oppenheimer approximation qualitatively fails to describe the levels of this system.

It can be seen in Figure 7 that the lowest energy level can be reasonably described by the $v = 0$ vibration associated with either the lower diabatic or lower Born-Oppenheimer potential. However, higher energy basis functions for the Born-Oppenheimer basis occur in nearly-degenerate pairs that become strongly mixed by non-adiabatic interactions. For this system, adiabatic approximations qualitatively fail to describe the correct level structure, predicting nearly degenerate pairs of levels that do not occur; the diabatic basis offers a better starting point for nonadiabatic dynamics in $\text{H}_2\text{N}_c$. Modeling the anisotropy with the diabatic basis states and energy levels predicts some decay of the anisotropy, however the linear coupling term (which is the non-adiabatic term in the diabatic representation) is required to correctly reproduce the data.

### 3.4 Discussion

The semi-classical Landau-Zener theory of electronic curve crossing emphasizes the role of vibrational wavepacket velocity in making the transition from one adiabatic electronic potential energy curve to another at an avoided crossing. The Landau-Zener treatment predicts that the curve-crossing probability for a single passage through an avoided crossing is

$$P = \exp\left(-\frac{2\pi H^2}{\hbar v |\Delta F|}\right), \quad (3.4.1)$$

where $H$ is the perturbing coupling that produces the avoided crossing, $v$ is the vibrational wavepacket velocity, and $|\Delta F|$ is the difference in force (potential slope) between the two unperturbed curves at the avoided crossing. According to Eq. (3.4.1), curve crossing becomes more probable for smaller couplings, higher wavepacket velocities, and larger differences in force. Although Eq. (3.4.1) suggests that the curve crossing probability vanishes at zero vibrational wavepacket velocity, it cannot be applied in this limit; a semi-classical theory
inherently assumes that the vibrational wavepacket width is negligible, a condition that can only be met (according to the uncertainty principle) by wavepackets with high momentum components. The Landau-Zener theory is self-consistent in predicting curve crossing within its domain of validity, but says nothing about low velocity vibrational wavepackets, wavepacket width in curve crossing phenomena, or actual intersections between curves.

When a vibrational wavepacket’s velocity is sufficiently low, its width will dominate the vibrational wavefunction derivative in the non-adiabatic coupling. Here, we expand on our previous discussion\textsuperscript{3,4} of electronic curve crossing dynamics at zero velocity. The discussion will concentrate on short time results, but use the quantum mechanical form of the lineshape function \( g(t) \) in Eq. (3.3.1) instead of the high temperature limit. In the high temperature limit, the distribution of vibrational coordinates can be regarded as an inhomogeneity, but the dynamics originating from excitation of the \( v = 0 \) wavefunction at zero temperature must be regarded as homogeneous. In the absence of damping, the second differential coefficient of the real part of the quantum lineshape function given by Eq. (5.23) of Tanimura and Mukamel\textsuperscript{55} is

\[
\frac{d^2 \text{Re}[g(t)]}{dt^2} \bigg|_{t=0} = (D\omega)\omega \coth(\beta\hbar\omega / 2)
= (\omega d)^2 \left[(1/2) \coth(\beta\hbar\omega / 2)\right]
\]

where \((D\omega)\) is the stabilization energy (in frequency units), \(\omega\) is the frequency, and \(\beta\) is the inverse temperature. The second line uses dimensionless normal coordinates, in which \(q = \pm 1\) at the classical turning points of the \(v = 0\) eigenstate. Here \(d\) is the displacement between harmonic curves and the width of the vibrational coordinate probability distribution is quantified by its variance \(\sigma^2 = (1/2) \coth(\beta\hbar\omega / 2)\). Recognizing that for \(V(q) = (1/2)\hbar\omega(q \pm d)^2\), the difference in force between the two curves at the conical intersection is \(|\Delta F| = 2\hbar\omega d\), the early time coherence decay can be written

\[
c_\perp(t) = \exp\left[-\frac{|\Delta F|}{\hbar} \frac{1}{\sigma^2(t^2 / 2)}\right]
\quad (3.4.2)
\]
revealing a universal fast dephasing driven by the product of the variance and the square of the difference in force of the energy tuning coordinates \( (b_{1g} \text{ in } D_{4h}, \text{ hence the subscript 1}) \). If several normal modes are involved, each acts independently on this timescale so that \(|\Delta F / \hbar|^2 \sigma^2\) should be replaced by \(\sum |\Delta F_i / \hbar|^2 \sigma^2_i\) (a result independent of the vibrational basis). A rotation of the electronic basis, always possible around a conical intersection, allows the result for dephasing driven by \( b_{1g} \) modes [Eq. (3.3.1)] to be applied to population transfer driven by \( b_{2g} \) modes. Because the dynamics along \( g \) and \( h \) are also independent to order \( r^2 \), one obtains

\[
d(t) = \exp[-|\Delta F_z / \hbar|^2 \sigma^2_z (t^2 / 2)], \quad (3.4.3)
\]
a fast population transfer driven by the product of the variance and the square of the difference in force on the derivative coupling coordinates \( (b_{2g} \text{ in } D_{4h}, \text{ hence the subscript 2}) \).

The vibrational frequency does not appear in Eqs. (3.4.2) and (3.4.3) due to the neglect of the higher order terms in the Taylor expansion of the lineshape function. In fact, it is possible for the reduced density matrix to reach equilibrium before such terms, or the interaction between \( g \)- and \( h \)-coordinate driven electronic processes, become significant. Near a conical intersection, the difference in forces arises from the coordinate dependence of the coupling [see Eq. (3.2.1)]. Eqs. (3.4.2) and (3.4.3) show that the variation of vibronic coupling across the width of the vibrational wavepacket can drive electronic equilibration on a timescale faster than vibrational wavepacket motion. This role of wavepacket width is a homogeneous effect, and occurs even when a minimum uncertainty wavepacket is placed on the conical intersection by excitation from the \( v = 0 \) level at zero temperature \([\sigma^2 = (1/2)]\). Vibrational wavepacket width is important because the coupling and energy gap are zero at the intersection itself – the wings of the vibrational wavepacket feel the driving force. Eqs. (3.4.2) and (3.4.3) do not rely on the entire surface being harmonic, but rather on three local assumptions: 1) a harmonic approximation to the curves along \( g \) and \( h \) over the width of the wavepacket; 2) wavepacket centering on the conical
intersection; and 3) the conical intersection reflection symmetries assumed in deriving Eq. (3.3.1).

The decay of population differences between diabatic basis states given by Eq. (3.4.3) is qualitatively different from the Landau-Zener probability for non-adiabatic curve crossing. However, neither formula is applicable in a parameter range where the other is valid. Comparisons involving both wavepacket width and wavepacket velocity effects may be possible by extending the harmonic approximation for the short-time dynamics to include off-center vibrational wavepackets using the multi-level nonlinear response functions derived by Sung and Silbey\textsuperscript{56} or Mukamel and Abramavicius.\textsuperscript{57}

3.5 Conclusion

Time resolved measurements of electronic wavefunction alignment with polarized light are a promising way to characterize the coupled vibronic dynamics at conical intersections and funnels. Such measurements reveal vibrations coupled to the electronic motion through their effect on electronic alignment. The vibrational quantum beat amplitude reflects the vibronic coupling strength and the anisotropy determines the vibrational symmetry. This symmetry determination is based on the same principle as the Raman depolarization ratio, but provides new information about excited state processes that complements and can sometimes predict the initial electronic alignment dynamics. However, recent calculations indicate that asymmetric vibrational quantum beats on the excited electronic state (but not on the ground electronic state) can be rapidly suppressed by small environmental asymmetries.\textsuperscript{58} Experiments on SiNc and H\textsubscript{2}Nc have highlighted the role of vibrational wavepacket width in rapidly driving electronic motion via conical intersections and funnels with small couplings.
3.6 References


CHAPTER 4

NODELESS WAVEFUNCTIONS AND NESTED FUNNELS IN A MODEL
PSEUDO-JAHN-TELLER HAMILTONIAN

4.0 Abstract

We present a visualization scheme to aid the interpretation of fully quantum mechanical nonadiabatic wavefunctions and dynamics and apply it to a model 2-state pseudo-Jahn-Teller Hamiltonian. Particular attention is placed on the exact treatment of electronic energy gaps of approximately one vibrational quantum. The stationary states have vibrational probability densities without zeros, indicating an underlying nodeless character. In regions of the vibrational coordinate where one would expect a vibrational node, there is instead a rapid change in electronic character without a significant drop in vibrational probability density. Exact nonadiabatic wavefunction dynamics show this nodeless behavior is associated with population transfer between zero-order electronic states. The combination of an electronic state separation of about one vibrational quantum with weak nonadiabatic coupling leads to a “nested funnel” which directs ultrafast population transfer to the lower adiabatic surface. A near-degeneracy between electronic-vibrational product basis states allows the rapid population transfer found by Smith et al., even for the relatively weak coupling of \( (D\omega)/\omega \approx 0.05 \).
**4.1 Introduction**

In the quantum description of molecular structure and dynamics, it is common to use an adiabatic approximation\(^2\), in which it is imagined that the nuclei move infinitely slowly compared to electrons (or the electrons infinitely quickly with respect to nuclei). If that were the case, as the nuclei moved, the electrons would always maintain equilibrium and the nuclear motion would not cause an electron in a stationary state to “jump” between electronic energy levels. In this sense the Born-Oppenheimer and related approximations are specific applications of the quantum mechanical adiabatic theorem\(^3\). Then we may solve an electronic Schrödinger equation with a “clamped nuclei” Hamiltonian\(^4\), which neglects the action of the nuclear kinetic energy operator on the electronic wavefunction, and may use its coordinate-dependent energy eigenvalues as potential functions for a series of nuclear Hamiltonians.

The electronic wavefunction is, however, a function of nuclear coordinates, and the neglected terms couple the vibrational and electronic wavefunctions. A useful physical picture for the breakdown of the adiabatic approximation is of an electronic wavefunction which does not “keep up” with changes in nuclear position,\(^5\) in the sense that it does not have sufficient time to create a standing wave before the nuclei move. This may happen when two electronic states are nearly degenerate. If a system is placed in a superposition of two nearly degenerate electronic states, the electronic wavefunction will oscillate at the difference frequency, and does not complete a full cycle of its motion until the reciprocal of that frequency. If this is comparable to or slower than the vibrational motion, the adiabatic approximation may fail, especially if there is a
resonance between electronic and vibrational degrees of freedom such that the electronic
difference frequency is close to a vibrational frequency.

One does not necessarily have to prepare such a superposition directly. For example, consider optically exciting to a bright state coupled to a dark state: the
eigenstates of the system will be of mixed character, but in any linear spectroscopic
experiment light will only interact with the bright components of those states. The system
will be in a superposition from the time it begins interacting with the light field until the
two excited states decohere.

The most widely used theoretical methods\textsuperscript{6} for propagating wavepackets in
nonadiabatic dynamics are semi-classical and rely on deriving a force for nuclear motion
from a potential energy curve set up by the electrons. Such curves may be diabatic or
adiabatic. Nonadiabatic effects are then introduced as a perturbation, and cause
transitions between curves. The dominant reason this is done, even when more accurate
methods\textsuperscript{7} are available, is for the physical intuition gained from a potential energy curve
and the relative ease of understanding the result from a semi-classical point of view.

Here we will describe full-quantum propagation of electronic-vibrational
wavepackets (vibronic wavepackets) and a visualization scheme to display the complete
electronic and vibrational motion without any reference to potential energy curves.
Plotting both the vibrational and electronic components of a wavefunction in a single
colored curve provides insight into the exact wavefunctions without recourse to low-
order perturbation expansions. Further, by plotting two dimensions of the dipole
expectation value for a wavepacket, we can understand the forces acting on a propagating
vibronic wavepacket without appeal to potential energy curves. We use these plots to
study the nonadiabatic wavefunctions of the two-state pseudo-Jahn-Teller linear coupling Hamiltonian\(^8\), and study its nonadiabatic dynamics in comparison to dynamics under an adiabatic approximation. This Hamiltonian has recently been used by Smith et al.\(^1\) to model femtosecond pump-probe polarization anisotropy experiments in a free base naphthalocyanine dye. We will pay particular attention to weak coupling for the case of an electronic energy splitting comparable to one vibrational quantum of energy.

We also study the applicability of the Condon approximation\(^9\) when calculating initial conditions for propagation. Under the Condon approximation, the vibrational coordinate-dependent electronic transition dipole of the adiabatic approximation is replaced with a constant, taken from the equilibrium nuclear configuration of the ground electronic state. We find that for even relatively weak coupling (Jahn-Teller stabilization energy \(D\omega\) roughly 5% of the vibrational frequency), the Condon approximation can produce qualitative errors that do not manifest key features of the dynamics.

The stationary eigenstates of the system are found to have nodeless vibrational wavefunctions; the only places where the probability of finding the nuclei vanishes are at infinity. The coupling of electronic and vibrational motions produces a change in electronic character, not a complete loss of vibrational probability density, wherever one would have expected a node. Nodeless wavefunctions have been noted in the context of nonadiabatic coupling before\(^10,11\), but to our knowledge have not been studied in near-degenerate systems. We are not aware of prior work discussing the nature of the electronic wavefunction where a vibrational node vanishes or the time-domain behavior of such systems.
4.2 Theory and Methods

4.2.1. Full Hamiltonian and the diabatic basis

The calculation of excited states starts with a linear coupling Hamiltonian for vibronic interaction between nearly degenerate electronic states with coupling along one asymmetric vibration. The electronic Hamiltonian includes the average vertical excitation energy, \( \omega_{eg} \), and a splitting, \( \delta \): \( \hat{H}_{\text{elec}} = \left( \omega_{eg} - \delta / 2 \right) |x\rangle \langle x| + \left( \omega_{eg} + \delta / 2 \right) |y\rangle \langle y| \). The electronic states are coupled through an asymmetric vibration, which in the absence of coupling is assumed to have the same equilibrium position and frequency in the two states, giving us a zero-order vibrational Hamiltonian

\[
\hat{H}_\text{vib} = \frac{\omega}{2} \left( \hat{p}^2 + \hat{q}^2 \right) (|x\rangle \langle x| + |y\rangle \langle y|).
\]

Here \( \omega \) is the vibrational frequency; \( \hat{p} \) and \( \hat{q} \) are dimensionless vibrational momentum and position operators. The linear, vibrational coordinate dependent, off-diagonal, electronic coupling is conveniently expressed as

\[
\hat{H}_{e-v} = \omega d \hat{q} (|x\rangle \langle y| + |y\rangle \langle x|)
\]

where \( D\omega = \frac{1}{2} \omega d^2 \) defines dimensionless displacement \( d \) in terms of the stabilization energy \( D\omega \). Combining these terms, pulling \( \omega_{eg} \) outside, and expressing as a matrix in the \( \{|x\rangle, |y\rangle\} \) electronic basis, the full Hamiltonian

\[
\hat{H}_\text{full} = \hat{H}_{\text{elec}} + \hat{H}_\text{vib} + \hat{H}_{e-v}
\]

becomes

\[
H_{\text{full}} = \omega_{eg} I + \begin{bmatrix}
-\frac{\delta}{2} + \frac{\omega}{2} (\hat{p}^2 + \hat{q}^2) & \omega d \hat{q} \\
\omega d \hat{q} & \frac{\delta}{2} + \frac{\omega}{2} (\hat{p}^2 + \hat{q}^2)
\end{bmatrix}.
\]  

(4.1)

Here \( I \) is the identity matrix for the \( \{|x\rangle, |y\rangle\} \) space and the subscript “full” on \( H \) indicates no approximation has been made to the full model Hamiltonian.
We refer to the \( \{|x\}, |y\rangle \) electronic basis as a set of diabatic electronic states\(^{12}\), as they are diagonal for the approximate Hamiltonian \( \hat{H}_{\text{elec}} + \hat{H}_{\text{vib}} \), which neglects coordinate-dependent coupling \( \hat{H}_{e-v} \), but fully includes the vibrational kinetic energy operator, \( (\omega/2) \hat{p}^2 \). Here, this could also be referred to as a crude adiabatic\(^{13,14}\) basis, since \(|x\rangle\) and \(|y\rangle\) are independent of the vibrational coordinate. Such a set of states can always be found and used for a zero-order basis; indeed, this approach underlies one approach to vibronic transitions in molecules\(^{15}\). We further assume \(|x\rangle\) and \(|y\rangle\) to have orthogonal transition dipoles of equal magnitude from the ground state, and label them by the direction of the transition dipole from the ground state:

\[
\langle x | \hat{\mathbf{E}} \cdot \hat{\mathbf{\mu}} | g \rangle = (\hat{\mathbf{E}} \cdot \hat{x}) \mu_{xg} \quad \text{and} \quad \langle y | \hat{\mathbf{E}} \cdot \hat{\mathbf{\mu}} | g \rangle = (\hat{\mathbf{E}} \cdot \hat{y}) \mu_{yg} .
\]

The Condon approximation holds between \(|g\rangle\) and the \( \{|x\}, |y\rangle \) basis states, since \(|x\rangle\) and \(|y\rangle\) are (somewhat artificially) chosen to be independent of the vibrational coordinate for simplicity.

4.2.2. Stationary states and energy levels

4.2.2a) diabatic states and energies

Vibronic diabatic basis state energies are obtained after taking a direct product with a vibrational basis set \( \{|v\rangle\} \), where \( \langle q | v \rangle = \phi_v(q) \) is the \( v^{th} \) harmonic oscillator eigenfunction of \( \hat{H}_{\text{vib}} \). This gives basis energies as

\[
E_{xv} = \omega_{eg} - \delta / 2 + \omega (v + \frac{1}{2}) \quad \text{for} \quad |x\rangle |v\rangle
\]

and

\[
E_{yv} = \omega_{eg} + \delta / 2 + \omega (v + \frac{1}{2}) \quad \text{for} \quad |y\rangle |v\rangle .
\]

For a product wavefunction with this bra-ket notation, completed angular brackets around the electronic wavefunction indicate
integration over electronic degrees of freedom only, and completed angular brackets
around vibrational wavefunctions indicate integration over vibrational coordinates only.
The ground state is assumed to have the same vibrational frequency and equilibrium
position as the $|x\rangle$ and $|y\rangle$ diabatic states; as a consequence only $\Delta v = 0$ transitions are
optically allowed between diabatic basis states under the Franck-Condon principle. The
excited state diabatic potential energy curves, vibronic energy levels, and vibrational
wavefunctions are illustrated in figure 4.1.

4.2.2b) adiabatic approximation

To obtain the adiabatic vibronic wavefunctions from Hamiltonian (4.1), we first
neglect vibrational momentum and treat the vibrational coordinate operator $\hat{q}$ as a
parameter $q$. In the diabatic $\{|x\rangle, |y\rangle\}$ basis, the adiabatic electronic Hamiltonian is

$$H_{elec}^a(q) = \omega_{eg} + \frac{1}{2} \frac{\delta^2}{\omega^2} + \omega dq \frac{\delta}{\omega} + \omega dq \frac{\omega}{\omega}.$$  \hspace{1cm} (4.2)

This Hamiltonian can be diagonalized to solve the electronic eigenvalue problem

$$\hat{H}_{elec}^a(q) |k(q)\rangle = \left( \omega_{eg} + U_k(q) \right) |k(q)\rangle.$$  \hspace{1cm} (4.3)

The eigenvalues are

$$U_k(q) = \frac{1}{2} \omega dq^2 \pm \sqrt{\left(\frac{\delta}{2}\right)^2 + \left(\omega dq\right)^2}.$$  \hspace{1cm} (4.4)

with normalized eigenvectors
Figure (4.1) Potential energy curves, energy levels, vibrational wavefunctions, and vibrational probability densities for the pseudo-Jahn-Teller Hamiltonian (4.1)
Figure (4.1)(a) shows the diabatic basis potential curves, vibrational and electronic state energies and vibrational wavefunctions for Hamiltonian (4.1) with parameters
\[ \delta = 110 \text{cm}^{-1}, \quad \omega = 176 \text{cm}^{-1} \quad \text{and} \quad D \omega = 9 \text{cm}^{-1}. \]
The electronic wavefunctions are indicated by color, with purple indicating \( |x\rangle \) and orange \( |y\rangle \); the vibrational wavefunctions have been offset vertically to coincide with basis state energies. The zero of energy has been set to midway between the minima of the potential curves. Panel (b) shows adiabatic potential curves, vibrational and electronic state energies and vibrational wavefunctions. The electronic wavefunction is again indicated by color, with the coordinate-dependent mixing angle mapped onto the color wheel shown in 1(c) in a way that encompasses real sign changes. \( |y\rangle \) is orange, with a transition through red to purple \( |x\rangle \), followed clockwise by blue for \(-|y\rangle\), green for \(-|x\rangle\) and a transition through yellow back to orange. The lower adiabatic potential then is colored magenta, corresponding to \( (|x\rangle + |y\rangle)/\sqrt{2} \), at \(-q\), and purple-blue, corresponding to \( (|x\rangle - |y\rangle)/\sqrt{2} \), at \(+q\). The upper adiabatic potential is orange-yellow, corresponding to \( (|y\rangle - |x\rangle)/\sqrt{2} \), at \(-q\), and red-orange, corresponding to \( (|y\rangle + |x\rangle)/\sqrt{2} \), at \(+q\). Compared to the diabatic basis, the lower adiabatic curve is softened and all vibrational energy levels are lower; the upper adiabatic curve has stiffened and all vibrational energy levels are higher than on the upper diabatic curve. Each adiabatic vibrational wave function has a coloring which matches its potential curve, indicating which electronic wavefunction it gets multiplied by to form an adiabatic electronic-vibrational product state. Figure 4.1(d) again shows the diabatic potential curve and vibrational energy levels, but now displays vibrational probability density (square modulus of the wavefunction) rather than the wavefunction. To compensate for the lost phase information when squaring a wavefunction, the coloring of the probability density has been rotated \( 180^\circ \) around the color wheel in regions where the vibrational wavefunction carries a negative sign. Since the overall wavefunction is a product wavefunction, this is equivalent to replacing the vibrational wavefunction with its modulus and moving its coordinate-dependent sign onto the electronic wavefunction. The values of all quantum mechanical observables are preserved under this procedure. Looking for example at either \( v = 1 \) state, we see that the probability density is symmetric about the origin but the color change indicates a phase change which indicates that the product wavefunction at \(-q\) is \( \pi \) out of phase with the product wavefunction at \(+q\).

Figure 4.1(e) shows the same procedure applied to adiabatic vibrational wavefunctions. Here the \( q \)-dependent coloring reveals how the overall product wavefunction depends on both vibrational and electronic composition. Figure 4.1(f) shows exact nonadiabatic vibrational probability density and energy levels, without potential curves as there is no potential energy surface in a fully nonadiabatic framework. Coloring again indicates the coordinate-dependent mixing of \( |x\rangle \) and \( |y\rangle \) basis states in such a way as to preserve overall vibrational-electronic phase information. Nonadiabatic states display a nodeless structure completely missed in either approximation scheme, and rapid variations in color indicate that electronic character oscillates between \( |x\rangle \) and \( |y\rangle \) during vibrational motion.
\[|\rangle = \cos(\theta^a(q))|x\rangle - \sin(\theta^a(q))|y\rangle \]
\[|+\rangle = \sin(\theta^a(q))|x\rangle + \cos(\theta^a(q))|y\rangle \]
\[\theta^a(q) = \text{atan2}\left(o \omega dq, \delta/2 + \sqrt{\left(\delta/2\right)^2 + (o \omega dq)^2}\right).\]  
(4.5)

where \(\text{atan2}(y, x)\) is an extended arctangent function with range \((-\pi, \pi]\) and
\[\text{atan2}(y, x) = \arctan\left(\frac{y}{x}\right)\] in the range \((-\pi/2, \pi/2)\).
\[|k(q)\rangle = \{\langle -\rangle, |+\rangle\}\] forms a new set of vibrational coordinate dependent electronic basis functions, the adiabatic electronic basis, which is orthonormal at each value of \(q\).

Having obtained adiabatic electronic wavefunctions, we re-introduce the vibrational momentum, replace \(q\) with \(\hat{q}\), and use \(U_\pm(\hat{q}) - U_\pm(q_e)\) as the potential energies for vibrational motion, where the equilibrium vibrational coordinate is \(q_e = 0\).

This gives a pair of adiabatic vibrational Hamiltonians for two new eigenvalue problems,
\[\hat{H}_v^k|v^k\rangle = \left(\frac{\omega^2}{2} \hat{p}^2 + U_k(\hat{q}) - U_\pm(0)\right)|v^k\rangle = E^k_v|v^k\rangle.\]  
(4.6)

To solve these anharmonic Hamiltonians, we expand in the same vibrational basis used for the diabatic calculation, that of the ground state vibrational wavefunctions. This allows us to fill in values for \(\hat{p}^2\) using well-known harmonic oscillator dimensionless momentum matrix elements:
\[\langle v|\hat{p}^2|v'\rangle = -\frac{1}{2} \sqrt{(v+1)(v+2)} \delta_{v,v+2} + (v+\frac{1}{2}) \delta_{v,v} - \frac{1}{2} \sqrt{v(v-1)} \delta_{v,v-2}.\]  
(4.7)
The cost incurred by this basis set choice is that we must numerically integrate the potential function matrix elements, \(U^\pm_{v,v'} = \langle v | \left(\frac{\omega_\delta \hat{q}^2}{2} \pm \sqrt{\left(\delta/2\right)^2 + (o \omega \hat{q})^2}\right) |v'\rangle\), then
numerically diagonalize the Hamiltonians to obtain adiabatic vibrational wavefunctions and energy levels.

These numerical integrations are accomplished with the DQDAGS routine, which is an adaptive quadrature routine available in the IMSL library; the DEVCRG routine (based on the QR algorithm) was used for matrix diagonalization, and is also included in the IMSL library. We find that integrating between \( q = \pm 9 \) and including 20 harmonic oscillator basis states ensures convergence for the lowest 7 vibrational states on each adiabatic electronic state to within \( 4 \times 10^{-5} \) cm\(^{-1}\) for the values of \( \omega, \delta, \) and \( D \omega \) investigated here. The resulting adiabatic vibrational state will be written as

\[
|v^k\rangle = \sum_{v'} c_{v'}^{k} |v'\rangle \quad \text{where} \quad k \in \{-, +\}, \quad v \text{ is a vibration quantum number for the adiabatic wavefunction, } v' \text{ is a vibrational quantum number for the basis function and} \quad c_{v'}^{k} = \langle v'^{k} | v' \rangle.
\]

The adiabatic potential energy curves (solutions to \( \hat{H}_{\text{elec}} \)), vibronic energy levels and vibrational wavefunctions are displayed in figure 4.1(B), with a coordinate-dependent coloring that reflects the mixing angle \( \theta(q) \) (eqn (4.5)). These wavefunctions are electronic-vibrational wavefunctions and can be expanded in the original diabatic basis as

\[
|\psi_{\pm v}\rangle = |\pm\rangle |v^-\rangle = (\cos \theta^a(q)|x\rangle - \sin \theta^a(q)|y\rangle) \left( \sum_{v'} c_{v'}^{-v} |v'\rangle \right) \quad \text{and} \quad |\psi_{\pm v}\rangle = |\pm\rangle |v^+\rangle = (\sin \theta^a(q)|x\rangle + \cos \theta^a(q)|y\rangle) \left( \sum_{v'} c_{v'}^{+v} |v'\rangle \right), \quad \text{where} \quad v' \text{ is the quantum number for the common vibrational basis. The total energy for the product wavefunction} \quad |k\rangle |v^k\rangle \quad \text{is given by}
\]
\[ E_{kv}^a = \omega_{eg} + U_k(q) + E_r^k = \omega_{eg} + \delta / 2 + E_r^k. \]  

(4.8)

4.2.2c) Exact nonadiabatic wavefunctions

To obtain the exact nonadiabatic energy levels and wavefunctions, we could proceed from either the diabatic basis or the adiabatic basis, and will do both as the physical insight gained from a calculation is often basis set dependent. To derive the nonadiabatic operator from the adiabatic basis, we allow the \( (\omega/2) \hat{p}^2 \) operator to act on an adiabatic product wavefunction, and by applying the product rule twice find one term which is equivalent to the use of \( (\omega/2) \hat{p}^2 \) in Hamiltonian (4.6), and two new terms which are missing in the adiabatic approximation\(^{14,19}\). The new terms are combined and called the nonadiabaticity operator \( \hat{\Lambda} \)\(^{14} \), which operates separately on adiabatic electronic and vibrational wavefunctions; because of that it needs to be expressed in a product basis. It is useful here to define a shorthand notation for taking the partial derivative of a wavefunction: let \( \left| \partial_{kv} k / \partial q \right\rangle = (\partial / \partial q) \left| v^{kt} \right\rangle \) and \( \left| \partial^n k(q) / \partial q^n \right\rangle = (\partial^n / \partial q^n) \left| k(q) \right\rangle \). Using this shorthand, the matrix elements are

\[
\tilde{\Lambda}_{kv,k'v'} = -\omega \left\langle v^k \left| k(q) \right| \partial k'(q) / \partial q \right\rangle \left| \partial v^{k'} / \partial q \right\rangle - \frac{1}{2} \omega \left\langle v^k \left| k(q) \right| \partial^2 k'(q) / \partial q^2 \right\rangle \left| v^{kt} \right\rangle ^{14}
\]

(4.9)

where \( \left| v^k \right\rangle \) can be any vibrational basis function belonging to \( \left| k \right\rangle \).

The term on the first line of the right hand side of eqn (4.9) is referred to as the radial derivative coupling and the term on the second line is commonly called the scalar coupling. If \( k = k' \), and the electronic wavefunctions are real, the first term vanishes (it is proportional to the expectation value of the momentum) and \( \Lambda_{kv,kv} \) is known as the
diagonal correction; various authors include this correction in the “Born-Oppenheimer” or “adiabatic” approximations to distinguish them\textsuperscript{20}; unfortunately there is not a uniformly accepted convention for which is adiabatic and which is Born-Oppenheimer. Following Born and Huang\textsuperscript{19}, we will call the basis which does not include this correction the “adiabatic” basis; we call the basis which does include it the “Born-Huang” basis because it was discussed in Born and Huang.\textsuperscript{19}

If \( k \neq k' \), both lines of eqn (4.9) must be included, as the terms are not individually Hermitian. For the real basis set used here, the scalar coupling is anti-symmetric \( \{ A_{ij} = -A_{ji} \} \) while the radial derivative coupling is neither symmetric nor anti-symmetric. \( \hat{\Lambda} \) is symmetric, however, so the radial coupling can be decomposed into a sum of symmetric and anti-symmetric parts, and its anti-symmetric part exactly cancels the scalar coupling. The Hermitian properties of components of \( \hat{\Lambda} \) have also been discussed in the electronic subspace\textsuperscript{21}, rather than as matrices in the electronic-vibrational product space; then too the individual terms in \( \hat{\Lambda} \) are not Hermitian but the detailed discussion is somewhat different.

To find the full nonadiabatic energy levels and wavefunctions, working from an adiabatic basis, we construct a block-diagonal adiabatic Hamiltonian containing both \( \hat{H}_{\text{elec}}^a \) and \( \hat{H}_{\text{vib}}^a \), then add the nonadiabaticity operator:

\[
H_{\text{full}}^a = \begin{bmatrix}
\omega_{eg} + U_{\text{e}}(0) + \hat{H}_{\text{vib}}^- & 0 \\
0 & \omega_{eg} + U_{\text{e}}(0) + \hat{H}_{\text{vib}}^+
\end{bmatrix} + \begin{bmatrix}
\hat{\Lambda}_{-,+} & \hat{\Lambda}_{-,-} \\
\hat{\Lambda}_{+,+} & \hat{\Lambda}_{+,+}
\end{bmatrix}
\]  

(4.10)

Where the “a” superscript on \( H \) indicates that it is expressed in the adiabatic electronic basis \( \{|-,+\} \) and the vibrational subscripts on \( \hat{\Lambda} \) have been dropped since eqn (4.10)
is not expressed in a vibrational basis. The form of \( \hat{\Lambda} \) presented in eqn (4.9) is used after expanding eqn (4.10) in a product basis.

Since our diabatic electronic basis is coordinate independent, we can carry out the \( q \)-derivatives of the adiabatic electronic functions and integrate over electronic degrees of freedom for the nonadiabaticity matrix elements by writing the adiabatic electronic wavefunctions as a linear combination of diabatic electronic wavefunctions.

\[
\left\langle + \left| \frac{\partial}{\partial q} \right| \left\langle - \right| \right\rangle = \sin \left( \theta^a(q) \right) \left( \frac{\partial}{\partial q} \right) \cos \left( \theta^a(q) \right) - \cos \left( \theta^a(q) \right) \left( \frac{\partial}{\partial q} \right) \sin \left( \theta^a(q) \right) \\
= -\sin^2 \left( \theta^a(q) \right) \frac{\partial \theta^a}{\partial q} - \cos^2 \left( \theta^a(q) \right) \frac{\partial \theta^a}{\partial q} \\
= -\frac{\partial \theta^a}{\partial q}
\]

(4.11.a)

Similarly,

\[
\left\langle - \left| \frac{\partial}{\partial q} \right| \left\langle + \right| \right\rangle = \frac{\partial \theta^a}{\partial q} \\
\left\langle - \left| \frac{\partial^2}{\partial q^2} \right| \left\langle + \right| \right\rangle = -\frac{\partial \theta^a}{\partial q} \\
\left\langle + \left| \frac{\partial^2}{\partial q^2} \right| \left\langle - \right| \right\rangle = -\frac{\partial^2 \theta^a}{\partial q^2} \\
\left\langle - \left| \frac{\partial^2}{\partial q^2} \right| \left\langle + \right| \right\rangle = \frac{\partial^2 \theta^a}{\partial q^2}
\]

(4.11.b, 4.11.c, 4.11.d, 4.11.e)

These nonadiabatic matrix elements remain expressed in the adiabatic electronic basis; to find a nonadiabatic matrix element between a pair of adiabatic vibrational-electronic states, this leaves only an integral over known functions of \( q \) to be done numerically.

Plugging equations (4.11) into equation (4.9), we find

\[
\Lambda_{v_v^+v^+} = \frac{\omega}{2} \left\langle v^+ \right| \frac{\partial \theta^a}{\partial q} \left| v^+ \right\rangle
\]

(4.12.a)
\[ \Lambda_{-v,v'} = \frac{\omega}{2} \langle v^- | \left( \frac{\partial^2 \theta^r}{\partial q^2} \right) | v^r \rangle \]  

(4.12.b)

\[ \Lambda_{v,v'} = \omega \langle v^+ | \left( \frac{\partial \theta^r}{\partial q} \right) | \frac{\partial v^-}{\partial q} \rangle + \frac{\omega}{2} \langle v^+ | \left( \frac{\partial^2 \theta^r}{\partial q^2} \right) | v^r \rangle \]  

(4.12.c)

\[ \Lambda_{v,-v'} = -\omega \langle v^- | \left( \frac{\partial \theta^r}{\partial q} \right) | \frac{\partial v^+}{\partial q} \rangle - \frac{\omega}{2} \langle v^- | \left( \frac{\partial^2 \theta^r}{\partial q^2} \right) | v^r \rangle \]  

(4.12.d)

where \( | v^k \rangle \) is any vibrational basis function belonging to the \( k \)th electronic state.

It is convenient to continue using the same vibrational basis used in solving \( \hat{H}^k_{\text{vib}} \), that of the ground electronic state vibrations. This allows the addition in equation (4.10) to occur in the same basis used for solving the adiabatic vibrational wavefunctions, so long as the matrices are added before diagonalizing. The IMSL\(^{18}\) routine QDAGP (an adaptive quadrature routine\(^{17}\) intended for use with functions containing known singularities) was used for evaluating integrals (4.12); typically a basis set of 25 ground state harmonic oscillator basis functions on each electronic state was enough to ensure energy convergence to within \( 7 \times 10^{-3} \text{cm}^{-1} \) for the lowest seven exact nonadiabatic eigenstates.

The cost of this basis choice is that the vibrationally off-diagonal matrix elements include both anharmonic and nonadiabatic coupling, which obfuscates the interpretation of electronically off-diagonal elements. If the matrix elements of the nonadiabaticity operator are to be found in the adiabatic basis, one must first expand equation (4.10) in the vibrational basis, then apply a unitary transformation to the matrices on the right hand side. These transformation matrices are assembled from the eigenvector matrices returned.
from the numerical diagonalization of $\hat{H}_{\text{vib}}^k$, since these were expressed in the same basis.

The transformation matrices are block-diagonal, with

$$C = \begin{bmatrix} c_{vv'} & 0 \\ 0 & c_{vv'}^* \end{bmatrix}$$

as the operator which transforms a ket (column vector) from the mixed adiabatic electronic but ground state vibrational basis to the fully adiabatic basis.

To obtain exact nonadiabatic wavefunctions, we could equally well have worked from a diabatic basis and filled in the off-diagonal parts of Hamiltonian (4.1). We use the same phase convention as for $\hat{p}^2$ to evaluate matrix elements of the dimensionless position operator, and obtain

$$H_{vv', vv''} = \omega d_{vv'} = \omega d \sqrt{(v/2)\delta_{v,v'+1}} + \omega d \sqrt{(v'/2)\delta_{v,v''-1}}$$

Exact energies $E_n$ and wavefunctions $|\psi_n\rangle$ are then obtained by expanding Hamiltonian (4.1) in the harmonic oscillator vibrational basis and numerically diagonalizing. The wavefunctions are of the form

$$|\psi_n\rangle = \sum_v b_{n,v} |x_v\rangle |v\rangle + \sum_y b_{n,y} |y_v\rangle |v\rangle.$$  \hfill (4.13)

The form presented in equation (4.13) is convenient for calculations, but for more insight we now seek to individually separate each nonadiabatic wavefunction into a single product of a purely vibrational wavefunction of $q$ alone and a normalized electronic wavefunction parametrically dependent on $q$. We start by writing the explicit $q$-dependent projections of the wavefunction onto $|x\rangle$ and $|y\rangle$: 
\begin{equation}
\langle x | \langle q | \psi_n \rangle = \sum_v b_{n,vx} \langle x | x \rangle \langle q | v \rangle + \sum_v b_{n,vy} \langle x | y \rangle \langle q | v \rangle \\
= \sum_v b_{n,vx} \varphi_x (q) \\
= \Phi_{n,x} (q) \\
\langle y | \langle q | \psi_n \rangle = \sum_v b_{n,vx} \langle y | x \rangle \langle q | v \rangle + \sum_v b_{n,vy} \langle y | y \rangle \langle q | v \rangle \\
= \sum_v b_{n,vy} \varphi_y (q) \\
= \Phi_{n,y} (q)
\end{equation}

With $\Phi_{n,x} (q)$ defining the $q$-dependent projection of $|\Psi_n \rangle$ onto $|x\rangle$ and $\Phi_{n,y} (q)$ defining the projection onto $|y\rangle$, we define a polar transformation at each value of $q$ and use it to define a new vibrational ket $|b_n \rangle$ and a new electronic ket $|K_n \rangle$:

$$
\Theta_n (q) = \text{atan2} \left( \Phi_{n,y} (q), \Phi_{n,x} (q) \right)
$$

$$
\langle q | b_n \rangle = b_n (q) = \sqrt{ \left( \Phi_{n,x} (q) \right)^2 + \left( \Phi_{n,y} (q) \right)^2 }
$$

$$
|K_n \rangle = \left[ \cos (\Theta_n (q)) |x\rangle + \sin (\Theta_n (q)) |y\rangle \right]
$$

$$
|\psi_n \rangle = |K_n \rangle |b_n \rangle.
$$

The product wavefunction $|K_n \rangle |b_n \rangle$ is an allowed wavefunction for the electronic-vibrational system. The new ket $|b_n \rangle$ may not generate an allowed vibrational wavefunction – a derivative discontinuity in $\langle q | b_n \rangle$ occurs if $\Phi_{n,x} (q) = \Phi_{n,y} (q) = 0$.

However, for diatomic molecules, it can be shown that analogous nonadiabatic vibrational wavefunctions do not have nodes. A similar problem occurs in the adiabatic framework, where in two dimensions $\phi^k (q_1, q_2)$ may be multi-valued and not admissible around a conical intersection (Berry’s phase), but the product $\phi^k (q_1, q_2) |k(q_1, q_2) \rangle$ is an allowed, single-valued, electronic-vibrational wavefunction.
The important difference between this and the adiabatic framework is that there is only one quantum number \( n \) which indexes both the electronic state and the vibrational state. By fully including vibrational momentum we end up with only one vibrational state, \( |p_n\rangle \), for each electronic state \( |k_n\rangle \), rather than a series of vibrational bound states for each electronic state; conversely we have a different electronic wavefunction for every vibrational state rather than having only two electronic states. Like the adiabatic electronic states, each nonadiabatic electronic state is normalized at each value of \( q \). However, unlike the adiabatic electronic states, the \( n \) electronic wavefunctions cannot be mutually orthogonal in the two-dimensional electronic subspace. Further, the \( n \) vibrational wavefunctions are not orthogonal in the vibrational subspace. Nonetheless, the product wavefunctions are orthogonal. As in the adiabatic framework, the \( q \)-dependent amplitude of the product wavefunction is contained in the vibrational wavefunction.

The results of diagonalizing Hamiltonian (4.1), then applying transformation (4.15) are displayed in figure 4.1(e). No potential curves are shown, as the nonadiabatic picture lacks the concept of each electronic state supporting a complete set of vibrational states. \( |\langle q | p_n \rangle|^2 \) is plotted to indicate the vibrational probability density, while the \( q \)-dependent coloring indicates \( \Theta_n(q) \) contains overall sign information and fully describes the \( q \)-dependence of the transition dipole from the ground electronic state. Note that this implies that the Condon approximation may fail due to a rotation of \( \tilde{\mu}_{kg} \), rather than the typical diatomic concerns about the magnitude of \( \tilde{\mu}_{kg} \).
4.2.3. Non-stationary states. Wavepacket propagation

To see what dynamics are contained in this Hamiltonian, we will take a look at time-dependent wavefunctions obtained under impulsive excitation from a zero-point vibration \((\nu=0)\) on the electronic ground state \(|g\rangle\). Calculations using the exact nonadiabatic solutions to Hamiltonian (4.1) will be contrasted to propagation using adiabatic product wavefunctions and energies. The effect of the Condon approximation on the dynamics through the initial conditions will also be examined. The calculations presented here will not take into account system-bath coupling, dephasing, or population transfer between eigenstates. This will allow us to propagate for sufficient lengths of time to study in detail the motions that are created by the Hamiltonian; for a large molecule in a condensed phase, these motions can be damped out on timescales ranging from a hundred to a few thousand femtoseconds.

4.2.3a) exact propagation

Impulsive laser excitation will project the electronic ground state vibrational wavepacket directly onto the electronic excited states. Explicit equations for the initial conditions are derived using first-order time dependent perturbation theory\(^{23}\), which has us operate on an initial ket \(|a\rangle\) with the operator \((1/\imath\hbar)\sum_n |\varphi_n\rangle \langle \varphi_n| (\mathbf{-E} \cdot \hat{\mathbf{\mu}})|a\rangle \langle a|\). We take our initial ket \(|a\rangle\) to be \(|g\rangle|0\rangle\) and assume \(\delta\)-function pulses, which have a spectrally constant electric field amplitude.
Here \(|\Psi(T)\rangle\) represents an excited-state vibronic wavepacket. The wavepacket at times after \(T=0\) is calculated using the time-dependent form of Schrödinger’s equation and the eigenvalues obtained by diagonalizing Hamiltonian (4.1).

\[
|\Psi(T)\rangle = (i/\hbar) \sum_n \langle \psi_n | (\hat{\mathbf{E}} \cdot \hat{\mathbf{\mu}}) |g\rangle |0\rangle \\
= (i/\hbar) \sum_n \mu_{n} \left( \sum_{v} b_{n,v} \langle v | x \rangle + \sum_{v} b_{n,v} \langle v | y \rangle \right) \left[ (\hat{\mathbf{E}} \cdot \hat{\mathbf{x}}) \hat{\mu}_x + (\hat{\mathbf{E}} \cdot \hat{\mathbf{y}}) \hat{\mu}_y \right] |g\rangle |0\rangle \\
= (i/\hbar) \mu_{x} \sum_n \left( b_{n,x} \hat{\mathbf{E}} \cdot \hat{\mathbf{x}} + b_{n,y} \hat{\mathbf{E}} \cdot \hat{\mathbf{y}} \right) |\psi_n\rangle
\]

Equation (4.16) is used for all nonadiabatic wavepacket calculations; however we seek to transform \(|\Psi(t)\rangle\) in a manner similar to the treatment of \(|\psi_n\rangle\), in order to apply the visualization scheme used in figure 4.1(f). A time-dependent generalization of transformation (4.15) is needed in order to separate the propagating wavepacket into a single product of a purely vibrational wavefunction and an electronic wavefunction whose \(q\)-dependence is described by the mixing angle \(\Theta(q,T)\). We proceed by defining

\[
\Phi_x(q,T) = \langle k | \langle q | \Psi(T) \rangle \\
= \sum_n b_n \langle k | \langle q | \psi_n \rangle \exp(-iE_n T / \hbar) \\
= \sum_n b_n \Phi_{n,k}(q) \exp(-iE_n T / \hbar)
\]

where \(|k\rangle \in \{|x\rangle, |y\rangle\}\), \(b_n = (b_{n,x} \hat{\mathbf{E}} \cdot \hat{\mathbf{x}} + b_{n,y} \hat{\mathbf{E}} \cdot \hat{\mathbf{y}})\) abbreviates the projection of the wavepacket onto eigenstates as in eqn (4.16), and \(|\Phi_x(q,T)\|^2 + |\Phi_y(q,T)\|^2\) is the time-dependent vibrational probability density. The projections \(\Phi_x(T)\) and \(\Phi_y(T)\) are time-dependent and therefore complex valued, preventing an unambiguous definition of the
mixing angle $\Theta(q, T)$. While arctangent is defined for complex arguments, it returns a complex angle which is not straightforwardly connected to experimental measurements. We chose instead to define $\Theta(q, T)$ using only the real parts of $\Phi_x(T)$ and $\Phi_y(T)$; this preserves the interpretation of $\Theta(q, T)$ as reflecting the vibrational coordinate dependence of the transition dipole to the ground state and reduces to transformation (4.15) at time zero, but loses information about the imaginary components of the wavepacket. The full transformation is

$$
\Theta(q, T) = \text{atan}2\left( \text{Re} \Phi_y(q), \text{Re} \Phi_x(q) \right)
$$

$$
\langle q | p_a(T) \rangle = \sqrt{\Phi_x(q, T)^2 + \Phi_y(q, T)^2}
$$

$$
|\Psi(T)\rangle = \left[ \cos\left(\Theta(q, T)\right) |x\rangle + \sin\left(\Theta(q, T)\right) |y\rangle \right] p_a(T) \rangle.
$$

4.2.3b) Adiabatic propagation

We first treat the approximate adiabatic propagation without making additional approximations; then we will simplify the initial conditions by invoking the Condon approximation. Our strategy will be the same: operate on the ground state with $\hat{E} \cdot \hat{\mu}$, then project onto excited states:

$$
|\Psi(T)\rangle^a = \left(1/\hbar\right) \sum_{k, v} \exp(-iE^a_{k, v} T / \hbar) |k\rangle \langle v^k | k\rangle \langle v^k | (E - \hat{E} \cdot \hat{\mu}) |g\rangle |0\rangle.
$$

The difference is that these states and energies will be adiabatic vibronic product states rather than exact nonadiabatic eigenstates. To obtain useful formulas for initial conditions, the bra $\langle v^k | k\rangle$ is expanded in the original diabatic electronic basis, for example as

$$
\langle v^k | k\rangle^+ = \langle v^k | (x|\sin \theta^x(q) + y|\cos \theta^x(q)) .
$$

The ket component $|k\rangle \langle v^k |$ of the projection
operator $|k\rangle\langle v^k|\langle v^k|k\rangle$ is left written in the adiabatic basis, but separated into $|+\rangle\langle v^+|$ and $|-\rangle\langle v^-|$ in order to make the difference in excitation probabilities for the two electronic states explicit.

$$
|\Psi(T)\rangle_a = (i/\hbar)\sum_v|+\rangle\langle v^+|\exp(-iE^a_vT/\hbar)\langle v^+|\left(\langle x|\sin\theta^a(q) + \langle y|\cos\theta^a(q)\right)(\vec{E}\cdot\hat{\mu})|g\rangle|0\rangle
$$

Taking the integral over electronic coordinates gives

$$
|\Psi(T)\rangle_a = (i/\hbar)\sum_v|+\rangle\langle v^+|\exp(-iE^a_vT/\hbar)\langle v^+|\left(\langle x|\sin\theta^a(q) + \langle y|\cos\theta^a(q)\right)(\vec{E}\cdot\hat{\mu})\mu_{sg}\sin\theta^a(q)\right)|0\rangle
$$

Now expanding the vibrational bra $\langle v^k|$ in the ground vibrational basis as $c_{v^k}^v$, and using $\mu_{sg} = \mu_{sg} = \mu_{eg}$, the adiabatic wavepacket is

$$
|\Psi(T)\rangle_a = (i/\hbar)\mu_{eg}\sum_{v,v'}\left(\langle \vec{E}\cdot\hat{x}\rangle c_{v'^v}^v\langle v^+|\sin\theta^a|0\rangle + \langle \vec{E}\cdot\hat{y}\rangle c_{v'^v}^v\langle v^+|\cos\theta^a|0\rangle\right)|+\rangle\langle v^+|\exp(-iE^a_vT/\hbar)
$$

The $q$-integrals $\langle v'|\cos\theta^a|0\rangle$ and $\langle v'|\sin\theta^a|0\rangle$ remaining in the last equation are evaluated numerically.

It is common to calculate initial conditions with the Condon approximation, in which the transition dipole is assumed constant along $q$. In the adiabatic derivation above, this amounts to replacing the adiabatic electronic expansion coefficients, $\sin\theta^a(q)$ and
\[
\cos \vartheta^r(q), \text{ with their values at } q = 0, \text{ where } \sin \vartheta^r|_{q=0} = 0 \text{ and } \cos \vartheta^r|_{q=0} = 1. \text{ Under the Condon approximation, the } q\text{-integrals remaining in the last line of equation (4.19) become equal to } \delta_{v0} \text{ and the sum collapses to give}
\]

\[
\left| \Psi^a(T) \right|_{\text{Condon}} = (i/\hbar) \mu_{eg} \left( \hat{\mathcal{E}} \cdot \hat{y} \right) \sum_{v} c_{v0}^+ \left| + \right> \left| v^+ \right> \exp(-iE_{v+}^a T / \hbar) \\
+ (i/\hbar) \mu_{eg} \left( \hat{\mathcal{E}} \cdot \hat{x} \right) \sum_{v} c_{v0}^- \left| - \right> \left| v^- \right> \exp(-iE_{v-}^a T / \hbar).
\]

\[
(4.20)
\]

4.3 Results and Discussion

4.3.1 Stationary states

The full nonadiabatic eigenstates of Hamiltonian (4.1) are shown in figure 4.1, and compared to both diabatic and adiabatic vibrational-electronic product wavefunctions. The parameters used are \( \delta = 110 \text{ cm}^{-1}, \) \( \omega = 176 \text{ cm}^{-1}, \) \( Dw = 9 \text{ cm}^{-1}, \) and \( \omega_{eg} = 0. \) These choices for splitting, vibrational frequency, and stabilization energy are the best fit parameters from Smith et al.\(^1\) In figure 4.1(f) the vibrational probability density is shown explicitly, while the vibrational phase and electronic composition of the wavefunction is indicated by color. In general the wavefunctions display rapid variations in color, indicating rapid variations in electronic composition, as the vibrational coordinate is varied. The lowest five nonadiabatic eigenstate energies and lowest five energies from each set of basis states are listed in table 4.1. The diabatic basis and the exact energies have an rms difference of \( 20 \text{ cm}^{-1}, \) while the adiabatic product state energies differ from the exact levels with an rms deviation of \( 41 \text{ cm}^{-1}. \) The lowest eigenenergy is within \( 6.5 \text{ cm}^{-1} \) with both basis sets.
| \( |\psi_n\rangle \) | Exact Energy \((cm^{-1})\) | Diabatic Energy \((cm^{-1})\) | Adiabatic Energy \((cm^{-1})\) |
|-----------------|-----------------|-----------------|-----------------|
| \( |\psi_0\rangle \) | 27.39 | 33 | 20.95 |
| \( |\psi_1\rangle \) | 122.60 | 143 | 153.96 |
| \( |\psi_2\rangle \) | 218.05 | 209 | 176.93 |
| \( |\psi_3\rangle \) | 287.69 | 319 | 338.11 |
| \( |\psi_4\rangle \) | 404.65 | 385 | 348.78 |

Table (4.1) Exact state and basis state energies for Hamiltonian (4.1)
Returning to figure 4.1(f), the lowest wavefunction \( |\psi_0\rangle \), nominally \( |x\rangle|v = 0\rangle \), is reasonably well described by the adiabatic approximation. It is mostly \( x \)-polarized, with small amounts of \( y \)-polarization mixed in-phase at negative \( q \) and out-of-phase at positive \( q \). The mixing-in of \( y \)-polarization is missed with a diabatic approximation, and slightly over-emphasized with the adiabatic approximation. The adiabatic calculation indicates the mixing angle reaches values of \( 22.7^\circ \geq -\theta^o \geq -22.7^\circ \) over the range of \( -1 \leq q \leq 1 \), while the lowest exact nonadiabatic state only reaches \( 10.9^\circ \geq \Theta_0 \geq -10.9^\circ \) over this range. The minus sign on \( \theta^o \) comes from the definition of \( - \) in equation (4.5).

The second and third levels are nominally \( |y\rangle|v = 0\rangle \) and \( |x\rangle|v = 1\rangle \) from a diabatic basis, or \( |+\rangle|v = 0\rangle \) and \( |-\rangle|v = 1\rangle \) from an adiabatic basis, and are heavily mixed due to their near-degeneracy. Comparing panels (e) and (f) in figure 4.1, \( |\psi_1\rangle \) looks qualitatively similar to \( |+\rangle|v = 0\rangle \) but with the electronic character change in the opposite sense: as \( q \) increases, \( |\psi_1\rangle \) changes from red to orange to yellow, while \( |+\rangle|v^+ = 0\rangle \) changes yellow to orange to red. This switch occurs because, in the adiabatic approximation, \( - \) is formed by \( |y\rangle \) interacting with an electronic state \( |x\rangle \) below it, while in the full nonadiabatic calculation \( |\psi_1\rangle \) is formed from \( |y\rangle|v = 0\rangle \) interacting with \( |x\rangle|v = 1\rangle \) above it, which causes a sign change in perturbation theory denominators.

Comparing panels (d) and (f), \( |\psi_2\rangle \) looks similar to \( |y\rangle|v = 0\rangle \) near \( q = 0 \), but resembles both \( |x\rangle|v = 1\rangle \) and \( |-\rangle|v^- = 1\rangle \) for both large positive and large negative values of \( q \).
These two wavefunctions are shown in greater detail in figure 4.2. Here we plot the two wavefunctions as in figure 4.1(f), but beneath each we show the $q$-dependence of the $|x\rangle$ and $|y\rangle$ components, $\Phi_{n,x}(q)$ and $\Phi_{n,y}(q)$. $\ket{\psi_1}$ is seen to be approximately $(|y\rangle|0\rangle - |x\rangle|1\rangle)/\sqrt{2}$, as expected from the above discussion. $\ket{\psi_2}$ is dominantly $(|x\rangle|1\rangle + |y\rangle|0\rangle)/\sqrt{2}$, but with enough $-|y\rangle|2\rangle$ mixed in to remove most of the amplitude from $\Phi_y$ in the wings. This results in an eigenstate which is almost $-|x\rangle$ at $-q$, $|y\rangle$ at $q=0$, and almost $+|x\rangle$ at $+q$.

In either the diabatic basis or the adiabatic approximation, we would expect the third eigenstate to have a node at $q=0$, as it corresponds to the first excited vibrational state on the lower surface. However, if we calculate the vibrational probability density using equations (4.13) and (4.14), $\left|\left\langle q | \psi_n \right\rangle\right|^2 = \left|\left\langle q | p_n \right\rangle\right|^2 = \Phi_{n,x}^2(q) + \Phi_{n,y}^2(q)$, the cross terms between $|x\rangle$ and $|y\rangle$ components vanish and no interference occurs between the vibrational wavefunctions belonging to different electronic states; it is the vibrational probability density from the coupled states that adds, not the wavefunctions. We are led to a picture where a perturbation “fills in” the nodes of one wavefunction with amplitude from another, leading to nodeless wavefunctions. This has been noticed before in the context of nonadiabatic coupling, however the previous studies were focused on ground state wavefunctions well isolated from other states, and nonadiabatic coupling was a small effect, except at adiabatic nodes.

Returning to figure 4.1(f), we examine the next pair of eigenstates, $\ket{\psi_3}$ and $\ket{\psi_4}$, we see multiple regions of rapid color changes; comparison to panels (d) and (e)
Figure (4.2) Detail of nonadiabatic eigenstates $|\psi_1\rangle$ and $|\psi_2\rangle$, constructed from Hamiltonian (4.1) with parameters $\delta = 110\text{ cm}^{-1}$, $\omega = 176\text{ cm}^{-1}$ and $D\omega = 9\text{ cm}^{-1}$. These two states can be understood mainly from the two-state interaction of $|y\rangle|0\rangle$ and $|x\rangle|1\rangle$, through a linear coupling $\hat{\omega}d\hat{q}$. Since $\hat{q}$ has positive matrix elements, the out-of-phase combination has lower energy than the in-phase combination. At the top of both panels the full vibronic wavefunction is displayed in the same manner as in figure 4.1(f). In the bottom of each panel the $q$-dependent projections of the full nonadiabatic wavefunction onto $|x\rangle$ and $|y\rangle$ electronic basis states are shown. Panel (a) shows the second lowest nonadiabatic eigenstate is dominantly $\left((|y\rangle|0\rangle - |x\rangle|1\rangle)/\sqrt{2}\right)$. Panel (b) shows the third lowest eigenstate to be dominantly $\left((|x\rangle|1\rangle + |y\rangle|0\rangle)/\sqrt{2}\right)$, although some $-|y\rangle|2\rangle$ character is evident in the wings. $|\psi_2\rangle$ would have a node under the diabatic or adiabatic approximations; the nonadiabatic mixing instead produces rapid color changes where the node was expected.
confirms that these occur in regions where one of the contributing basis functions has a node. This causes the electronic wavefunction to change its character rapidly as a function of vibrational coordinate. Indeed, \( |\psi_i\rangle \), which is dominantly \( |x\rangle|2\rangle \), travels more than one complete cycle around the color wheel, from \( \theta^\ast = 3.5^\circ \), through zero to -90, 180, 90, and through zero again to -3.5, in the range \(-\sqrt{5} \leq q \leq \sqrt{5}\), the classical turning points for a \( v=2 \) vibrational state.

These rapid color changes are a result of the nodeless quality of the wavefunctions, which arises from having mixed character with appreciable amplitude from both \( |x\rangle \) and \( |y\rangle \). The question arises, then, of under what conditions can we expect this behavior? Also, we could equally well have used an adiabatic electronic basis,

\[
|q\rangle |\psi_n\rangle = |\Phi_{n,\cdot}(q)|-\rangle + |\Phi_{n,\cdot}(q)|+\rangle = \Phi_{n,\cdot}(q) + \Phi_{n,\cdot}(q),
\]

leading to the question of with which basis is it easier to identify situations in which a nodeless wavefunction may be important?

To explore these questions, we have plotted in figure 4.3(a) the height of \( |\psi_1\rangle \) and \( |\psi_2\rangle \), evaluated at \( q=0 \), as the electronic splitting parameter is varied from 0 to 300 cm\(^{-1}\). This tunes from exact degeneracy, where nonadiabatic effects are known to be important, through a resonance at \( \delta = \omega \) and into the regime where \( \delta > \omega \) and nonadiabatic effects become relatively weak. We see that when the electronic splitting is large compared to the vibrational frequency, \( \omega = 176cm^{-1} \), there is almost a node in \( |\psi_1\rangle \), which corresponds to \( |x\rangle|1\rangle \) in the range of \( \delta > \omega \). The wave function does not change sign, but the vibrational probability density at \( q=0 \) has already dropped to below 0.04 when \( \delta = 3\omega / 2 = 264cm^{-1} \). For reference, a normalized harmonic oscillator
Figure (4.3) Properties of nonadiabatic electronic-vibrational wavefunctions of Hamiltonian (4.1) with parameters $\omega = 176\text{cm}^{-1}$ and $D\omega = 9\text{cm}^{-1}$, as the electronic basis state splitting $\delta$ is tuned from 0 to 300 cm$^{-1}$. Panel (a) shows the vibrational probability amplitude of the second and third lowest nonadiabatic wavefunctions at $q=0$. In the diabatic and adiabatic approximations, one of these wavefunctions always has a node at $q=0$. $|\psi_1\rangle$ is dominantly $|y\rangle|0\rangle$ at small splittings and dominantly $|x\rangle|1\rangle$ at large splittings; only at large splittings does it effectively have a node. $|\psi_2\rangle$ is dominantly $|y\rangle|0\rangle$ at large splittings; as $\delta$ shrinks it becomes nominally $|x\rangle|1\rangle$ but does not develop a node as $\delta \to 0$ due to interaction with both $|y\rangle|0\rangle$ and $|y\rangle|2\rangle$. The lines cross at 147 cm$^{-1}$, where $|\psi_1\rangle$ and $|\psi_2\rangle$ have equal probability density at $q=0$.

Panel (b) shows stick spectra showing lowest four transition probabilities originating from $v=0$ of the ground state to exact nonadiabatic levels, colored orange for $y$-polarized transitions and purple for $x$-polarized transitions. The zero of energy has been set to midway between the minima of the potential curves. When $\delta = 0$ the two electronic states are degenerate and can have any in-plane polarization. As $\delta$ increases, oscillator strength moves from the second level to the third and from the fourth (nominally $|y\rangle|1\rangle$) to the first. $|\psi_1\rangle$ and $|\psi_2\rangle$ have equal transition strength at $\delta = 167\text{cm}^{-1}$. 
probability density in dimensionless coordinates, $|\phi_v(q)|^2 = (\pi^{-1/4} (2^v v!)^{-1/2} e^{-q^2/2} H_v(q))^2$, evaluated at $q=0$ is $|\phi_0(q = 0)|^2 = 0.564$ for $v=0$, $|\phi_v(q = 0)|^2 = 0$ for odd states, and $|\phi_2(q = 0)|^2 = 0.282$ for $v=2$. $H_v(q)$ is the $v^{th}$ Hermite polynomial. We see that as the electronic splitting gets smaller and approaches the vibrational frequency, nodeless character develops in the sense that neither nonadiabatic vibrational probability density is small at the origin. The two wavefunctions have equal probability density at $q=0$ when $\delta = 147 \text{cm}^{-1}$. If we had chosen a different pair of wavefunctions to compare, the curves would cross at a different splitting. As the splitting continues to get smaller, neither wavefunction fully develops a node at $q=0$. From the point of view of a dominantly $|\Psi_1\rangle\rangle$ state, as $\delta \rightarrow 0$ the wavefunction replaces some of its $|\Psi_0\rangle\rangle$ component with a $-|\Psi_2\rangle\rangle$ component, which is in-phase with $|\Psi_0\rangle\rangle$ at $q=0$. That the maximum nodeless character, or minimum display of a node-like feature by either eigenstate, occurs at finite $\delta$ indicates an electronic-vibrational resonance causes more significant nodeless behavior than a purely electronic degeneracy.

As $\delta \rightarrow 0$, there is another way to understand why $|\Psi_2\rangle\rangle$ does not develop a node-like feature similar to the case of $\delta > \omega$. When the splitting vanishes we can transform Hamiltonian 1.1 into an electronic basis consisting of $(|x\rangle + |y\rangle)/\sqrt{2}$ and $(|x\rangle - |y\rangle)/\sqrt{2}$. In this basis the electronically diagonal elements are $\gamma x \omega (\hat{p}^2 + \hat{q}^2) \pm \omega d \hat{q}$, and there is a diabatic basis of uncoupled harmonic oscillators displaced $\pm d$ from the origin; the $v=1$ vibrational levels on these electronic states have nodes at $q = \pm d$ rather than at $q=0$. This transformation does not give uncoupled states with nodes unless $\delta = 0$, but it does
suggest that at small values of the splitting, we can understand the nodeless character as arising from the coupling between an electronic state which has vibrational nodes at \(-d\) with a state which has nodes at \(+d\). This coupling involves a \(\Delta v = 1\) rule between 
\[
\left(\left| x \right\rangle + \left| y \right\rangle\right)/\sqrt{2} \quad \text{and} \quad \left(\left| x \right\rangle - \left| y \right\rangle\right)/\sqrt{2}.
\]

As noted above, \(\left| \psi_1 \right\rangle\) and \(\left| \psi_2 \right\rangle\) have equal probability density at \(q=0\) when \(\delta = 147 \text{cm}^{-1}\); we emphasize that this does not mean the two wavefunctions are composed of equal \(v=0\) and \(v=1\) character. Figure 4.3(b) shows optical stick spectra for transitions from the ground state to those described by Hamiltonian (4.1) with the same parameters used in panel (a). For transitions originating from \(v=0\) on the ground electronic state, the spectra reduce to plotting the values of \(b_{n,x,0}^2 + b_{n,y,0}^2\) from equation (4.13). When \(\delta = 0\) the two electronic states are degenerate and the linear coupling between \(\left| y \right\rangle\) and \(\left| x \right\rangle\) can be diagonalized by a transformation to \(\left(\left| x \right\rangle + \left| y \right\rangle\right)/\sqrt{2} \quad \text{and} \quad \left(\left| x \right\rangle - \left| y \right\rangle\right)/\sqrt{2}\) electronic states; in this basis\(^{25}\) the \(\omega d q\) term becomes a Franck-Condon active stabilization, which allows weak transitions to \(v' = 1\). For nonzero splitting, the transitions are dominantly \(x\) or \(y\) polarized. The \(x\)-polarized intensity is concentrated in \(\left| \psi_0 \right\rangle\), which is dominantly \(\left| x \right\rangle\left| 0 \right\rangle\), and in \(\left| \psi_3 \right\rangle\), which is dominantly \(\left| y \right\rangle\left| 1 \right\rangle\). As the splitting increases, the interaction between \(\left| x \right\rangle\left| 0 \right\rangle\) and \(\left| y \right\rangle\left| 1 \right\rangle\) weakens, and the intensity borrowing by \(\left| \psi_3 \right\rangle\) from \(\left| \psi_0 \right\rangle\) lessens. The \(y\)-polarized intensity is concentrated in \(\left| \psi_1 \right\rangle\) and \(\left| \psi_2 \right\rangle\), which are dominantly \(\left| y \right\rangle\left| v = 0 \right\rangle\) and \(\left| x \right\rangle\left| v = 1 \right\rangle\). Spectral mixing between \(\left| y \right\rangle\left| v = 0 \right\rangle\) and \(\left| x \right\rangle\left| v = 1 \right\rangle\) occurs through the full range of splitting shown; transition intensities for \(\left| \psi_1 \right\rangle\) and \(\left| \psi_2 \right\rangle\) are
equal when $\delta = 167\text{cm}^{-1}$. This corresponds to $\delta \approx \omega - \lambda$ (rather than the splitting $\delta = \omega$ which would have been expected from a two-state interaction) because $|x\rangle|1\rangle$ also interacts with $|y\rangle|2\rangle$.

Viewing the nonadiabatic wavefunctions from an adiabatic point of view, the rapid color changes seen in eigenstates $|\psi_x\rangle$ and above are clearly derived from a coupling between the adiabatic electronic states, but the color of the plot alone tells us nothing about electronically diagonal nonadiabatic effects. In perturbation theory, electronically diagonal correction terms lead to first and second order corrections in both energies and wavefunctions, while electronically off-diagonal nonadiabatic coupling affects wavefunctions at first order but energies only at second order. We plot important matrix elements of the nonadiabaticity operator $\hat{\Lambda}$ in figure 4.4, along with diabatic, adiabatic and nonadiabatic energy levels, as the electronic energy level splitting $\delta$ varies from 0 to 300 cm$^{-1}$.

In figure 4.4(a) fully diagonal (electronically and vibrationally) matrix elements are shown for $v=0$ and $v=1$ on each adiabatic surface. These matrix elements are the first-order energy corrections of perturbation theory. The corrections for $v=0$ are shown as solid lines, and become quite large for $\delta < \omega / 2$, from 10s to 100s of wavenumbers. For $\delta = 110\text{cm}^{-1}$, these matrix elements are $\Lambda_{-0,0} = 13.61\text{cm}^{-1}$, $\Lambda_{-1,-1} = 5.63\text{cm}^{-1}$ and $\Lambda_{+0,+0} = 14.5\text{cm}^{-1}$. Electronically diagonal but vibrationally off-diagonal terms contribute to second order energy corrections and amount to corrections of less than 3 cm$^{-1}$ for the states shown here.
Figure (4.4) Nonadiabatic matrix elements evaluated in an adiabatic basis and comparison of approximate and exact state energies of Hamiltonian (4.1) with parameters $\omega = 176\,\text{cm}^{-1}$ and $D\omega = 9\,\text{cm}^{-1}$, as the electronic basis state splitting $\delta$ is tuned from 40 to $300\,\text{cm}^{-1}$. In panel (a) the first-order energy corrections (electronically and vibrationally diagonal matrix elements of the nonadiabaticity operator) are shown for the lowest two vibrational levels on each adiabatic electronic state. Purple lines indicate $|->\rangle$, orange lines indicate $|+\rangle$, solid lines refer to $|v^k\rangle = 0$ and dashed lines indicate $|v^k\rangle = 1$. Electronically diagonal but vibrationally off-diagonal energy corrections contribute at second order and are less than $3\,\text{cm}^{-1}$ for the levels shown. When the electronic splitting is $\delta \approx \omega / 2$ and larger the diagonal non-BO correction is less than $20\,\text{cm}^{-1}$ for $v^k=0$ and less than $10\,\text{cm}^{-1}$ for $v^k=1$; for smaller values of electronic splitting the non-BO correction can become quite large. Panel (b) shows electronically off-diagonal nonadiabaticity matrix elements, focusing on $|v^k\rangle = 1$ for both the upper and lower adiabatic electronic states. Dark orange lines indicate the dominant coupling terms affecting $v^k=1$ on the upper adiabatic electronic state: solid orange gives $\Lambda_{+1,-0}$, dashed orange shows $\Lambda_{+1,-2}$. Dark purple lines indicate the dominant coupling terms affecting $v^k=1$ on the lower adiabatic electronic state: solid purple gives $\Lambda_{-1,0}$, dashed purple shows $\Lambda_{-1,-2}$. These matrix elements contribute to wavefunction corrections at first order but only affect energy levels at second order. These couplings are seen to be of comparable magnitude; the difference seen in perturbation of, e.g., $|->\rangle|0\rangle$ and $|+\rangle|0\rangle$ stem from a significant difference in energy gaps between these states and the relevant $v^k=1$ states. Panel (c) shows the energies of the lowest 3 eigenstates treated at different levels of approximation: diabatic (black), adiabatic (green) and nonadiabatic (red). The diabatic basis has a degeneracy between $|x\rangle|1\rangle$ and $|y\rangle|0\rangle$ at $\delta = 176\,\text{cm}^{-1}$, while the adiabatic basis has a degeneracy between $|->\rangle|1\rangle$ and $|+\rangle|0\rangle$ around $140\,\text{cm}^{-1}$. The $\Lambda_{+1,-0}$ off-diagonal couplings seen in panel (b) strongly perturb the system near the degeneracy in the adiabatic basis (avoided crossing in red).
We can get a sense of the effect of off-diagonal corrections by comparing these matrix elements to table 1, where the total energy corrections are available by taking differences between adiabatic energies and exact nonadiabatic energies. For example, the lowest nonadiabatic eigenstate has an energy of 27.39 cm\(^{-1}\) while the lowest adiabatic state is at 20.95 cm\(^{-1}\). The total energy corrections must account for 6.44 cm\(^{-1}\); we have already mentioned the first order correction, \(\Lambda_{0,0} = 13.61 \text{ cm}^{-1}\), meaning that higher order terms must add -7.17 cm\(^{-1}\). The second order correction is smaller than the first, providing some reason to hope a low-order perturbation expansion might be successful in describing this state. For the higher states, however, this is not so. Considering the second lowest nonadiabatic eigenstate, which is nominally \(|+\rangle\langle 0|\), the total energy difference between the basis state and the exact state is -31.36 cm\(^{-1}\) while the first order energy correction is 14.5 cm\(^{-1}\). The second and higher terms must account for -45.86 cm\(^{-1}\), which is significantly larger than the first order correction. A similar situation holds for \(|\psi_3\rangle\), which is nominally \(|-\rangle\langle 0|\): the first order correction is 5.63 cm\(^{-1}\) while the total energy correction is 41.12 cm\(^{-1}\). For all but the lowest level of the excited state, the dominant nonadiabatic perturbation arises from electronically off-diagonal coupling terms.

Panel 4(b) shows the magnitudes of electronically off-diagonal elements of \(\hat{\Lambda}\), focusing on those giving first-order wavefunctions corrections for \(|-\rangle\langle 1|\) and \(|+\rangle\langle 1|\). These matrix elements are seen to be on the order of several tens of wavenumbers, and decrease monotonically with increasing splitting. Any resonant effect, such as the peak nodeless feature in figure 4.3(a), must therefore be attributed to a near-degeneracy. In figure 4.4(b) we show the values of adiabatic basis state energies, diabatic basis state...
energies, and exact nonadiabatic energies. In the adiabatic basis, the second and third levels come into a degeneracy near $\delta = 140 \text{cm}^{-1}$, well below the crossing of the second and third diabatic levels at a splitting of $\delta = 176 \text{cm}^{-1}$. The difference stems from the softening of the lower adiabatic potential and hardening of the upper, with respect to the diabatic basis. The adiabatic degeneracy is slightly below the peak nodeless feature in figure 4.3(a), but is close enough to suggest that for this model Hamiltonian, strong nodeless behavior stems from near degeneracy between $\Delta \nu = 1$ adiabatic basis states. However, it is not clear to us why the $q=0$ probability density crossover in figure 4.3(a) shows up exactly at the value of $\delta$ that it does.

4.3.2) Time-dependent behavior

4.3.2a) Initial Conditions

Before we compare the propagation of a wavepacket under the full nonadiabatic Hamiltonian to that under the adiabatic approximation, we consider the role of the Condon approximation in dynamical calculations. The Condon approximation affects only the initial conditions, not the time-domain evolution of the wavepacket, dictated by the Hamiltonian. Nevertheless, the initial conditions assumed for the excited state vibronic wavepacket can have a dramatic effect on the wavepacket dynamics.

The Condon approximation is automatically valid for “crude adiabatic” states, which is the basis Hamiltonian (4.1) is written in, since the electronic wavefunctions are explicitly independent of vibrational coordinate. For an excited wavepacket composed of exact nonadiabatic eigenstates $|\psi_n\rangle$, expanded as a coordinate-independent linear combination of crude adiabatic states as in equation (4.13), it is not obvious how to apply
the Condon approximation. The nonadiabatic states, even though composed of crude adiabatic basis states, have strong vibrational coordinate and level dependent dipoles. This likely makes them bad candidates for any further Condon-type approximation.

Under the adiabatic approximation, however, excited state wavefunctions are a coordinate-dependent linear combination of the diabatic basis states, and therefore have a coordinate-dependent transition dipole from the ground electronic state. In this case the Condon approximation can be applied to the adiabatic eigenstates, by examining expansion coefficients only at \( q=0 \), in addition to applying the Condon approximation to the crude adiabatic basis states. In this sense, we can calculate excitation probabilities for adiabatic electronic-vibrational product states by integrating

\[
\langle v' | \langle k | \hat{E} \cdot \hat{\mu}(q) | g \rangle | v'' \rangle = \langle v' | \hat{E} \cdot \hat{\mu}_{gg}(q) | v'' \rangle \quad \text{(equation (4.19))},
\]

or make the Condon approximation and move the transition dipole out of the \( q \)-integral:

\[
\langle v' | \langle k | \hat{E} \cdot \hat{\mu}(q) | g \rangle | v'' \rangle \approx \left( \hat{E} \cdot \hat{\mu}_{gg}(q_0) \right) \langle v' | v'' \rangle \quad \text{(equation (4.20))}. \]

This choice changes the expansion coefficients when we express an excited state wavepacket as a linear combination of adiabatic basis functions.

This is illustrated in figure 4.5, where we show the initial wavepacket as calculated without approximation and with the Condon approximation applied to adiabatic excited states. Panel (a) shows a wavepacket prepared when the incident light is polarized along the molecular \( x \) axis, which is parallel to the transition dipole for the lower adiabatic state if evaluated at \( q=0 \). The dashed black line shows the \( v=0 \) vibrational probability density of the ground state, which (to within a constant multiplier) will be the initial vibrational probability density for an excited state wavepacket created under
Figure (4.5) Probability density at time zero for wavepackets produced under impulsive excitation with polarized light, calculated with and without the Condon approximation. Dashed, black curves show a \( v=0 \) ground state wavefunction, which gets transferred to the excited state manifold for a short laser pulse. The initial wavepacket is identical whether the excited state manifold is taken to be a complete set of nonadiabatic states or a complete set of adiabatic states. Blue shows the square of the projection of the initial wavepacket onto the lower adiabatic electronic state, \( |\Phi_{-}(q)|^2 \), while red shows the projection onto the upper state, \( |\Phi_{+}(q)|^2 \). Panel (a) shows the square of the initial wavepacket following excitation with a pulse polarized along the molecular \( x \) axis, which has \( q \)-dependent projections onto \( \psi_- \) and \( \psi_+ \). At \( q=0 \), an \( x \)-polarized pulse excites the \( \psi_- \) state, and no population density is excited to \( \psi_+ \). At positive \( q \) some \( x \) character is added to \( \psi_+ \), and at \( -q \) some \( -x \) character is added to \( \psi_- \). Panel (b) shows the wavepackets constructed under the same conditions, but using the Condon approximation which sets the transition dipoles everywhere equal to those at \( q=0 \); this then over-estimates the width of the wavepacket on \( \psi_- \) and misses the probability density created on \( \psi_+ \).

Wavepackets created with light polarized along the molecular \( y \) axis are similar at time zero, but with \( \psi_+ \) and \( \psi_- \) interchanged; the difference strongly affects subsequent dynamics. Panel (c) shows the excited state wavepacket excited with polarization parallel to \( (\hat{x} + \hat{y})/\sqrt{2} \) in the molecular frame. There is equal total probability density in both adiabatic electronic states, but each state has its projection shifted away from \( q=0 \) according to the overlap between \( |g\rangle |0\rangle \) and the region where the mixing angle approaches the laser polarization: \( \psi_- \) has \( |y\rangle \) added in-phase at \( -q \), while \( \psi_+ \) gets \( |x\rangle \) added in-phase at \( +q \). Panel (d) shows the excited state wavepackets excited under the same conditions, but in the Condon approximation. Although the Condon approximation does correctly excite equal probability to both surfaces, by replacing the transition dipole everywhere with that at \( q=0 \), it incorrectly generates excited state wavepackets which are centered at the origin on both potential curves.
impulsive excitation. The blue line gives the component of the vibrational probability density which arises from the $|\rightarrow\rangle$ adiabatic electronic state. It looks quite similar to the ground $\nu=0$ density, but is somewhat narrower because, at larger $q$, the transition dipole is no longer exactly parallel to the incident radiation, and correspondingly less of the available ground state density gets excited to $|\rightarrow\rangle$. This missing probability density is excited to $|\leftarrow\rangle$. The red line shows the component of the excited state vibrational probability density from excitation to the $|\leftarrow\rangle$ adiabatic electronic state. No probability density is created on this electronic state at $q=0$, because the transition dipole is perpendicular to the incident radiation; away from the origin the transition dipole is nonzero and is an odd function of $q$, as it comes from the $\sin \theta |x\rangle$ component of $|\leftarrow\rangle$.

The probability density created on $|\leftarrow\rangle$ must then be composed entirely of odd vibrational quantum numbers. In panel (b) we show a wavepacket calculated under the Condon approximation with the same incident radiation. Transition dipoles are set equal to those evaluated at $q=0$, which can excite $|\rightarrow\rangle$ but not $|\leftarrow\rangle$. Without a coordinate-dependent dipole strength, the wavepacket created on $|\rightarrow\rangle$ is an undistorted copy of the ground state vibrational probability density, and the blue line lies on top of the black line. The red line is zero everywhere, as the $|\leftarrow\rangle$ electronic state is perpendicular under this approximation.

The effect of the Condon approximation on the adiabatic dynamics can be anticipated by imagining the initial forces which would be applied to the wavepackets of fig 4.5(a) and 4.5(b) by the potential curves shown in fig 4.1(b). The potential curve for the $|\rightarrow\rangle$ electronic state is softer than the curve for the ground state (which is identical to
the curves in fig 4.1(a) for the diabatic basis); a wavepacket matching $v=0$ on the ground state would initially expand, as it would be narrower than $|\pm\rangle |0\rangle$. Since the vibrational density on $|\pm\rangle$ is narrower in fig 4.5(a) than in fig 4.5(b), this expansion, and the subsequent quantum beats, would be under-emphasized with a Condon approximation. Given the $q$-dependence of the electronic mixing angle, there should be an increase in overall $|y\rangle$ character as the wavepacket expands. The potential curve (fig 4.1(b)) for the $|\pm\rangle$ electronic state is significantly narrower than that of the ground state, so the component of the excited state wavepacket represented by the red line in fig 4.5(a) will feel a compressive force, accentuated by the fact that only population from the wings of the ground state distribution is transferred to this curve. This should cause a rapid shrinking of the wavepacket, and with it an increase in $|y\rangle$ electronic character; this motion is completely missing under the Condon approximation. Given the vibrational motions of both electronic components of the wavepacket, we expect the wavepacket width quantum beats should partially cancel. The quantum beats in electronic character on both surfaces are in phase, subsequently we expect much larger electronic quantum beats without the Condon approximation than with one.

Panels (c) and (d) in fig 4.5 show initial wavepackets constructed for laser polarization projecting onto $(\hat{x} + \hat{y})/\sqrt{2}$ in the $x$-$y$ molecular plane for exact and Condon-approximation excitation probabilities. The exact initial conditions show equal amounts of vibrational density on each surface, with the component coming from $|\pm\rangle$ centered at $q=-0.31$ and the $|\pm\rangle$ component at $q=0.31$. This can be understood by looking again at
the potential curves of fig 4.1(b), noting that the lower potential curve becomes red at $-q$
while the upper curve becomes red at $+q$, and noting from fig 4.1(c) that red indicates an
in-phase combination of $x$ and $y$. Each individual adiabatic surface receives a wavepacket
based on the overlap between the ground state $v=0$ wavefunction and the region where
the $q$-dependent transition dipole aligns with the incident field. This is a non-Condon
effect, and panel (d) shows the initial wavepacket as calculated under the Condon
approximation. We see again equal amplitude on $|+\rangle$ and $|−\rangle$, but with no variation of
the transition moment along $q$ allowed in the calculation, the probability density on each
surface has the position and width of the ground state $v=0$ wavefunction.

4.3.2b) Wavepacket motion

We show the vibrational and electronic structure of wavepackets propagating
under the exact nonadiabatic Hamiltonian for laser polarization parallel to molecular $x$
and $y$ axes in figure 4.6. The wavepacket is shown at 9 time steps of 25 fs each, for a total
run of 200 fs. This is roughly a half-period of the dominant motions seen in the $y$-
polarized calculation. Panel (a) shows the wavepacket dynamics after excitation with $x$-
polarized light; the only apparent motion in this plot is a low-amplitude breathing motion.
With exact nonadiabatic eigenstates expressed as a linear combination of diabatic basis
states, as in eqn (4.13), the transition strength under these polarization conditions comes
from the $|x\rangle|0\rangle$ component; the wavepacket then develops a small amount of $|y\rangle|1\rangle$
character, from the $|x\rangle|0\rangle \leftrightarrow |y\rangle|1\rangle$ coupling, leading to a wider wavepacket. This can
also be understood from an adiabatic perspective, by noting that the lower adiabatic
potential curve is wider than the ground state potential, so the initial motion should be to
Figure (4.6) Excited state wavepacket, $|\Psi(T)\rangle$, propagation after a $v=0$ ground state is excited with an impulsive, polarized laser pulse. Excited states are described by Hamiltonian (4.1) with parameters $\delta = 110 \text{cm}^{-1}$, $\omega = 176 \text{cm}^{-1}$ and $D\omega = 9 \text{cm}^{-1}$. Under impulsive excitation eigenstates are populated proportionally to their projections onto $|x\rangle|0\rangle$ (left) and $|y\rangle|0\rangle$ (right). The zero of energy has been set to the lowest eigenvalue, so that the $|\psi_0\rangle$ component of each wavepacket does not oscillate (i.e. $\exp(-iE_0t/\hbar) \equiv 1$).

Vibrational probability density, $|\langle q |\Psi(T)\rangle|^2 = |\Phi_x(q)|^2 + |\Phi_y(q)|^2$, is plotted as a function of propagation time and vibrational coordinate. The coloring of the curves indicates the time- and coordinate-dependent electronic character, taken from $\Theta(q,T) = \tan^{-1}\left[\langle y |\langle q |\Psi(T)\rangle/\langle x |\langle q |\Psi(T)\rangle\right]$ and mapped onto the color wheel of figure 4.1(c). Panel (a) shows wavepacket motion after $x$-polarized excitation. The wavepacket undergoes low-amplitude breathing motions, remaining centered at $q=0$. Panel (b) shows wavepacket motion after $y$-polarized excitation. Here we see that, over the course of about 200 fs, the wavepacket changes from completely $|y\rangle|0\rangle$ character, to almost completely $|x\rangle|1\rangle$ character, remaining centered at $q=0$. In the adiabatic framework, one would have low-amplitude breathing motions on the $|+\rangle$ surface similar to what was seen in panel (a) for the $|-\rangle$ surface. These dynamics can be understood from a nonadiabatic point of view, as the $|y\rangle|0\rangle$ oscillator strength is concentrated mainly in $|\psi_1\rangle$ and $|\psi_2\rangle$, which both have significant $|x\rangle|1\rangle$ character. The difference between panels (a) and (b) are due to the differences in the energy gap between $|x\rangle|0\rangle$ and $|y\rangle|1\rangle$, in contrast to that between $|y\rangle|0\rangle$ and $|x\rangle|1\rangle$. 
spread out. In the adiabatic approximation, this motion comes from a \(|-\rangle|0\rangle \leftrightarrow |-\rangle|2\rangle\) superposition. Typically, a \(\Delta \nu = 1\) superposition leads to a wavepacket translation, for example when the negative region of a \(\nu=1\) state destructively interferes with a \(\nu=0\) state, but the positive region interferes constructively. A \(\Delta \nu = 1\) superposition here, however, leads to a width modulation because the probability densities add instead of the wavefunctions, 
\[
|\langle q|\Psi(T)\rangle|^2 = |\Phi_\nu |x\rangle + \Phi_\nu |y\rangle|^2 .
\]
That the dynamics can be rationalized using either nonadiabatic or adiabatic arguments suggests that the lowest excited state, \(|\psi_0\rangle\), is not strongly perturbed by nonadiabatic effects.

Figure 4.6(b) shows wavepacket dynamics under \(\gamma\)-polarized excitation. It can be seen that the wavepacket spreads significantly and develops strong \(x\) character within 75 fs, and has converted almost completely to \(|x\rangle|1\rangle\) character by 200 fs. Under the adiabatic approximation, population would be mainly prepared on the upper surface \(|+\rangle\) with some amount along the wings prepared onto the lower surface \(|-\rangle\). The component on the \(|+\rangle\) surface would be expected to feel a compressive force, and become more \(\gamma\)-polarized as it compresses. At no point in an adiabatic calculation would the wavepacket be expected to become more \(|x\rangle\)-like than \(|\nu\rangle\)-like. There are strong qualitative discrepancies from the adiabatic approximation, which indicates that the exact dynamics are intrinsically nonadiabatic, and these discrepancies appear within 75 fs.
4.3.2c) time-dependence of observable and projections

To gain more insight into the wavepacket dynamics, we calculate expectation values for the wavepacket vibrational coordinate and variance as well as $q$-integrated projections onto diabatic and adiabatic electronic basis states as a function of propagation time. The coordinate expectation value for position is calculated as

$$\langle q(T) \rangle = \langle \Psi(T) | \hat{q} | \Psi(T) \rangle,$$

and wavepacket variance is represented by the second central moment,

$$\sigma^2(T) = \langle \Psi(T) | (\hat{q} - \langle q(T) \rangle)^2 | \Psi(T) \rangle.$$

Electronic dynamics are followed by the time-dependent, $q$-integrated projection onto the diabatic state $| x \rangle$ and the adiabatic state $| - \rangle$, given by $| x \rangle | \Psi(T) \rangle^2$ and $| - \rangle | \Psi(T) \rangle^2$, respectively. These observables are calculated at 10 fs increments for 1001 steps. The time traces are then Fourier transformed, yielding a frequency resolution of 3.3 cm$^{-1}$ and range of 1667 cm$^{-1}$; this is sufficient to identify which eigenstate superpositions are driving the relevant motions.

In Figure 4.7 we show the time dependence of vibrational and electronic degrees of freedom for the case of $y$-polarized excitation, and compare exact nonadiabatic propagation, adiabatic propagation with exact initial conditions, and adiabatic propagation with initial conditions calculated under the Condon approximation. Under $y$ polarization, the exact excited state wavepacket is dominantly a superposition of $| \psi_1 \rangle$ and $| \psi_2 \rangle$, which contain the bulk of the $| y \rangle | 0 \rangle$ character. Panel (a) shows the time dependence of the vibrational wavepacket variance, which begins at 0.5, the variance of the ground state $v=0$ wavefunction. The exact calculation (red) shows little movement for the first 25 fs, then begins to drastically expand as the coupling between $| y \rangle | 0 \rangle$ and
Figure (4.7) Detail of excited state wavepacket dynamics following impulsive excitation polarized along the molecular $y$ axis. Red traces display wavepacket propagation using the full nonadiabatic Hamiltonian. Black and blue traces are propagated using the adiabatic approximation. Initial conditions for red and black traces are exact, while initial conditions for blue traces are calculated under the Condon approximation. Under $y$ polarization, the Condon approximation only populates the adiabatic $|\pm\rangle$ potential curve.

In panel (a) we show the time dependence of the wavepacket variance. For reference, an unperturbed $v=0$ state has a variance of 0.5, and an unperturbed $v=1$ state has a variance of 1.5; panel (b) shows Fourier transforms of the traces in panel (a). The exact calculation shows an oscillation from 0.5 to 1.42, with a frequency of 95 cm$^{-1}$, corresponding to the energy difference between $|\psi_1\rangle$ and $|\psi_2\rangle$. Propagation under an adiabatic Hamiltonian shows much smaller beating, dominated by $\Delta v = 2$ vibrational superpositions. Panel (c) shows the integrated projection onto the $|x\rangle$ electronic state, with the Fourier transforms of these traces shown in panel (d). The nonadiabatic electronic character oscillates in phase with the nuclear motion, with significantly larger amplitude than expected under the adiabatic approximation. In panel (e) we show the projection onto the lower adiabatic electronic state. Since blue and black curves are propagated under an adiabatic Hamiltonian, they remain constant in this plot. The exact nonadiabatic calculation, however, shows a strong oscillation between the two adiabatic electronic states. This plot demonstrates coupling between adiabatic electronic states.
\( |x\rangle|1\rangle \) takes effect, increasing to a variance of 1.42, nearly the value of 1.5 expected for a purely \( v=1 \) wavefunction. Under the adiabatic approximation (black) the wavepacket initially expands faster than the exact nonadiabatic wavepacket, ceases to expand at 50 fs and begins to compress. This motion is happening mainly on the lower adiabatic potential curve, and beats at the superposition frequency of \( E_{a-3}^a - E_{a-1}^a = 324 cm^{-1} \). A wavepacket prepared under the Condon approximation (blue) shrinks instead of expanding. This can be understood by noting that under a Condon approximation, we evaluate the transition dipole at \( q=0 \), which will then populate the upper adiabatic potential curve with the entire ground-state wave packet. The upper adiabatic potential curve is narrower than the ground state potential, and would exert a compressive force if the entire ground state wavepacket were transferred there. The Condon approximation, then, fails qualitatively to describe the vibrational behavior even at the earliest times, before any coupling can be felt. Adiabatic propagation from exact initial conditions recovers the correct initial force (expansion), but fails quantitatively from the beginning and vastly underestimates the expansion of the wavepacket for times longer than 50 fs.

In order to focus on electronic behavior, panel (c) of figure 4.7, shows the projection of the wavepacket onto the diabatic \( |x\rangle \) electronic state. In red we see that, when propagated under the exact Hamiltonian, electronic character oscillates with the same dominant frequency and phase as the wavepacket width seen in panel (a). This indicates the tight coupling between electronic and vibrational motion, which comes from the \( |y\rangle|0\rangle \) and \( |x\rangle|1\rangle \) interaction. The blue curve, which due to the Condon approximation contains population only on the upper adiabatic surface, shows an
electronic character oscillating in step with the wavepacket width under the Condon approximation: as the wavepacket compresses and covers less of the mixing angle seen in the color variation in figure 4.1(b), the amount of $x$-character drops. These are small oscillations, at the same frequency as seen in the wavepacket width beating under the Condon approximation. The adiabatic black curve shows richer dynamics, with a small amplitude fast oscillation and a large amplitude slow oscillation. This slow oscillation occurs at the difference frequency of $|{-}\rangle |1\rangle$ and $|{+}\rangle |0\rangle$. In the adiabatic picture, at time zero the wavepacket is entirely $y$-polarized, which requires probability density on both the upper and lower curve. The component of the wavepacket on the lower curve then expands, increasing its $y$-character, while the component on the upper curve also expands slightly, increasing its $x$-character. The overall wavepacket then shows very little change in electronic character for the first 100 fs. The vibrational probability densities on both $|{-}\rangle$ and $|{+}\rangle$ curves both initially expand and are initially oscillating in-phase (at first), but the oscillation frequencies on the two curves are slightly different, such that the two components of the wavepacket are oscillating roughly out of phase by 700 fs. At this point the diabatic $|x\rangle$ character reaches its maximum level, then begins to drop as the vibrational wavepackets on the two surfaces begin to oscillate in-phase again.

Panel (e) shows the projection of the propagating wavepackets onto the adiabatic $|{-}\rangle$ state. As the black and blue traces are propagated under an adiabatic Hamiltonian, their projections onto adiabatic basis states do not change. The nonadiabatic wavepacket, however, shows very large oscillations from dominantly $|{+}\rangle$ character to dominantly $|{-}\rangle$ character, at the same frequency and in phase with the oscillations seen in panels (a) and
This panel demonstrates that coupling between adiabatic electronic states is responsible for the dynamics, and rules out the possibility that these dynamics are caused by the electronically diagonal nonadiabatic correction.

In figure 4.8 we examine nonadiabatic wavepacket propagation following $x$-polarized excitation. Under the adiabatic approximation, $x$-polarized light excites probability density mainly to the $\ket{-}$ surface; under a Condon approximation only this electronic state is excited. The vibrational dynamics are qualitatively comparable in both cases, with low amplitude oscillations at roughly $2\omega$. All calculated wavepackets initially expand, up to a variance ranging from 0.63 under the Condon approximation to 0.75 for the nonadiabatic wavepacket. Both adiabatic calculations oscillate at the superposition frequency between $\ket{-}\bra{0}$ and $\ket{-}\bra{2}$. The nonadiabatic propagation (red) has a richer structure, due to the coupling of both $\ket{x}\bra{0}$ and $\ket{x}\bra{2}$ to $\ket{y}\bra{1}$, oscillating at the superposition frequencies $E_3 - E_0 = 260\text{ cm}^{-1}$, $E_4 - E_0 = 377\text{ cm}^{-1}$, and $E_4 - E_3 = 117\text{ cm}^{-1}$; The red trace repeatedly dips briefly below 0.5, indicating a squeezed state. The involvement of $\ket{x}\bra{2}$ is a second-order effect when viewed from a diabatic basis: the excited basis state which is optically accessible is $\ket{x}\bra{0}$, which is not directly coupled to $\ket{x}\bra{2}$. The vibrational dynamics as a whole are only slightly perturbed by the nonadiabatic effects.

Panel (c) of figure 4.8 shows the projection of each wavepacket onto the diabatic $\ket{x}$ electronic basis state. The nonadiabatic propagation shows electronic character oscillating at the same frequencies as its wavepacket variance oscillation. The $260\text{ cm}^{-1}$
Figure (4.8) Detail of excited state wavepacket dynamics following impulsive excitation polarized along the molecular $x$ axis. Red traces display wavepacket propagation using the full nonadiabatic Hamiltonian. Black and blue traces are propagated using the adiabatic approximation. Initial conditions for red and black traces are exact, while initial conditions for blue traces are calculated with the Condon approximation. Under $x$ polarization, the Condon approximation only populates the lower $|\rangle$ potential curve. In panel (a) we show the time dependence of the wavepacket variance, measured in dimensionless normal coordinate of the diabatic basis; panel (b) shows Fourier transforms of the traces in panel (a). All three traces in panel (a) show an initial expansion in wavepacket variance, and subsequent oscillations at about twice the vibrational frequency. In panel (c) we show the time dependence of the integrated projections onto $|x\rangle$, in order to study changes in electronic character; panel (d) shows Fourier transforms of the traces in (c). The nonadiabatic propagation shows electronic character oscillating at the same frequencies as its wavepacket variance oscillation. The reduction in amplitude compared to 7(c) stems from the significantly larger energy gap between coupled states here. The blue trace shows very weak oscillations, again at the same frequency and out of phase with the wavepacket width beating. The black trace, however, which propagates a wavepacket on both adiabatic potential curves, shows a strong oscillation coming from a $|-\rangle|0\rangle \leftrightarrow |+\rangle|1\rangle$ superposition. This is qualitatively similar to the superposition in the exact calculation, but is strongly over-emphasized by the adiabatic approximation. Panel (e) shows the projection onto the lower adiabatic electronic state. The exact calculation initially oscillates toward the lower adiabatic state (panel e), and away from the lower diabatic state (panel c).
component corresponding to the gap between $|\psi_3\rangle$ and $|\psi_0\rangle$, nominally $|x\rangle|0\rangle$ and $|y\rangle|1\rangle$, is out of phase with vibrational variance ($|x\rangle$ character decreases when vibrational variance increases, easiest to see by looking at the first 128 fs period) showing that increases in variance are coming dominantly from the $|x\rangle|0\rangle \leftrightarrow |y\rangle|1\rangle$ coupling. The reduction in amplitude compared to figure 4.7(c), which shows the same projection but for dynamics following $y$-polarized excitation, stems from the significantly larger energy gap between coupled states here. Under the Condon approximation (blue) there are very weak oscillations, again at the same frequency and out of phase with the wavepacket width beating; this beating arises from the vibrational wavepacket reaching more $y$ character when covering a larger region of $q$. An adiabatic approximation without the Condon approximation, however, (black line) propagates a wavepacket on both adiabatic potential curves and shows a strong oscillation coming from a $|--\rangle|0\rangle \leftrightarrow |+\rangle|1\rangle$ superposition. This is qualitatively similar to the superposition in the exact calculation, but is strongly over-emphasized by the adiabatic approximation. In panel (e) the projection onto the lower adiabatic surface is shown for each wavepacket. Interestingly, although the excitation polarization is chosen to maximally excite the lower adiabatic surface (which is dominantly $x$ in character), the nonadiabatic coupling acts to increase the $|--\rangle$ character beyond what can be directly prepared by an impulsive laser pulse.

In figure 4.9 we show wavepacket dynamics following impulsive excitation polarized along $(\hat{x} + \hat{y})/\sqrt{2}$ in the molecular frame. We note that when the excitation polarization is not parallel to $x$ or $y$, wavepackets may be created in an asymmetrical way, leading to a motion of the center of the wavepacket, as opposed to the width oscillations.
Figure (4.9) Detail of excited state wavepacket dynamics following impulsive excitation polarized along $(\hat{x} + \hat{y})/\sqrt{2}$ in the molecular frame. Red traces display wavepacket propagation using the full nonadiabatic Hamiltonian. Black and blue traces are propagated using the adiabatic approximation. Initial conditions for red and black traces are exact, while initial conditions for blue traces are calculated with the Condon approximation. In panel (a) we show the time-dependent expectation value of the wavepacket center, and in panel (b) corresponding Fourier transforms. Traces with exact initial conditions show wavepacket oscillations arising from nominally $\Delta v = 1$ superposition on a single electronic surface, while the Condon approximation completely misses the vibrational dynamics by keeping $\bar{q} = 0$ at all times. Panels (c) and (d) show the time-dependent projections onto the diabatic electronic state $|x\rangle$. The initial motion in both adiabatic calculations is toward less $|x\rangle$ character, while in the exact calculation it is toward increased $|x\rangle$ character. In panel (e) we show the projection onto BO electronic states, and see the exact calculation moving strongly toward the lower potential curve.
seen above. In panel (a) we show the time-dependent expectation values of the wavepacket center, and in panel (b) corresponding Fourier transforms. The Condon approximation completely misses the vibrational dynamics by keeping $\langle q \rangle = 0$ at all times. While the expectation value $\langle q \rangle$ oscillates in both the exact calculation and the adiabatic approximation, this motion is dependent on setting up initial conditions correctly. The Condon approximation makes it impossible to create a wavepacket which oscillates side-to-side on an undisplaced excited state.

The nonadiabatic wavepacket shows strong oscillations at $E_1 - E_0 = 95 \text{cm}^{-1}$ and $E_2 - E_0 = 190 \text{cm}^{-1}$, which are of a $|x\rangle|0\rangle \leftrightarrow |x\rangle|1\rangle$ character (recall the $|x\rangle|1\rangle$ basis state is split into eigenstates $|\psi_1\rangle$ and $|\psi_2\rangle$). There is also a smaller peak at $E_3 - E_1 = 165 \text{cm}^{-1}$, which is of a $|y\rangle|0\rangle \leftrightarrow |y\rangle|1\rangle$ character. The adiabatic approximation without the Condon approximation (black) shows slightly smaller oscillations, arising from $|-\rangle|0\rangle \leftrightarrow |-\rangle|1\rangle$ and $|+\rangle|0\rangle \leftrightarrow |+\rangle|1\rangle$ interference. Panels (c) and (d) show the time-dependent projections onto the diabatic electronic state $|x\rangle$. The exact calculation is dominated by a superposition between $|\psi_1\rangle$ and $|\psi_2\rangle$, which comes from the $y$-polarized component of the excitation pulse. The adiabatic black trace shows a fast oscillation from a $|+\rangle|1\rangle \leftrightarrow |-\rangle|0\rangle$ superposition and a slow oscillation from the superposition of $|-\rangle|1\rangle$ and $|+\rangle|0\rangle$. Interestingly, although the adiabatic calculation with exact initial conditions agreed with the nonadiabatic results about the direction of the initial force on the electronic degrees of freedom under purely $x$ or purely $y$ excitation, the adiabatic approximation fails already at the earliest times for this $(\hat{x} + \hat{y})/\sqrt{2}$ excitation. The
initial motion in both adiabatic calculations is toward less $|x\rangle$ character, while in the exact calculation it is toward increased $|x\rangle$ character.

In panel (e) we show the projection onto adiabatic electronic states, and see the exact calculation moving strongly toward the lower potential curve. Comparing the projections onto adiabatic states after excitation with $\hat{x}$ polarization (figure 4.8(e)), $\hat{y}$ polarization (figure 4.7(e)), and $(\hat{x} + \hat{y})/\sqrt{2}$ polarization (figure 4.9(e)), we see the initial electronic motion, when nonadiabatic coupling is accounted for, is always toward the lower adiabatic surface, regardless of whether the electronic motion viewed from a diabatic point of view is toward $|x\rangle$ or $|y\rangle$, and regardless of whether or not the wavepacket moves away from $\langle q \rangle = 0$.

That the electronic motion is always toward the lower adiabatic surface stems from the relative isolation of $|−\rangle|0\rangle$ state compared to any other basis state; this can be seen in figures 4.1(b) and (d). At any given polarization, some population density will be created on the upper adiabatic surface and some on the lower. Due to the smallness of the stabilization energy, $(D\omega)/\omega \approx 0.05$, the excited state wavepacket will be composed mainly of $v=0$ states. Population in $|−\rangle|0\rangle$ essentially stays in that state, while population in $|+\rangle|0\rangle$ couples immediately to $|−\rangle|1\rangle$. This then gives an overall net increase in $|−\rangle$ character, for any laser polarization.

Surprisingly, a critical condition for this efficient population transfer to the lower adiabatic curve is for the nonadiabatic coupling, as parameterized by $D\omega$, to be weak. If $D\omega$ were large enough to significantly distort the potential energy curves, the Franck-
Condon factors would begin to favor optical excitation to higher vibrational levels. If exciting, for example, to \( v=1 \) states, the population in \( -|l\rangle \) would couple to \( +|0\rangle \), and the population in \( +|l\rangle \) would couple to \( -|2\rangle \), giving no strong preference for population to flow to one curve or the other. The critical conditions for this “funneling” of population from the higher adiabatic surface to the lower are for 1) the energy gap between zero-order electronic states to be roughly equal to the vibrational frequency, and 2) the excited state stabilization energy to be weak enough that optical excitation strongly favors excitation to \( v=0 \) states.

In nonadiabatic language, it is sometimes useful to distinguish between conical intersections and conical funnels. A conical intersection has a point of degeneracy where two adiabatic potential energy surfaces intersect; a conical funnel efficiently transfers population from one adiabatic surface to another faster than vibrational relaxation. A funnel may or may not have a point of degeneracy, and a conical intersection may or may not efficiently funnel population between curves. In this language, our system appears to be operating like a conical funnel, although we cannot use the term “conical” as there is only one vibrational mode in the model Hamiltonian.

To emphasize that the ultrafast directional transfer of population between adiabatic surfaces which we describe requires weak coupling we use the term “nested funnel.” The directionality of the transfer from the upper surface to the lower is lost if the optical transition strength is not concentrated in \( v=0 \) on the excited states. The transfer is ultrafast and potentially efficient even for weak coupling due to a near degeneracy; critically, the necessary near degeneracy is between \( v=1 \) on one electronic state and \( v=0 \) on another.
4.4 Conclusions

The stationary states and wavepacket dynamics of a model 2-state linear pseudo-Jahn-Teller Hamiltonian have been investigated for the case of weak coupling with an electronic energy gap roughly equal to the vibrational frequency. The near-degeneracy of $v=1$ on the lower electronic state with $v=0$ on the upper electronic state causes ultrafast transfer of population preferentially toward the lower adiabatic surface. This population transfer requires weak coupling in order to efficient.
4.5 References


18 Visual Numerics IMSL numerical libraries (Rogue Wave Software, Boulder, CO).


CHAPTER 5
NONADIABATIC COUPLING IN EXCITONIC HAMILTONIANS AND NESTED
INTERMOLECULAR FUNNELS

5.0 Abstract

The singly excited states of a two-site Coulombically coupled pigment model Hamiltonian is considered under the condition that the electronic energy difference of the two sites roughly matches a vibrational mode. If there is a small vibrational displacement upon excitation of an isolated pigment, this vibronic stabilization transforms into a nonadiabatic off-diagonal coupling between the excitonic electronic states. Weak nonadiabatic coupling and a near-degeneracy between \( v=0 \) on one pigment and \( v=1 \) on the other is found to create a nested intermolecular funnel, which guides an ultrafast energy transfer toward the lower energy pigment. This energy transfer is driven by nonadiabatic coupling when the individual pigment’s vibrational displacement is small enough that the \( \Delta v = 0 \) transition contains the majority of the pigment’s electronic transition strength.
5.1 Introduction

Photosynthesis, which powers life on our planet, is initiated when sunlight is captured by antenna proteins containing light absorbing pigments. The antenna protein positions the pigments to couple them and alters their electronic energies to direct electronic energy transfer toward a reaction center, which stores this energy chemically. Photosynthetic energy transfer is remarkably fast and efficient, often with quantum yields equal to one within experimental error\textsuperscript{1,2} Even with atomic resolution structures of several antennas and advances in quantum chemistry that provide the electronic structure and couplings between pigments\textsuperscript{3}, full understanding of the energy transfer mechanism and design principles has remained elusive.

Recent experiments\textsuperscript{1,4} have provided evidence that energy transfer through some parts of the photosynthetic apparatus may occur coherently, commonly referred to as wave-like motion, rather than incoherently, commonly called a hopping or diffusive motion.\textsuperscript{5} The assignment of the longest coherences (up to a few picoseconds) in these reports has been disputed\textsuperscript{6}, but timescales have been observed\textsuperscript{7,8} in the 100 -400 fs range which is comparable to prior reports\textsuperscript{9} of electronic dephasing in dye molecules with conjugated ring structures similar to chlorophylls. The reports have renewed interest in modelling coherent effects in photosynthetic energy transfer.

A pair of coupled pigments in the photosynthetic apparatus can be considered as a super-molecule; from this viewpoint the transfer of energy from one pigment to another can be considered to be an internal conversion process of the super-molecule. This leads to a picture of (potentially intersecting) potential energy surfaces connecting a state with energy localized on one pigment to a state with energy localized on the other; Förster\textsuperscript{10}
has considered this problem, and realized that the relevant vibrational coordinates for the
potential energy surfaces are delocalized linear combinations of local vibrations on each
pigment: $q_+ = (q_A + q_B)/\sqrt{2}$ and $q_- = (q_A - q_B)/\sqrt{2}$, where $q_A$ and $q_B$ represent the same
vibration on different pigment molecules, named $A$ and $B$. This transformation projects
localized motions onto delocalized modes, picking out the correlated and anti-correlated
components of motion which may or may not have any intrinsic correlation. Förster
recognized that $q_-$, the delocalized, anti-correlated vibration, since it tunes the electronic
energy gap between pigments, is the relevant vibrational coordinate for driving energy
transfer at all coupling strengths, regardless of the extent of electronic delocalization.

In this chapter we discuss energy transfer from the viewpoint of internal
conversion, using a model Hamiltonian previously used to qualitatively reproduce key
features of the experiments mentioned above. This model describes a Coulombically
coupled two-pigment system with one weakly stabilizing vibrational mode on each
pigment, where the difference between electronic energy levels on the two pigments
roughly matches the vibrational frequency. Model parameters have been chosen to
qualitatively match key features of the lowest excitonic levels of the FMO complex, but
no attempt has been made to quantitatively model any real system. We find that
nonadiabatic coupling along the anti-correlated vibration $q_-$ directs ultrafast energy
transfer to the lower-energy pigment in a funnel-like fashion.

“Conical funnels,” where electronic potential energy surfaces approach so
closely that the adiabatic approximation breaks down, play an important role in
photochemistry, and often funnel molecules to lower energy electronic states
(internal conversion). A conical funnel may be either a conical intersection between
adiabatic potential surfaces or a “near miss”, but must allow a change in electronic state before vibrational equilibration. The funnel which appears in our model Hamiltonian cannot be described as “conical,” because there is only one coordinate described; however the efficient funnelling of energy we describe relies on a weak vibronic coupling such that one excited state potential energy curve lies nested within a lower excited state potential energy curve, so we call this a “nested funnel.”

5.2 Theory

5.2.1) Electronic wavefunctions; basis choices

5.2.1a) Full Hamiltonian for coupled pigments and the site basis

The Hamiltonian for the system describes two pigments, each with a Franck-Condon active vibrational normal mode, interacting through a dipolar Coulombic coupling. The pigments are allowed to have different vertical excitation energies, but are assumed to have the same vibrational frequency and stabilization energy. The Hamiltonian for pigment A is

$$\hat{H}_A = \frac{1}{2} \omega (\hat{p}_A^2 + \hat{q}_A^2) \hat{I}_A + (E_A + \omega d \hat{q}_A) |A\rangle \langle A|.$$  

$\hat{I}_A$ is the identity operator for the electronic space spanning ground and excited states of pigment A, $|A\rangle$ is the excited state, $E_A$ is the vertical electronic excitation energy, $\omega$ is the vibrational frequency, $\hat{p}_A$ and $\hat{q}_A$ are dimensionless vibrational momentum and coordinate operators. The dimensionless displacement $d$ (note the sign on $d$ is opposite that previously used$^6$) is related to stabilization energy by $\lambda = (1/2)\omega d^2$. The Hamiltonian for pigment B has the same form.
We assume $|A\rangle$ and $|B\rangle$ to have orthogonal transition dipoles of equal magnitude from the ground state, and choose the molecular frame $x$ axis parallel to the transition dipole for $|A\rangle$; the molecular frame $y$ axis is chosen parallel to the transition dipole for $|B\rangle$. We further assume the Condon approximation$^{13}$ holds for the isolated pigments:

$$
\langle A | \vec{\mathcal{E}} \cdot \hat{\mu}(q_A) | g \rangle = \mathcal{E}_A \mu_{A_g}(q_A = 0) \quad \text{and} \quad \langle B | \vec{\mathcal{E}} \cdot \hat{\mu}(q_B) | g \rangle = \mathcal{E}_B \mu_{B_g}(q_B = 0).
$$

The two pigment system has a single electronic ground state $|0_{AB}\rangle$, two singly excited electronic states $|A\rangle|0_B\rangle$ and $|0_A\rangle|B\rangle$, and a doubly excited electronic state $|A\rangle|B\rangle$. In this chapter we restrict our attention to singly excited states, neglecting both the global ground state and the doubly excited state; we then abbreviate $|A\rangle|0_B\rangle \equiv |A\rangle$ and $|0_A\rangle|B\rangle \equiv |B\rangle$. With this abbreviation, when we write $|A\rangle$, the pigment B ground state $|0_B\rangle$ is also present and has vibrational energy through $\omega(\hat{p}_B^2 + \hat{q}_B^2)/2$.

If either pigment is excited, the two pigments interact through a Coulombic coupling,$^{10}$ so that $\hat{H}_{exc} = \hat{H}_A + \hat{H}_B + J(|A\rangle\langle A| + |B\rangle\langle B|)$, where the subscript “exc” indicates we restrict our attention to singly excited states. At long range the Coulombic coupling can be calculated via the transition dipole approximation, although this might not be accurate for realistic modelling of photosynthetic systems. Using equation 3.11 of Förster,$^{10}$ the transition dipole approximation and the Condon approximation for the isolated pigments force $J$ to be independent of the intra-molecular normal coordinates $q_A$ and $q_B$. 

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It is convenient to separate out an average excitation energy \( (E_A + E_B)/2 = \omega_{eg} \), leaving in an energy gap \( (E_B - E_A)/2 = \delta/2 \). Expressing \( \hat{H}_{\text{exc}} \) as a matrix in the \(|A\rangle,|B\rangle\rangle \) electronic basis, our Hamiltonian becomes

\[
\hat{H}_{\text{exc}} = \omega_{eg} \mathbf{I} + \begin{bmatrix}
\frac{\omega}{2}(\hat{p}_A^2 + \hat{q}_A^2) + \omega d \hat{q}_A - \frac{\delta}{2} & J \\
J & \frac{\omega}{2}(\hat{p}_B^2 + \hat{q}_B^2) + \omega d \hat{q}_B + \frac{\delta}{2}
\end{bmatrix}.
\]

(5.1)

Here \( \mathbf{I} \) is the identity matrix for the singly excited states of the site basis.

It is further convenient to transform the vibrational coordinates to correlated and anti-correlated components: \( q_+ = (q_A + q_B)/\sqrt{2} \) and \( q_- = (q_A - q_B)/\sqrt{2} \). In the language of conical intersections, \( q_- \) is the “tuning coordinate” \( g \), and \( q_+ \) belongs to the “seam” space. A “coupling coordinate” \( h \) is not present in this Hamiltonian; it would correspond to an inter-pigment coordinate that changes the coupling \( J \). Carrying out this vibrational coordinate transformation, we rewrite our Hamiltonian as \( \hat{H}_{\text{exc}} = \hat{H}_{\text{corr}} + \hat{H}_{\text{int}} \), with

\[
\hat{H}_{\text{corr}} = \left( \omega_{eg} + \frac{\omega}{2}(\hat{p}_+^2 + \hat{q}_+^2) + \frac{\omega d \hat{q}_+}{\sqrt{2}} \right) \mathbf{I},
\]

(5.2)

and

\[
\hat{H}_{\text{int}} = \begin{bmatrix}
\frac{\omega}{2}(\hat{p}_-^2 + \hat{q}_-^2) + \frac{\omega d \hat{q}_-}{\sqrt{2}} - \frac{\delta}{2} & J \\
J & \frac{\omega}{2}(\hat{p}_+^2 + \hat{q}_+^2) - \frac{\omega d \hat{q}_+}{\sqrt{2}} + \frac{\delta}{2}
\end{bmatrix}.
\]

(5.3)

For this chapter we will restrict our attention to \( \hat{H}_{\text{int}} \), which contains all of the inter-pigment information. For convenience, we will drop the subscript “int”, and
consider (5.3) to represent $\hat{H}$, the Hamiltonian of interest. From this point of view, the vibrational coordinate transformation has reduced the dimensionality of the problem from two coordinates to one. The diagonal elements define the “site” basis, because it solves $\hat{H}$ if the pigment-pigment coupling $J$ is neglected.

Figure 5.1 displays the potential energy curves along coordinate $q$ and its vibrational energy levels for the site basis in dashed lines, constructed from parameters $\omega = 200\, cm^{-1}$, $\delta = 150\, cm^{-1}$ and $\lambda = 5\, cm^{-1}$ (which gives $d = 0.224$). $J$ is not used in constructing the site basis, but is set to $66.14\, cm^{-1}$. The figure shows a dashed purple line representing the potential curve along the anti-correlated coordinate when pigment A is excited and pigment B is in its ground state; the curve is displaced $-d/\sqrt{2}$ from the origin, where the $\sqrt{2}$ comes from the coordinate transformation from $q_A$ and $q_B$ to $q+$ and $q$. Vibrational energy levels are $\omega\left(v + \frac{1}{2}\right)$ above the minimum of the potential, which is $-\delta/2 - \omega d^2/4$. The orange dashed line shows the potential curve and vibrational energy levels when pigment B is excited and pigment A is in its ground state; the curve is displaced $d/\sqrt{2}$ from the origin and has a minima at energy $\delta/2 - \omega d^2/4$.

5.2.1b) the excitonic electronic basis and potential curves

The dipolar coupling constant in this work, $J = 66.14\, cm^{-1}$, is a significant fraction of both the vibrational frequency $\omega = 200\, cm^{-1}$ and the pigment energy gap $\delta = 150\, cm^{-1}$, while the electronic-vibrational stabilization energy $\lambda = 5\, cm^{-1}$ is relatively small. It would be advantageous to work from a basis in which $J$ is diagonal, then treat $\lambda$ as a perturbation (which will be included without terminating the expansion at low order).
Figure (5.1) Potential energy curves and product state energies for site and excitonic diabatic electronic bases (Hamiltonians (5.3) and (5.6)), with parameters $\omega = 200\text{ cm}^{-1}$, $\delta = 150\text{ cm}^{-1}$, $\lambda = 5\text{ cm}^{-1}$ and $J = 66.14\text{ cm}^{-1}$. Both basis sets include harmonic wells offset slightly from $q=0$, with a frequency of $200\text{ cm}^{-1}$. The splitting $\delta = 150\text{ cm}^{-1}$ between site energies becomes a splitting of $\Delta_{\text{ex}} = 200\text{ cm}^{-1}$ in the excitonic basis. Site potential curves and energy levels are shown as dashed lines, purple for $|A\rangle$ and orange for $|B\rangle$. The excitonic basis curves are solid lines colored according to the $q$-independent, purely electronic excitonic mixing angle, $\theta^d = 20.7^\circ$. Because the lower exciton, $|\alpha\rangle$, is an out-of-phase combination, the transition dipole to $|\alpha\rangle$ from $|g\rangle$ is at $-\theta^d$ in the $xy$ plane; this makes the curve a darker, more bluish purple than used for site $|A\rangle$. The upper excitonic curve $|\beta\rangle$ is orthogonal to the lower exciton and is colored red to indicate $90^\circ - \theta^d$. The excitonic curves are very similar to the adiabatic curves seen in figure 5.2(b) and 5.2(d); a consequence of the parameters $\lambda << J$. The total stabilization energy of each pigment, 5 cm$^{-1}$, is split between correlated and anti-correlated combinations of pigment-localized vibrations, so there is only 2.5 cm$^{-1}$ stabilization energy in the relevant anti-correlated mode. On transforming to an excitonic basis, this energy gets further divided into a diagonal component of 1.4 cm$^{-1}$ and a coupling component of 1.1 cm$^{-1}$; the diagonal component shifts the minima of the excitonic curves away from $q=0$, while the coupling component (which is 0.5% of a vibrational quantum) causes nonadiabatic mixing between states.
If we neglect the $\omega d\hat{q}_- / \sqrt{2}$ terms, Hamiltonian (5.3) can be diagonalized by usual 2x2 methods, yielding new, excitonic electronic states

$$
|\alpha\rangle = \cos \theta^d |A\rangle - \sin \theta^d |B\rangle \\
|\beta\rangle = \sin \theta^d |A\rangle + \cos \theta^d |B\rangle
$$

(5.4)

$$
\theta^d = \text{atan2} \left( J, \delta / 2 + \sqrt{\left( \delta / 2 \right)^2 + J^2} \right).
$$

where $\text{atan2}(y, x)$ is an extended arctangent function with range $(-\pi, \pi]$ and $\text{atan2}(y, x) = \arctan(y / x)$ in the range $(-\pi / 2, \pi / 2)$. The “d” superscript on the mixing angle indicates that $\{|\alpha\rangle, |\beta\rangle\}$ are a set of diabatic electronic states$^{14}$, as they are eigenvectors of Hamiltonian (5.6) if $\omega d\hat{q}_- / \sqrt{2}$ is the only neglected term. These states are diagonal with both the vibrational kinetic energy operator, $(\omega / 2) \hat{p}^2$ and the Coulombic coupling between pigments $J$ fully included.

To express Hamiltonian(5.3), including the $\omega d\hat{q}_- / \sqrt{2}$ terms, in this new excitonic, diabatic basis, unitary transforms are derived from equations (5.4);

$$
\mathbf{D} = \begin{bmatrix} \cos \theta^d & -\sin \theta^d \\ \sin \theta^d & \cos \theta^d \end{bmatrix}
$$

(5.5)

is the matrix which transforms a column vector in the site basis to a column vector in the excitonic basis. Using that to transform Hamiltonian (5.3) we get

$$
\mathbf{\tilde{H}} = \mathbf{D} \mathbf{H} \mathbf{D}^{-1}
$$

(5.6)
where the bar on $\bar{\mathbf{H}}$ indicates that it has been transformed to the excitonic diabatic electronic basis, $d_s = \left( \cos^2 \theta^d - \sin^2 \theta^d \right) d / \sqrt{2}$ and $d_c = \left( 2 \cos \theta^d \sin \theta^d \right) d / \sqrt{2}$ (the subscript “s” indicates a splitting between excitonic states and the subscript “c” indicates coupling between excitonic states).

The projection of the Franck-Condon active vibrational stabilization of the individual pigments onto an anti-correlated delocalized vibrational mode goes over to become both an excitonic stabilization (diagonal) and a coordinate-dependent coupling (off-diagonal) on transformation to a delocalized electronic basis. $\omega d_s \hat{q}_-$ gives the amount of $\omega d \hat{q}_- / \sqrt{2}$ which becomes the excitonic stabilization and $\omega d_c \hat{q}_-$ give the amount of $\omega d \hat{q}_- / \sqrt{2}$ which becomes the coordinate dependent coupling between excitonic states.

This is unavoidable: if there is a change in equilibrium position upon electronic excitation in individual pigments, there will be a coordinate-dependent coupling (which is how nonadiabatic effects appear in a diabatic basis) in the excitonic system.

In Figure 5.1 potential energy curves for the excitonic diabatic basis are shown as solid lines, with the excitonic stabilization terms $\omega d_s \hat{q}_-$ included, so that the figure shows the diagonal terms of Hamiltonian (5.6). Parameters are $\omega = 200 \text{cm}^{-1}$, $\delta = 150 \text{cm}^{-1}$ and $\lambda = 5 \text{cm}^{-1}$, and $J = 66.14 \text{cm}^{-1}$. The curves are colored according to the projections (5.4) onto $|A\rangle$ and $|B\rangle$. The lower excitonic surface, $|\alpha\rangle$, is a bluish purple, projecting at $-21^\circ$ on the inset color wheel; the minimum is located at coordinate $q_0 = -d_s$ and energy $E_\alpha = -\sqrt{\delta^2/2 + J^2} - \omega d^2_s / 2$. The upper excitonic curve, $|\beta\rangle$, projects at $69^\circ$ in the $\{ |A\rangle, |B\rangle \}$-plane and has a red color. The minima of this curve is located at coordinate $q$. 


\[ E_\beta = +\sqrt{\left(\frac{\delta}{2}\right)^2 + J^2} - \omega d_s^2/2. \] The transformation leaves the new basis curves parabolic, and vibrational energy levels lie \( \omega \left(\nu + \frac{1}{2}\right) \) above respective minima.

With the choice of parameters used for figure 5.1, the nonadiabatic coupling in this excitonic basis is quite weak. Of the original 5 cm\(^{-1}\) stabilization energy per pigment, half goes into the correlated motion \( q_+ \), and half into the anti-correlated motion \( q_- \). The transformation of the inter-pigment Hamiltonian (5.3) into an excitonic basis, (5.6) further separates the \( q_- \) component into a splitting of 1.4 cm\(^{-1}\) (\( \omega d_s^2/2 \)) and a coupling of 1.1 cm\(^{-1}\) (\( \omega d_s^2/2 \)). From the point of view of the excitonic diabatic basis, it is only this last 1.1 cm\(^{-1}\) (about 0.5% of the vibrational frequency) which drives nonadiabatic dynamics.

5.2.1c) adiabatic electronic basis and potential curves

To obtain the adiabatic vibronic wavefunctions from Hamiltonian (5.3), we first neglect vibrational momentum and treat the vibrational coordinate operator \( \hat{q} \) as a parameter \( q \):

\[ H_{\text{elec}}^a(q) = \begin{bmatrix} \frac{\omega}{2} q^2 & \frac{\omega dq_- - \delta}{\sqrt{2}} & J \\ J & \frac{\omega}{2} q^2 & -\frac{\omega dq_- + \delta}{\sqrt{2}} \end{bmatrix}. \] (5.7)

The superscript “a” indicates that this electronic Hamiltonian is under an adiabatic approximation. This Hamiltonian can be diagonalized to solve the eigenvalue problem

\[ \hat{H}_{\text{elec}}^a(q_-)|k(q_-)\rangle = U_k(q_-)|k(q_-)\rangle. \] (5.8)
The eigenvalues are
\[ U_\pm(q_-) = \frac{1}{2} \omega q_-^2 \pm \sqrt{\left( \delta/2 - \omega dq_- / \sqrt{2} \right)^2 + J^2} \] (5.9)

with eigenvectors
\[ |\pm\rangle = \cos\left( \theta^\alpha(q_-) \right) |x\rangle - \sin\left( \theta^\alpha(q_-) \right) |y\rangle \]
\[ |+\rangle = \sin\left( \theta^\alpha(q_-) \right) |x\rangle + \cos\left( \theta^\alpha(q_-) \right) |y\rangle \]
\[ \theta^\alpha(q_-) = \arctan \left( J, \left( \delta/2 - \omega dq_- / \sqrt{2} \right) + \sqrt{\left( \delta/2 - \omega dq_- / \sqrt{2} \right)^2 + J^2} \right). \] (5.10)

\[ |k(q_-)\rangle = \{ |\pm\rangle, |+\rangle \} \] forms a new set of vibrational coordinate dependent electronic basis functions, the adiabatic electronic basis, which is orthonormal at each value of \( q_- \).

Potential energy curves within an adiabatic approximation are shown in figure 5.2(b). Parameters are \( \omega = 200 \text{cm}^{-1} \), \( \delta = 150 \text{cm}^{-1} \) and \( \lambda = 5 \text{cm}^{-1} \), and \( J = 66.14 \text{cm}^{-1} \). The coloring of the curves reflects the coordinate-dependent mixing angle \( \theta^\alpha(q_-) \), which ranges from 15° to 27° in between classical turning points of the lower adiabatic curve \( |\pm\rangle \); note that the minus sign in (5.10) means \( |\pm\rangle \) projects at \( -\theta^\alpha(q_-) \) in the \{A, B\}-plane. The upper curve \( |+\rangle \) is orthogonal to \( |\pm\rangle \) at every point in \( q_- \); it projects at \( -\theta^\alpha(q_-) + \pi/2 \).

The vibrational Hamiltonian in the adiabatic approximation is found by using the \( q_- \)-dependent electronic energy as the potential:
\[ \hat{H}_{\text{vib}}^k |v^k\rangle = \left( \frac{\omega}{2} \hat{P}_z^2 + U_k(q_-) - U_k(q_-^{\text{min}}) \right) |v^k\rangle = E_k^v |v^k\rangle \] (5.11)

where \( q_k^{\text{min}} \) is the coordinate of the minimum of the \( k \)-th potential energy curve, and
\( U_k(q_k^{\text{min}}) \) is subtracted off so that eigenvalues of \( \hat{H}_{\text{vib}}^k \) represent purely vibrational
Figure (5.2) Potential energy curves, energy levels, vibrational wavefunctions and vibrational probability densities for Hamiltonian (5.3)
Figure (5.2) Potential energy curves, energy levels, vibrational wavefunctions and vibrational probability densities for Hamiltonian (5.3), with parameters $\omega = 200 \text{cm}^{-1}$, $\delta = 150 \text{cm}^{-1}$, $\lambda = 5 \text{cm}^{-1}$ and $J = 66.14 \text{cm}^{-1}$. The zero of energy has been set to midway between potential minima for the site basis. Panel (a) shows the potential energy curves, vibrational energy levels, and vibrational wavefunctions for each pigment, each of which is vertically offset such that its origin coincides with its energy level; the product electronic and vibrational wavefunctions define the site basis. The purple curve represents the excited state of pigment $A$, and the purple curve represents the excited state of pigment $B$. Panel (b) shows the adiabatic potential curves, energy levels and vibrational wavefunctions which define the adiabatic basis. The adiabatic electronic mixing angle, which defines the adiabatic electronic wavefunctions in equation (5.10), is indicated by mapping onto the color wheel in panel (c); at $q=0$ the lower curve is dark purple, representing the mixing angle $-\theta^d = -20.7^\circ$, and the upper curve is red, indicating $-\theta^d + 90^\circ = 69.3^\circ$. Away from $q=0$ the adiabatic potential curves change color, most rapidly in the region near the crossing of the curves in the site basis. At $q=2.37$, the site curves cross and the adiabatic curves have a vertical splitting of $2J = 132 \text{cm}^{-1}$. Panel (c) shows an alternative representation of panel (a): we plot the vibrational probability density instead of the vibrational wavefunction, and indicate the lost phase information from regions where the wavefunction is negative by assigning a color which is $180^\circ$ around the color wheel. This is equivalent to replacing the vibrational wavefunction everywhere by its modulus and moving its sign to the electronic wavefunction; such a procedure preserves the values of all quantum mechanical observables. Looking for example at $|A\rangle |1\rangle$, in the region to the left of its $v=1$ node the vibrational probability density is colored green instead of purple, indicating $-|A\rangle$ instead of $|A\rangle$. Similarly, the vibrational probability density for $|B\rangle |1\rangle$ is colored light blue instead of orange in regions where the vibrational wavefunction for $|B\rangle |1\rangle$ carries a negative sign. In panel (e) the same procedure is applied to the adiabatic wavefunctions; due to the slow color change at negative $q$ (far from the avoided crossing), the regions of inverted color appear similar to those in the site basis. Panel (f) shows the vibrational probability density for exact nonadiabatic wavefunctions, with a coloring to indicate the $q$-dependence of the nonadiabatic electronic wavefunction, expressed as a nonadiabatic mixing angle $\Theta_n(q)$ (equation (5.22)). The vibrational probability density has been vertically offset such that each eigenstate’s energy serves as the origin. Nonadiabatic wavefunctions, except for the lowest $|\psi_o\rangle$, do not resemble either site or adiabatic basis states in color or shape; due to the near-degeneracy of the adiabatic levels the eigenstates are heavily mixed. These nonadiabatic states show rapid color changes as the vibrational coordinate is varied and have no zeros in the probability density that would indicate a node.
energies in the adiabatic approximation. The potential curves are not quite harmonic, and vibrational wavefunctions and energy levels are found numerically.

To solve these anharmonic Hamiltonians, we expand in the ground state vibrational basis set. This basis is useful for calculating excitation probabilities later on. Matrix elements of dimensionless momentum are filled in with known relations:

\[ \langle v \mid \hat{p}^2 \mid v' \rangle = -\frac{1}{2} \sqrt{(v+1)(v+2)} \delta_{v,v+2} + (v+\frac{1}{2}) \delta_{v,v} - \frac{1}{2} \sqrt{v(v-1)} \delta_{v,v-2} \]  

(5.12)

The potential energy matrix elements are numerically integrated, \( U_{vv'}^k = \langle v \mid U_k(q_-) \mid v' \rangle \), then the \( H_{vib}^k \) are numerically diagonalized to obtain adiabatic vibrational wavefunctions and energy levels. The resulting adiabatic vibrational state will be written as

\[ \langle v^k \rangle = \sum_{v'} c_{v,v'}^k \langle v' \rangle \]  

where \( k \in \{-,+\} \), \( v \) is a vibration quantum number for the adiabatic wavefunction, \( v' \) is a vibrational quantum number for the basis function and

\[ c_{v,v'}^k = \langle v^k \rangle |v'\rangle \]. Adiabatic product states \( |k\rangle |v^k\rangle \) have total energies of \( E_{v}^k = U_k(q_{v}^{\min}) + E_v^k \).

5.2.2) form of the coupling from different bases

5.2.2a) site electronic basis

To fully describe coupled vibrational-electronic states, Hamiltonian (5.3) is expanded to explicitly include vibrational levels on each electronic state. It is conceptually easiest to add vibrational eigenstates on each surface, forming product wavefunctions of the form \( |A\rangle |v^A\rangle \) and \( |B\rangle |v^B\rangle \). Here \( \langle q_- |v^A\rangle = \phi_v^A(q_-) \) is the \( v \)th harmonic oscillator wavefunction on the \( |A\rangle \) electronic state, which is centered at \( q_- = -d/\sqrt{2} \), and \( |v^B\rangle \) is defined similarly, except being centered at \( q_- = d/\sqrt{2} \). As
noted above, the assumption that the Condon approximation holds for isolated pigments leaves $J$ independent of $q$, so that the coupling between vibronic wavefunctions is
\[
\langle v^A | \langle A | \hat{H} | B \rangle | v^B \rangle = J \langle v^A | v^B \rangle.
\]
We refer to this vibrational basis as a “shifted basis,” as the vibrational wavefunctions are not centered at $q = 0$ but are shifted to match their respective curves.

In the shifted vibrational basis, every vibrational level on one pigment is coupled to every vibrational level on the other pigment, with the coupling screened by a vibrational overlap integral $\langle v^A | v^B \rangle$. These vibrational overlaps can be calculated recursively, for example using equations I and II from Manneback.\(^{17}\)

The Hamiltonian is simpler to express if we choose a common vibrational basis for use with both singly excited states. This amounts to neglecting $\hat{q}^2 / \sqrt{2}$ as well as $J$ when writing down basis energies, and taking a direct product of $\{|A\rangle, |B\rangle\}$ with the vibrational basis of the ground electronic state (recalling from the definition of $\hat{H}_A$ that the ground electronic state of $A$ has the same frequency and is centered at $q_A = 0$). We refer to this as the “undisplaced” vibrational basis, $\{|v^u\rangle\}$, as $\langle q^- | v^u \rangle = \phi_i(q_-)$ are wavefunctions centered at $q = 0$. In this undisplaced vibrational basis, $J$ is electronically off-diagonal but vibrationally diagonal,
\[
\langle v^u | \langle A | \hat{H} | B \rangle | v^v \rangle = J \delta_{uv}.
\]
(5.13)
The $\hat{q}^2 / \sqrt{2}$ term is electronically diagonal but vibrationally off-diagonal; these terms can be filled in by using standard values for the coordinate operator $\hat{q}$.\(^{16}\)
The undisplaced vibrational basis is not the most natural basis for considering the excited state of an isolated pigment, as it does not represent vibrational eigenstates of the isolated pigment excited states, however the undisplaced basis has two important advantages for the calculations presented here. The first advantage is that under optical excitation only dipole transitions with $\Delta v = 0$ are allowed, in this vibrational basis, under the Franck-Condon principle. The second advantage comes from the $q$-independence of the dipolar Coulombic coupling $J$, which then also has a $\Delta v = 0$ rule if the vibrational basis is the same for both singly excited states (i.e. if we use a direct product basis). The undisplaced vibrational basis is used for all nonadiabatic calculations presented in this chapter.

5.2.2b) diabatic excitonic electronic basis

The electronically off-diagonal term in the diabatic excitonic basis (Hamiltonian (5.6)) is $odq$ $q$ $q$, since $J$ is diagonalized with transformation (5.5). Using the undisplaced basis of the ground electronic state vibrational wavefunctions as a common vibrational basis for both excitonic electronic states, $q$ $q$ obeys the usual $\Delta v = 1$ selection rule; $q$ $q$ retains its $\Delta v = 1$ rule for the electronically diagonal $odq$ $q$ $q$ term. In this diabatic excitonic electronic basis and unshifted ground state vibrational basis, there are electronically diagonal but vibrationally off-diagonal elements,
in addition to coupling elements that are both electronically and vibrationally off-diagonal,

\[ H_{v,v'} = \omega d_c q_{v'} = \omega d_c \sqrt{(v'/2)} \delta_{v,v'+1} + \omega d_c \sqrt{(v'/2)} \delta_{v,v'-1}. \]  

(5.16)

5.2.2c) adiabatic basis

The adiabatic electronic-vibrational product states are coupled to one another, both within the same electronic state and between electronic states, with the so-called nonadiabaticity operator \( \hat{\Lambda} \). To derive the nonadiabatic operator from the adiabatic basis, we allow the \( (\omega/2) \hat{p}^2 \) operator to act on an adiabatic product wavefunction, and by applying the product rule twice find one term which is equivalent to the use of \( (\omega/2) \hat{p}^2 \) in the adiabatic vibrational Hamiltonian (5.11), and two new terms which are missing in the adiabatic approximation. The new terms are combined and called the nonadiabaticity operator \( \hat{\Lambda} \), which operates separately on adiabatic electronic and vibrational wavefunctions; because of that it needs to be expressed in a product basis. It is useful here to define a shorthand notation for taking the partial derivative of a wavefunction: let \( \partial v^k / \partial q \equiv (\partial / \partial q) \left| v^k \right\rangle \) and \( \partial^n k(q) / \partial q^n \equiv (\partial^n / \partial q^n) \left| k(q) \right\rangle \). Using this shorthand, the matrix elements are

\[ \bar{\Lambda}_{v,v'} = -\omega \langle v' | (k(q) \partial v^k / \partial q) | v^k \rangle \]

\[ \quad -\frac{\omega}{2} \langle v' | (k(q) \partial^2 v^k / \partial q^2) | v^k \rangle \]

(5.17)

where \( \left| v^k \right\rangle \) can be any vibrational basis function belonging to \( k \).

The term on the first line right hand side of eqn (5.17) is referred to as the radial derivative coupling and the term on the second line is commonly called the scalar
coupling. If \( k = k' \), and the electronic wavefunctions are real, the first term vanishes\(^{19}\) and \( \Lambda_{kv,kv'} \) is known as the diagonal correction; various authors include this correction in the “Born-Oppenheimer” or “adiabatic” approximations to distinguish them\(^{20}\); unfortunately there is not a uniformly accepted definition for which is adiabatic and which is Born-Oppenheimer. Following Born and Huang\(^{19}\), we will call the basis which does not include this correction the “adiabatic” basis; we call the basis which does include it the “Born-Huang” basis because it was discussed by Born and Huang.\(^{19}\)

If \( k \neq k' \), both lines of eqn (5.17) must be included, as the terms are not individually Hermitian. For the real electronic and vibrational basis set used here, the scalar coupling is anti-symmetric \( \left( A_{ij} = -A_{ji} \right) \) while the radial derivative coupling is neither symmetric nor anti-symmetric. \( \hat{\Lambda} \) is symmetric, however, so the radial coupling can be decomposed into a sum of symmetric and anti-symmetric parts, and its anti-symmetric part exactly cancels the scalar coupling. The Hermitian properties of components of \( \hat{\Lambda} \) have also been discussed in the electronic subspace\(^{21}\), rather than as matrices in the electronic-vibrational product space; then too the individual terms in \( \hat{\Lambda} \) are not Hermitian but the detailed discussion is somewhat different.

To find the full nonadiabatic energy levels and wavefunctions, working from an adiabatic basis, we construct a block-diagonal adiabatic Hamiltonian containing both \( \hat{H}_{\text{elec}}^a \) and \( \hat{H}_{\text{vib}}^a \), then add the nonadiabaticity operator:

\[
\hat{H} = \begin{bmatrix}
U_{\text{elec}}(q_{\text{min}}^+) + \hat{H}_{\text{vib}}^{-}
& 0 \\
0 & U_{\text{vib}}(q_{\text{min}}^+) + \hat{H}_{\text{vib}}^{+}
\end{bmatrix} + \begin{bmatrix}
\hat{\Lambda}_{-,+} & \hat{\Lambda}_{+,+} \\
\hat{\Lambda}_{-,+} & \hat{\Lambda}_{-,+}
\end{bmatrix}
\]  

(5.18)
Where the tilde on $\tilde{\hat{H}}$ indicates that it is expressed in the adiabatic electronic basis and the vibrational subscripts on $\hat{A}$ have been dropped since eqn (5.18) is not expressed in a vibrational basis. The form of $\hat{A}$ presented in eqn (5.17) is used after expanding eqn (5.18) in a product basis.

5.2.3) exact nonadiabatic wavefunctions

Exact nonadiabatic wavefunctions will be calculated by proceeding from the site electronic basis, Hamiltonian (5.3), with off-diagonal elements evaluated as (5.13) and (5.14). We could have worked from an adiabatic basis and evaluated the nonadiabaticity operator (5.17), which simplifies to a manageable form if a crude adiabatic approximation is made for states $|A\rangle$ and $|B\rangle$. [chapter 4 of this thesis] The crude adiabatic approximation neglects any dependence of $|A\rangle$ and $|B\rangle$ on the vibrational coordinate $\hat{q}_v$, and is more restrictive than the Condon approximation, which it implies.

With three undisplaced vibrational wavefunctions on the site electronic basis functions explicitly shown, Hamiltonian (5.3) is

$$
\begin{bmatrix}
\frac{\omega}{2} - \frac{\delta}{2} & \frac{\omega \delta}{\sqrt{2}} & 0 & J & 0 & 0 \\
\frac{\omega \delta}{\sqrt{2}} & \frac{3\omega}{2} - \frac{\delta}{2} & \omega \delta & 0 & J & 0 \\
0 & \omega \delta & \frac{5\omega}{2} - \frac{\delta}{2} & \ldots & 0 & 0 & J \\
J & 0 & 0 & \frac{\omega}{2} + \frac{\delta}{2} & -\frac{\omega \delta}{\sqrt{2}} & 0 \\
0 & J & 0 & -\frac{\omega \delta}{\sqrt{2}} & \frac{3\omega}{2} + \frac{\delta}{2} & -\omega \delta \\
0 & 0 & J & 0 & -\omega \delta & \frac{5\omega}{2} + \frac{\delta}{2} & \ldots \\
& & & & & & \ddots \end{bmatrix}
$$

(5.19)
Exact energies $E_n$ and wavefunctions $|\psi_n\rangle$ are obtained by numerically diagonalizing this matrix. The wavefunctions are of the form

$$|\psi_n\rangle = \sum_v b_{n,Av} |A\rangle |v\rangle + \sum_v b_{n,Bv} |B\rangle |v\rangle.$$  \hspace{1cm} (5.20)

The form presented in equation (5.20) is convenient for calculations, but for more insight we now seek to individually separate each nonadiabatic wavefunction into a single product of a purely vibrational wavefunction of $q_-$ alone and a normalized electronic wavefunction parametrically dependent on $q_-$. We start by writing the explicit $q$-dependent projections of the wavefunction onto $|A\rangle$ and $|B\rangle$:

$$\langle A | q_- | \psi_n \rangle = \sum_v b_{n,Av} \langle A | A \rangle \langle q_- | v \rangle + \sum_v b_{n,Av} \langle A | B \rangle \langle q_- | v \rangle$$

$$= \sum_v b_{n,Av} \varphi_v (q_-)$$

$$= \Phi_{n,A}(q_-)$$

$$\langle B | q_- | \psi_n \rangle = \sum_v b_{n,Bv} \langle B | A \rangle \langle q_- | v \rangle + \sum_v b_{n,Bv} \langle B | B \rangle \langle q_- | v \rangle$$

$$= \sum_v b_{n,Bv} \varphi_v (q_-)$$

$$= \Phi_{n,B}(q_-)$$  \hspace{1cm} (5.21)

With $\Phi_{n,A}(q_-)$ defining the $q$-dependent projection of $|\psi_n\rangle$ onto $|A\rangle$ and $\Phi_{n,B}(q_-)$ defining the projection onto $|B\rangle$, we define a polar transformation at each value of $q_-$ and use it to define a new vibrational ket $|p_n\rangle$ and a new electronic ket $|K_n\rangle$:

$$\Theta_n(q_-) = \text{atan2}(\Phi_{n,A}(q_-), \Phi_{n,B}(q_-))$$

$$\langle q_- | p_n \rangle = p_n(q_-) = \sqrt{(\Phi_{n,A}(q_-))^2 + (\Phi_{n,B}(q_-))^2}$$

$$|K_n\rangle = [\cos(\Theta_n(q_-)) |A\rangle + \sin(\Theta_n(q_-)) |B\rangle]$$

$$|\psi_n\rangle = |K_n\rangle |p_n\rangle.$$  \hspace{1cm} (5.22)
The product wavefunction \( |K_n\rangle |\Psi_n\rangle \) is an allowed wavefunction for the electronic-vibrational system. The new ket \( |\Psi_n\rangle \) may not generate an allowed vibrational wavefunction -- a derivative discontinuity in \( \langle q |\Psi_n\rangle \) occurs if \( \Phi_{n,d}(q_-) = \Phi_{n,a}(q_-) = 0 \).

However, for diatomic molecules, it can be shown that analogous nonadiabatic vibrational wavefunctions do not have nodes.

A similar problem occurs in the adiabatic framework, where in two dimensions \( \phi^k(q_1,q_2) \) may be multi-valued and not be admissible around a conical intersection (Berry’s phase), but the product \( \phi^k(q_1,q_2) |k(q_1,q_2)\rangle \) is an allowed, single-valued, electronic-vibrational wavefunction.

The important difference between this and the adiabatic framework is that there is only one quantum number \( n \) which indexes both the electronic state and the vibrational state. By fully including vibrational momentum we end up with only one vibrational state, \( |\Psi_n\rangle \), for each electronic state \( |K_n\rangle \), rather than a series of vibrational bound states for each electronic state; conversely we have a different electronic wavefunction for every vibrational state rather than having only two electronic states. Like the adiabatic states, each nonadiabatic electronic state is normalized at each value of \( q_- \). However, unlike the adiabatic electronic states, the electronic wavefunctions cannot be mutually orthogonal in the two-dimensional electronic subspace. Further, the vibrational wavefunctions are not orthogonal in the vibrational subspace. Nonetheless, the product wavefunctions are orthogonal. As in the adiabatic framework, the \( q_- \)-dependent amplitude of the product wavefunction is contained in the vibrational wavefunction.

The results of diagonalizing Hamiltonian (5.19), then applying transformation (5.22) are displayed in figure 5.2(f). No potential curves are shown, as the nonadiabatic
picture lacks the concept of each electronic state supporting a complete set of vibrational states. $|\langle q_+ | \mathbf{p}_n \rangle|^2$ is plotted to indicate the vibrational wavefunction, while the $q_+$-dependent coloring indicates $\Theta_n(q_+)$ contains overall sign information and fully describes the $q_+$-dependence of the transition dipole from the ground electronic state. Note that this implies that the Condon approximation may fail due to a rotation of $\mu_{kg}$, rather than the usual diatomic concerns about the magnitude of $\mu_{kg}$.

5.2.4) nonstationary states. wavepacket propagation

To see what dynamics are contained in this Hamiltonian, we will take a look at time-dependent wavefunctions obtained under impulsive excitation from a zero-point vibration ($v=0$) on the electronic ground state $|g\rangle$. Calculations using the exact nonadiabatic solutions to the inter-pigment Hamiltonian (5.3) will be contrasted to propagation using adiabatic product wavefunctions and energies. The calculations presented here will not take into account dephasing or population transfer between eigenstates. This will allow us to propagate for sufficient lengths of time to study in detail the motions that are created by the Hamiltonian; for a large molecule in a condensed phase these motions can be damped out on timescales ranging from a hundred to a few thousand femtoseconds.

5.2.4a) exact nonadiabatic propagation

Impulsive laser excitation will project the electronic ground state vibrational wavepacket directly onto the electronic excited states. Explicit equations for the initial conditions are derived using first-order time dependent perturbation theory$^{24}$, which has
us operate on an initial ket $|a\rangle$ with the operator $(1/\hbar)\sum_n |\psi_n\rangle \langle \psi_n |(-\hat{E} \cdot \hat{\mu})|a\rangle \langle a|$, where $\hat{E}$ is the incident electric field. We take our initial ket $|a\rangle$ to be $|g\rangle|0\rangle$ and assume $\delta$-function pulses, which have a spectrally constant electric field amplitude.

$$|\Psi(T = 0)\rangle = (1/\hbar)\sum_n |\psi_n\rangle \langle \psi_n |(-\hat{E} \cdot \hat{\mu})|g\rangle|0\rangle$$

$$= (i/\hbar) \sum_n |\psi_n\rangle \left[ \sum_v b_{n,v}\langle v |\langle A | + \sum_v b_{n,v}\langle v |\langle B | \right] \left[ (\hat{E} \cdot \hat{x})\hat{\mu}_x + (\hat{E} \cdot \hat{y})\hat{\mu}_y \right]|g\rangle|0\rangle$$

$$= (i/\hbar) \mu_{g}\sum_n \left( b_{n,A0}(\hat{E} \cdot \hat{x}) + b_{n,B0}(\hat{E} \cdot \hat{y}) \right)|\psi_n\rangle$$

Here $|\Psi(T)\rangle$ represents an excited-state vibronic wavepacket. The wavepacket at times after $T=0$ is calculated using the time-dependent form of Schrödinger’s equation and the eigenvalues obtained by diagonalizing Hamiltonian (5.3), as expressed in (5.19).

$$|\Psi(T)\rangle = (i/\hbar) \mu_{g}\sum_n \left( b_{n,A0}(\hat{E} \cdot \hat{x}) + b_{n,B0}(\hat{E} \cdot \hat{y}) \right)|\psi_n\rangle \exp(-iE_n T/\hbar) \quad (5.23)$$

Equation (5.23) is used for all nonadiabatic wavepacket calculations; however we seek to transform $|\Psi(t)\rangle$ in a manner similar to the treatment of $|\psi_n\rangle$, in order to apply the visualization scheme used in figure 5.1(f). A time-dependent generalization of transformation (5.22) is needed in order to separate the propagating wavepacket into a single product of a purely vibrational wavefunction and an electronic wavefunction whose $q$-dependence is described by the mixing angle $\Theta(q,T)$. We proceed by defining

$$\Phi_k(q_-,T) = \langle k | q_- | \Psi(T) \rangle$$

$$= \sum_n b_n \langle k | q_- | \psi_n \rangle \exp(-iE_n T/\hbar) \quad (5.24)$$

$$= \sum_n b_n \Phi_{n,k}(q_-) \exp(-iE_n T/\hbar)$$
where \( |k \rangle \in \{ |A \rangle, |B \rangle \} \), \( b_n = \left( b_{n,00} (\vec{E} \cdot \hat{x}) + b_{n,00} (\vec{E} \cdot \hat{y}) \right) \) abbreviates the projection of the wavepacket onto eigenstates as in eqn (5.23), and \( |\Phi_A(q_c, T)|^2 + |\Phi_B(q_c, T)|^2 \) is the time dependent vibrational probability density. The projections \( \Phi_A(q_c, T) \) and \( \Phi_B(q_c, T) \) are time-dependent and therefore complex valued, preventing an unambiguous definition of the mixing angle \( \Theta(q_c, T) \). While arctangent is defined for complex arguments, it returns a complex angle which is not straightforwardly connected to experimental measurements. We chose instead to define \( \Theta(q_c, T) \) using only the real parts of \( \Phi_A(q_c, T) \) and \( \Phi_B(q_c, T) \); this preserves the interpretation of \( \Theta(q_c, T) \) as reflecting the vibrational coordinate dependence of the transition dipole direction to the ground state and reduces to transformation (5.22) at time zero, but loses information about the imaginary components of the wavepacket. The full transformation is

\[
\Theta(q_c, T) = \text{atan2}(\text{Re} \Phi_B(q_c, T), \text{Re} \Phi_A(q_c, T))
\]

\[
\langle q | \Psi(T) \rangle = \sqrt{|\Phi_A(q_c, T)|^2 + |\Phi_B(q_c, T)|^2}
\]

\[
|K(T)\rangle = \left[ \cos(\Theta(q_c, T)) |A\rangle + \sin(\Theta(q_c, T)) |B\rangle \right]
\]

\[
|\Psi(T)\rangle = |K(T)\rangle |\Psi(T)\rangle.
\]

5.2.4b) Adiabatic propagation

For propagation under an adiabatic Hamiltonian, our strategy will be the same: operate on the ground state with \( \frac{1}{i\hbar} (-\vec{E} \cdot \hat{\mu}) \), then project onto excited states:
\[ |\Psi(T)\rangle = \frac{1}{\sqrt{\hbar}} \sum_{k,v} \exp(-iE_k^a T / \hbar)|k\rangle\langle v^k|\left( -\overrightarrow{E} \cdot \hat{\mu} \right) |g\rangle |0\rangle. \]

The difference is that these states and energies of the projection operator will be adiabatic vibronic product states rather than exact nonadiabatic eigenstates. To obtain useful formulas for initial conditions, the bra \( \langle v^k| \) is expanded in the original diabatic electronic basis, for example as \( \langle v^+| = \langle v^+| (\langle A| \sin \theta^a (q_-) + \langle B| \cos \theta^a (q_-) ). \) The ket component \( |k\rangle\langle v^k| \) of the projection operator \( |k\rangle\langle v^k|\langle k| \) is left written in the adiabatic basis, but the sum over \( k \) is separated into \( |+\rangle|v^+\rangle \) and \( |-\rangle|v^-\rangle \) in order to make the difference in excitation probabilities for the two electronic states explicit.

\[ |\Psi(T)\rangle = (i / \hbar) \sum_{v} |v^+\rangle \exp(-iE_v^a T / \hbar) \langle v^+| \left( \langle A| \sin \theta^a (q_-) + \langle B| \cos \theta^a (q_-) \right) \left( \overrightarrow{E} \cdot \hat{\mu} \right) |g\rangle |0\rangle + (i / \hbar) \sum_{v} |v^-\rangle \exp(-iE_v^a T / \hbar) \langle v^-| \left( \langle A| \cos \theta^a (q_-) - \langle B| \sin \theta^a (q_-) \right) \left( \overrightarrow{E} \cdot \hat{\mu} \right) |g\rangle |0\rangle. \]

Taking the integral over electronic coordinates gives

\[ |\Psi(T)\rangle = (i / \hbar) \sum_{v} |v^+\rangle \exp(-iE_v^a T / \hbar) \langle v^+| \left( \overrightarrow{E} \cdot \hat{\mu}_a \sin \theta^a (q_-) + \overrightarrow{E} \cdot \hat{\mu}_b \cos \theta^a (q_-) \right) |0\rangle + (i / \hbar) \sum_{v} |v^-\rangle \exp(-iE_v^a T / \hbar) \langle v^-| \left( \overrightarrow{E} \cdot \hat{\mu}_a \cos \theta^a (q_-) - \overrightarrow{E} \cdot \hat{\mu}_b \sin \theta^a (q_-) \right) |0\rangle. \]

Now expanding the vibrational bra \( \langle v^k| \) in the ground vibrational basis as

\[ \langle v^k| = \sum_{v} c_{v^k} \langle v|, \] and assuming \( \mu_{eg} = \mu_{Ag} = \mu_{Bg}, \) the adiabatic wavepacket is
\[ |\psi(T)\rangle = \frac{i}{\hbar} \mu_x \sum_{v,v'} \left( (\vec{E} \cdot \hat{x}) c_{v,v'}^+ \langle v'| \sin \theta^v(q_-)|0\rangle + (\vec{E} \cdot \hat{y}) c_{v,v'}^+ \langle v'| \cos \theta^v(q_-)|0\rangle \right) |v\rangle \exp(-iE^v_{\omega} T / \hbar) + \frac{i}{\hbar} \mu_x \sum_{v,v'} \left( (\vec{E} \cdot \hat{x}) c_{v,v'}^- \langle v'| \cos \theta^v(q_-)|0\rangle - (\vec{E} \cdot \hat{y}) c_{v,v'}^- \langle v'| \sin \theta^v(q_-)|0\rangle \right) |v\rangle \exp(-iE^v_{\omega} T / \hbar). \] (5.26)

The \( q \)-integrals \( \langle v' | \cos \theta^v(q_-) | 0 \rangle \) and \( \langle v' | \sin \theta^v(q_-) | 0 \rangle \) remaining in the last equation are evaluated numerically.

5.3 Methods

All calculations were done using parameters of \( \omega = 200cm^{-1}, \delta = 150cm^{-1}, \)
\( J = 66.14cm^{-1} \) and \( \lambda = 5cm^{-1}. \) Numerical techniques were performed using pre-packaged routines from the Visual Numerics IMSL library.\(^{25}\) Numerical integrations were accomplished with the DQDAGS routine, which is an adaptive quadrature algorithm.\(^{26}\) We find that integrating from \( q = \pm 9 \) converges to within \( 1 \times 10^{-11} \) \( cm^{-1} \) for the lowest 15 vibrational states on each adiabatic curve. Matrix diagonalization was accomplished with the routine DEVCRG, which is based on the QR algorithm.\(^{26}\) Inclusion of 20 vibrational levels on each pigment (40 total) was found to converge the lowest 30 eigenvalues of Hamiltonian (5.19) to within \( 1 \times 10^{-4} \) \( cm^{-1}. \) This was sufficient to converge the lowest 20 wavefunctions to with \( 1 \times 10^{-10}, \) with convergence tested by \( 1 - \int_{-\infty}^{\infty} \Phi_n (q_-) \Phi'_n (q_-) dq_- . \) where \( \Phi'_n (q_-) \) is the same nonadiabatic vibrational wavefunction as \( \Phi_n (q_-), \) but calculated with twice as many basis states.
5.4 Results

5.4.1) Stationary states

Using parameters of $\omega = 200 \text{cm}^{-1}$, $\delta = 150 \text{cm}^{-1}$, $J = 66.14 \text{cm}^{-1}$ and $\lambda = 5 \text{cm}^{-1}$ the lowest 5 eigenvalues of the full non-adiabatic Hamiltonian (5.19) are shown in table 5.1. For reference we also show the lowest 5 vibronic basis state energies in the site electronic basis, the diabatic excitonic electronic basis, and the adiabatic basis. The basis state energies of the site basis are always far from the exact answer; this is due to the Coulombic coupling, which is too large to be taken as a perturbation. It can be seen that the lowest eigenstate, nominally $|\text{-}\rangle|0\rangle$ is reasonably well described by either the diabatic excitonic or adiabatic approximation, with neither approximation more than 0.6 cm$^{-1}$ from the exact answer. In both the diabatic excitonic and adiabatic approximations the higher lying basis states come in nearly-degenerate pairs.

We can estimate the values of the nonadiabatic coupling without directly evaluating $\hat{A}$ by taking the pair of $|\psi_1\rangle$ and $|\psi_2\rangle$ and treating it as a 2-state system with average energy $(E_2 + E_1)/2 = 198.014 \text{cm}^{-1}$ and splitting $E_2 - E_1 = 29.135 \text{cm}^{-1}$. For the adiabatic basis states, $|+\rangle|0\rangle$ and $|\text{-}\rangle|1\rangle$ start with an average energy of $(E_{a0}^+ + E_{a1}^-)/2 = 197.532 \text{cm}^{-1}$, so we estimate diagonal nonadiabatic corrections to contribute about 0.5 cm$^{-1}$ for these states. These basis states $|+\rangle|0\rangle$ and $|\text{-}\rangle|1\rangle$ have an energy gap $E_{a0}^+ - E_{a1}^- = 4.683 \text{cm}^{-1}$; using the relation $\Delta_f = \sqrt{\Delta_i^2 + 4V^2}$ to relate the final energy gap $\Delta_f$ to the initial energy gap $\Delta_i$ and coupling $V$ for a two-state interaction, we
<table>
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<th>Exact Level</th>
<th>Energy (cm$^{-1}$)</th>
<th>Site Basis</th>
<th>Energy (cm$^{-1}$)</th>
<th>Exciton Basis</th>
<th>Energy (cm$^{-1}$)</th>
<th>Adiabatic Basis</th>
<th>Energy (cm$^{-1}$)</th>
</tr>
</thead>
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<td>$</td>
<td>\psi_0\rangle$</td>
<td>-1.956</td>
<td>$</td>
<td>A\rangle</td>
<td>0\rangle$</td>
<td>22.5</td>
<td>$</td>
</tr>
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<td>$</td>
<td>B\rangle</td>
<td>0\rangle$</td>
<td>172.5</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>\psi_2\rangle$</td>
<td>212.582</td>
<td>$</td>
<td>A\rangle</td>
<td>1\rangle$</td>
<td>222.5</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>\psi_3\rangle$</td>
<td>377.701</td>
<td>$</td>
<td>B\rangle</td>
<td>1\rangle$</td>
<td>372.5</td>
<td>$</td>
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<tr>
<td>$</td>
<td>\psi_4\rangle$</td>
<td>418.261</td>
<td>$</td>
<td>A\rangle</td>
<td>2\rangle$</td>
<td>422.5</td>
<td>$</td>
</tr>
</tbody>
</table>

Table (5.1) Exact nonadiabatic energies and approximate basis state energies for Hamiltonian (5.3).
estimate the effective nonadiabatic coupling between $|+\rangle|0\rangle$ and $|-\rangle|1\rangle$ to be about 14 cm$^{-1}$.

Figure 5.2(f) shows the vibrational-coordinate dependence of the exact nonadiabatic wavefunctions. The amplitude of the curves indicates the vibrational probability density for exact nonadiabatic wavefunctions. The coloring indicates the $q$-dependence of the nonadiabatic electronic wavefunction, expressed as a nonadiabatic mixing angle $\Theta(q)$ (equation (5.22)). No potential energy curve is shown, as a fully nonadiabatic framework does not separate purely electronic energy as a driving force for vibrational motion. The vibrational probability density has been vertically offset such that each eigenstate’s energy serves as the origin. The lowest excited state $|\psi_0\rangle$ looks similar to the lowest adiabatic state $|-\rangle|0\rangle$, with slightly less color variation indicating slightly less coordinate-dependence to the electronic mixing. The site mixing of the lowest adiabatic state, $|-\rangle|0\rangle$ ranges from $-15.5^\circ \geq -\theta(q) \geq -27.4^\circ$ in between classical turning points, while that for $|\psi_0\rangle$ ranges $-17.6^\circ \geq \Theta(q) \geq -23.5^\circ$ over the same range of $q$.

Other nonadiabatic wavefunctions do not resemble either site, excitonic or adiabatic basis states in color or shape; due to the near-degeneracy of the adiabatic levels the eigenstates are heavily mixed. These nonadiabatic states show rapid color changes as the vibrational coordinate is varied and have no zeros in the probability density that would indicate a node. Nodeless wavefunctions have been noted in the context of nonadiabatic coupling before$^{22,27}$, but to our knowledge have not been studied in systems with near vibronic degeneracy.
In figure 5.3 we focus on the second and third eigenstates, $|\psi_1\rangle$ and $|\psi_2\rangle$. As can be seen in table 1, these arise dominantly from a 2-state interaction between either $|\alpha\rangle|1\rangle$ and $|\beta\rangle|0\rangle$ in an excitonic basis or between $|+\rangle|0\rangle$ and $|-\rangle|1\rangle$ in the adiabatic basis. The situation from the site basis is less clear, as $|\psi_1\rangle$ and $|\psi_2\rangle$ are closer in energy than the basis functions $|A\rangle|1\rangle$ and $|B\rangle|0\rangle$ are, indicating that other levels are involved as well. To take a close look at these eigenstates, they have been projected onto each electronic basis and the projections plotted in figure 5.3. At the top of each panel the exact nonadiabatic eigenstate is shown as in figure 5.2(f); the bottom of each panel shows the decomposition into an electronic basis, $\langle q | \psi_n \rangle = \langle k | q | \psi_n \rangle + \langle k^* | q | \psi_n \rangle$, where the electronic basis is site $\{|A\rangle, |B\rangle\}$ (first column), excitonic $\{|\alpha\rangle, |\beta\rangle\}$ (second column), or adiabatic $\{|-\rangle, |+\rangle\}$ (third column).

Figure 5.3(a) shows $|\psi_1\rangle$ decomposed into $\{|A\rangle, |B\rangle\}$; based on proximity to final state energies, we expect $|B\rangle|0\rangle$ and $|A\rangle|1\rangle$ to contribute most strongly. $\Phi_{1B}$ follows this expectation and looks similar to a $v=0$ state, except shifted too far toward positive $q$- due to the involvement of $|B\rangle|1\rangle$. $\Phi_{1A}$ is dominated by a $v=1$ component, but the positive region has significantly more area than the negative and its node is at positive $q$, rather than negative $q$, revealing the involvement of $|A\rangle|0\rangle$. Panel (b) shows the $\{|A\rangle, |B\rangle\}$ decomposition of $|\psi_2\rangle$, also expected to dominated by $|B\rangle|0\rangle$ and $|A\rangle|1\rangle$; again we see evidence of significant contributions from $|B\rangle|1\rangle$ and $|A\rangle|0\rangle$. The significant involvement of basis states 200 cm$^{-1}$ higher and lower than the two expected to contribute
Figure (5.3) Detail of 2nd and 3rd eigenstates: At the top of each panel the exact nonadiabatic eigenstate is shown as in figure 5.2(f); the bottom of each panel shows the projections onto electronic basis functions, \( \langle k | \langle q | \psi_n \rangle \), where the electronic basis is site \( \{|A\},|B\rangle \), excitonic \( \{|\alpha\},|\beta\rangle \), or adiabatic \( \{|-,+\}\). Panel (a) shows \( |\psi_1\rangle \) decomposed into \( \{|A\},|B\rangle \); \( \Phi_{1B} \) is composed of \( |B\rangle|0\rangle \) and \( |B\rangle|1\rangle \) while \( \Phi_{1A} \) shows \( |A\rangle|0\rangle \) and \( |A\rangle|1\rangle \), making this state a mixture of four basis functions. Panels (c) and (d) show decompositions into the \( \{|\alpha\},|\beta\rangle \) excitonic basis. In panel (c) we see that \( |\psi_1\rangle \) is dominantly \( \left( |\beta\rangle|0\rangle - |\alpha\rangle|1\rangle \right)/\sqrt{2} \), with \( \Phi_{1\beta} \) centered at \( q_-=d_s \) and \( \Phi_{1\alpha} \) with a node at \( q_+=d_s \). Panel (d) shows \( |\psi_2\rangle \) to be dominantly \( \left( |\alpha\rangle|1\rangle + |\beta\rangle|0\rangle \right)/\sqrt{2} \). Panels (e) and (f) give the decomposition of \( |\psi_1\rangle \) and \( |\psi_2\rangle \) into adiabatic electronic states, which is seen to be very similar to the excitonic decomposition. From an adiabatic point of view, the two eigenstates arise dominantly from the interaction between \( |-\rangle|1\rangle \) and \( |+\rangle|0\rangle \).
most strongly to $|\psi_1\rangle$ and $|\psi_2\rangle$ arises from the large off-diagonal (in a site basis) Coulombic coupling.

Given the difficulty in analyzing nonadiabatic wavefunctions as a linear combination of site basis functions, we next analyze them in the excitonic diabatic basis, in which the Coulombic coupling is electronically diagonal and the stabilization energy develops both diagonal and off-diagonal character; only the diagonal component is kept for the definition of the excitonic diabatic basis. Panels (c) and (d) shows decompositions into this $\{ |\alpha\rangle, |\beta\rangle \}$ electronic basis, shows that $|\psi_1\rangle$ and $|\psi_2\rangle$ arise from $|\beta\rangle|0\rangle$ and $|\alpha\rangle|1\rangle$ with little involvement of more distant states. In panel (c) we see that $|\psi_1\rangle$ is dominantly $(|\beta\rangle|0\rangle - |\alpha\rangle|1\rangle)/\sqrt{2}$, with $\Phi_{1\beta}$ centered at $q = d_s$ and $\Phi_{1\alpha}$ with a node at $q = -d_s$. Panel (d) shows $|\psi_2\rangle$ to be dominantly $(|\alpha\rangle|1\rangle + |\beta\rangle|0\rangle)/\sqrt{2}$. Both wavefunctions have a nodeless character, with probability density from $|\beta\rangle$ “filling in” the node from $|\alpha\rangle$; consequently, both wavefunctions show a rapid color change when moving from $-q$ to $+q$, indicating an electronic character which is strongly dependent on vibrational coordinate.

If we consider this excitonic basis to give rise to an adiabatic basis through the action of the excitonically off-diagonal stabilization energy of 1.1 cm$^{-1}$, we expect a very weak coordinate-dependence of the mixing angle (in the diabatic excitonic basis, $D\omega/\omega = 0.0055$ where $D\omega$ is the off-diagonal Jahn-Teller stabilization energy of 1.1 cm$^{-1}$). Panels (e) and (f) give the decomposition of $|\psi_1\rangle$ and $|\psi_2\rangle$ onto the adiabatic electronic states, which is seen to be very similar to the excitonic decomposition. $\Phi_{1\alpha}$ is
slightly narrower than $\Phi_{1\beta}$, while $\Phi_{1\alpha}$ is correspondingly wider than $\Phi_{1\alpha}$; the situation in reversed for $|\psi_2\rangle$. The adiabatic projections, then, are very similar to the excitonic diabatic projections; the heavy mixing of basis states to produce the nonadiabatic eigenstates is dependent on the near-degeneracy of the individual product electronic-vibrational basis states, not due to a degeneracy of the electronic states or to strong nonadiabatic coupling.

Figure 5.4 shows the projections of the next pair of eigenstates $|\psi_3\rangle$ and $|\psi_4\rangle$ onto the excitonic basis functions, plotted in the same manner as for figure 5.3. These eigenstates are dominantly a 2-state interaction between $|\alpha\rangle|2\rangle$ and $|\beta\rangle|1\rangle$. Panel (a) shows $|\psi_3\rangle \approx (|\beta\rangle|1\rangle - |\alpha\rangle|2\rangle)/\sqrt{2}$, which is $-|A\rangle$ (green) at large $-q$, moves through $-|B\rangle$ (light blue) to become $(|A\rangle - |B\rangle)/\sqrt{2}$ (dark blue) at $-q = 0$, and continues through $|A\rangle$ and $|B\rangle$ to become $(|B\rangle - |A\rangle)/\sqrt{2}$ (yellow) at large $+q$. This rapid electronic variation, moving almost a complete circle around the color wheel, does not occur in an adiabatic model. Interestingly, there is a node-like feature at $q = 0.45$, where neither contributing basis function has a node; the vibrational probability density drops to a value of 0.06. For reference, a $v = 0$ probability density in dimensionless coordinates drops to this value at $q = 1.5$ (classical turning points are at $q = 1$).

Panel (b) shows the excitonic decomposition of the 5th wavefunction to be $|\psi_4\rangle \approx (|\beta\rangle|1\rangle + |\alpha\rangle|2\rangle)/\sqrt{2}$, which covers a similar sweep of the color wheel as $|\psi_3\rangle$ but travelling counter-clockwise instead. A dip in vibrational probability density at $q = 0.3$ appears in this wavefunction, near the dip at $q = 0.45$ seen in $|\psi_3\rangle$. Although the exact
Figure (5.4) Detail of 4th and 5th nonadiabatic eigenstates. At the top of each panel the exact nonadiabatic eigenstate is shown as in figure 5.2(f); the bottom of each panel shows the decomposition into the excitonic electronic basis, \( \langle \alpha | q | \psi_n \rangle \) and \( \langle \beta | q | \psi_n \rangle \). These eigenstates are dominantly a 2-state interaction between \( |\alpha\rangle |2\rangle \) and \( |\beta\rangle |1\rangle \). Panel (a) shows \( |\psi_3\rangle \approx (|\beta\rangle |1\rangle - |\alpha\rangle |2\rangle) / \sqrt{2} \), which is \( -|A\rangle \) (green) at large \(-q\), moves through \(-|B\rangle \) (light blue) to become \( (|A\rangle - |B\rangle) / \sqrt{2} \) (dark blue) at \(-q=0\), and continues through \( |A\rangle \) and \( |B\rangle \) to become \( (|B\rangle - |A\rangle) / \sqrt{2} \) (yellow) at large \(+q\). This rapid electronic variation, moving almost a complete circle around the color wheel, does not occur in a 2-electronic state, single vibration adiabatic model. There is a node-like feature at \( q_c=0.45 \), where neither contributing basis function has a node. Panel (b) shows the excitonic decomposition of the 5th wavefunction to be \( |\psi_4\rangle \approx (|\beta\rangle |1\rangle + |\alpha\rangle |2\rangle) / \sqrt{2} \), which covers a similar sweep of the color wheel as \( |\psi_3\rangle \) but travelling counter-clockwise instead. A dip in vibrational probability density at \( q_c=0.3 \) appears in this wavefunction.
nonadiabatic eigenstates are nodeless, it appears that “pseudo-nodes” can develop in
regions near, but not necessarily at, the nodes in contributing basis functions, and that
similar “pseudo-nodes” can appear in consecutive wavefunctions. In the adiabatic
approximation, an increase in quantum number is always accompanied by a change in the
number of nodes; for low vibration quantum numbers this is accompanied by relatively
large changes in the positions of nodes.

5.4.2) Nonadiabatic propagation of wavepackets

To learn what dynamics are associated with the near-degenerate, nodeless
wavefunctions discussed above, figure 5.5 shows the propagation of a wavepacket
created under impulsive excitation with a laser polarized parallel to the transition dipole
for pigment $A$. Panel (c) shows the initial wavepacket, at time zero, and its projections
onto adiabatic surfaces. The purple dashed line (colored purple to indicate that it aligns
with pigment $A$) shows the ground state $v=0$ vibrational probability density, which will
be projected onto the excited states by impulsive excitation. The probability density
excited to the lower adiabatic surface is shown in dark purple (with the slowly varying
color of the adiabatic curves in figure 5.2(b)); the lower surface is populated
preferentially at slightly negative values of $q$. while the upper surface is shifted to slightly
positive values of $q$. Looking at figure 5.2(b), this is understood to be caused by the
rotation of the transition dipole (displayed as a color variation), which causes the lower
curve to project onto the laser polarization better at $-q$. and the upper curve to project
better onto the laser polarization at $+q$. This is a non-Condon effect; the Condon
approximation would neglect the variation in transition dipole direction along $q$. 
Figure (5.5) Wavepacket dynamics following excitation with laser polarization parallel to the transition dipole for pigment A
Figure (5.5) Wavepacket dynamics following excitation with laser polarization parallel to the transition dipole for pigment A. Panel(a) shows the full wavepacket propagation, with amplitude representing vibrational probability density and color indicating electronic composition of the real part of the wavefunction, using the color wheel of figure 5.2(c). The zero of energy has been set to the lowest eigenvalue of Hamiltonian (5.19), $E_0$, so that the $|\psi_0\rangle$ component of the wavepacket does not oscillate. Dynamics are shown for the first 600 fs, which corresponds to a half-period of the dominant nonadiabatic motions. Vibrational oscillations and color variations arise from the superposition of $|\psi_0\rangle$, $|\psi_1\rangle$ and $|\psi_2\rangle$. Panel (b) shows propagation under an adiabatic Hamiltonian, starting from the same initial conditions, with $E^a_0$ set as the zero of energy. Similar but weaker motions appear from the superposition of $|\psi_0\rangle$, $|\psi_1\rangle$, and $|\psi_2\rangle$. Panel (c) shows the initial wavepacket at time zero; the dashed line shows the ground state $\nu=0$ vibrational density distribution colored according to the laser polarization in the $xy$ plane, which dictates the electronic superposition excited. Dark purple shows the population density excited to the lower adiabatic surface and red shows the population density on the upper adiabatic surface. Panel (d) shows $\langle q(T) \rangle = \langle \Psi(T) | \hat{q} | \Psi(T) \rangle$ for nonadiabatic propagation in red and adiabatic propagation in black. The red nonadiabatic curve shows significantly larger oscillations than the adiabatic, arising from the $|\alpha\rangle |0\rangle \leftrightarrow |\alpha\rangle |1\rangle$ character of the superpositions $|\psi_0\rangle \leftrightarrow |\psi_1\rangle$ and $|\psi_0\rangle \leftrightarrow |\psi_2\rangle$. Panel (e) shows $\langle A | \Psi \rangle^2 = \int_{-\infty}^{\infty} \Phi^2 dq_+$, the integrated projection onto pigment $A$. Both the nonadiabatic and the adiabatic curves show deep excitonic oscillations occurring at about 200 cm$^{-1}$. Nonadiabatic effects cause an interference which damps the excitonic oscillation at from 400 – 600 fs in the red curve. Panel (f) shows the projection of the wavepackets onto the lower adiabatic surface, $\langle [-|\Psi|]_2 = \int_{-\infty}^{\infty} \Phi^2 dq_+$. The projection onto the lower adiabatic state is dominated by an oscillation at the superposition frequency between $|\psi_1\rangle$ and $|\psi_2\rangle$. 

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The assumption that the Condon approximation holds for isolated pigments causes \(|g\rangle|0\rangle\) to project onto the excited states without distortion of the vibrational probability density so long as we include all excited states. This assumption does not imply that the Condon approximation holds for the full dimer; however, despite the shifted initial conditions in panel (c), the Condon approximation was found to cause only small quantitative errors in the adiabatic calculations discussed here. All presented calculations were done without applying the Condon approximation to the full system.

Figure 5.5(a) shows the full wavepacket propagation, with amplitude given by \(|\mathbf{p}(T)\rangle\) and color taken from \(\Theta(q_-, T)\), defined in equation (5.25). The zero of energy has been set to the lowest eigenvalue of Hamiltonian (5.19), \(E_0\), so that the \(|\psi_0\rangle\) component of the wavepacket does not oscillate. Dynamics are shown for the first 600 fs, which corresponds to a half-period of the dominant nonadiabatic motions. Side-to-side oscillations and breathing motions can be seen, as well as some color variation; these motions arise from the superposition of \(|\psi_0\rangle\), \(|\psi_1\rangle\) and \(|\psi_2\rangle\). The overall color oscillation from blue to purple is the phase evolution of \(|\psi_1\rangle\) and \(|\psi_2\rangle\) with respect to \(|\psi_0\rangle\). Panel (b) shows propagation under an adiabatic Hamiltonian, starting from the same initial conditions. Similar motions, although weaker and more regular, appear in the adiabatic calculation; the states involved are dominantly \(|-\rangle|0\rangle\) and \(|+\rangle|0\rangle\), although the displacement of the adiabatic curves allows some \(v=1\) to be created as well. Here the energy of \(|-\rangle|0\rangle\) has been set to zero, so that the color changes indicate the phase evolution of \(|+\rangle|0\rangle\).
The detailed dynamics are easier to see if we calculate observables. Panel (d) shows \( \langle q(T) \rangle = \langle \Psi(T) | \hat{q} | \Psi(T) \rangle \) for nonadiabatic propagation in red and adiabatic propagation in black. The adiabatic curve oscillates toward the negative, as the dominant portion of the population density is on the \( | - \rangle \) potential curve, which has its minimum shifted toward \(-q\). The red nonadiabatic curve shows significantly larger oscillations arising from both the \( | \psi_0 \rangle \leftrightarrow | \psi_1 \rangle \) superposition and the \( | \psi_0 \rangle \leftrightarrow | \psi_2 \rangle \) superposition. Both \( | \psi_1 \rangle \) and \( | \psi_2 \rangle \) contain significant \( | \alpha \rangle | 1 \rangle \) character, while \( | \psi_0 \rangle \) is almost entirely \( | \alpha \rangle | 0 \rangle \), which gives this motion a dominantly \( \Delta v = 1 \) character. These superpositions give oscillations at \( E_1 - E_0 = 185 \text{cm}^{-1} \) and \( E_2 - E_0 = 215 \text{cm}^{-1} \), leading to a 30 cm\(^{-1}\) beat frequency in the wavepacket oscillations, with wavepacket oscillations from the origin growing for 600 fs, then fading away again.

To focus on electronic motions, panels (e) and (f) show projections onto electronic basis states. Panel (e) shows \( \int_{-\infty}^{\infty} \Phi_A^2 dq \), the integrated projection onto pigment \( A \). Both the nonadiabatic and the adiabatic curves show deep oscillations occurring at about 200 cm\(^{-1}\). For the adiabatic calculation, this oscillation can be understood as coming from the excitonic nature of the system. Using the excitonic transformation (5.5) and neglecting vibrational levels to simplify the algebra (the excitonic and adiabatic levels and potential curves are similar), a pulse polarized along \( A \) prepares the superposition \( \cos \theta | \alpha \rangle + \sin \theta | \beta \rangle \approx 0.935 | \alpha \rangle + 0.354 | \beta \rangle \); this coherently evolves to become \( 0.935 | \alpha \rangle - 0.354 | \beta \rangle \), which can be transformed back to the site basis to find about 56% \( | A \rangle \) character remains. This is the “wave-like” transport in which the
excitonic nature of the system causes a coherent oscillation between sites;\textsuperscript{10} the electronic energy gap $\delta$ limits the depth of the oscillation and prevents complete transfer to $|B\rangle$.

The projection of the nonadiabatic dynamics onto pigment $|A\rangle$ begins with the same oscillation; in this case it arises from the same superpositions seen in the vibrational motion, $|\psi_0\rangle \leftrightarrow |\psi_1\rangle$ and $|\psi_0\rangle \leftrightarrow |\psi_2\rangle$. In light of the discussion of the adiabatic calculation, however, we assign the electronic beating to the $|\beta\rangle |0\rangle$ components of $|\psi_1\rangle$ and $|\psi_2\rangle$, rather than the $|\alpha\rangle |1\rangle$ components. The same $30 \text{ cm}^{-1}$ beating phenomena occurs, although because it is the $|\beta\rangle |0\rangle$ components which are causing the electronic character oscillations, the $30 \text{ cm}^{-1}$ beat frequency is out of phase with that seen in the vibrational position: the electronic oscillations are large near time zero, fade away near 600 fs, then grow back in.

In panel (f) we show the projection of the wavepackets onto the lower adiabatic surface, $|\langle -|\Psi\rangle|^2 = \int_{-\infty}^{\infty} \Phi^2 dq_-$. In the adiabatic calculation this is an integration over eigenstates, so the populations never change and the black line is perfectly straight. In the nonadiabatic calculation, adiabatic states are basis states whose populations can change (the populations of the exact eigenstates remain constant, but quantum interference allows basis state “populations” to change). The projection onto the lower adiabatic state shows weak oscillations at about $200 \text{ cm}^{-1}$, but is dominated by an oscillation at the superposition frequency between $|\psi_1\rangle$ and $|\psi_2\rangle$ (this can be distinguished from a beat between $|\psi_0\rangle \leftrightarrow |\psi_1\rangle$ and $|\psi_0\rangle \leftrightarrow |\psi_2\rangle$ because a beat between two oscillations cannot have larger amplitude than the sum of the component oscillations).
The coupled vibrational and electronic dynamics are polarization dependent. In figure 5.6 dynamics following impulsive excitation with light polarized parallel to the transition dipole for the lower excitonic state (or the lower adiabatic state at \(q_\perp = 0\)) is shown with propagation under both adiabatic and nonadiabatic Hamiltonians. Panel (c) shows the initial wavepacket and its projections onto the adiabatic electronic states. The red line depicting the upper adiabatic state is not exactly zero anywhere except \(q_\perp = 0\), however it has negligible population density.

Figure 5.6(a) depicts the full wavepacket, with weak side-to-side and breathing motions, although they are difficult to see in this plot as the wavepacket is dominantly \(|\psi_0\rangle\). Panel (b) shows the dynamics following the same excitation pulse, but propagated under an adiabatic approximation. The color changes in the wings come from a \(\Delta v = 1\) superposition, which appear blue at positive \(q_\perp\) and pink at negative \(q_\perp\). Panel (d) shows the side-to-side motions of the wavepacket; in the adiabatic calculation these arise from the same \(\Delta v = 1\) superposition mentioned above. In the exact nonadiabatic dynamics we again see the superposition frequencies between \(|\psi_0\rangle \leftrightarrow |\psi_1\rangle\) and \(|\psi_0\rangle \leftrightarrow |\psi_2\rangle\) and a beating between them. Panel (e) shows the projections onto the \(|A\rangle\) basis state. This time the adiabatic calculation shows less excitonic beating or wave-like transfer than was seen in figure 5.5 following excitation straight to \(|A\rangle\), because the laser polarization for figure 5.6 was chosen to maximally excite the \(|\alpha\rangle|0\rangle\) diabatic excitonic eigenstate. The weak oscillations seen in the black trace arise from the wavepacket moving back and forth on the lower adiabatic curve, which has a weak coordinate-dependence to its mixing angle \(\theta^a(q_\perp)\). The exact nonadiabatic calculation again shows a beating between two
Figure (5.6) Wavepacket dynamics following excitation with laser polarization parallel to the transition dipole to the lower diabatic excitonic surface
Figure (5.6) Wavepacket dynamics following excitation with laser polarization parallel to the transition dipole to the lower diabatic excitonic surface. Panel (a) shows the full wavepacket propagation, with amplitude representing vibrational probability density and color indicating electronic composition of the real part of the wavefunction, using the color wheel of figure 5.2(c). The zero of energy has been set to the lowest eigenvalue of Hamiltonian (5.19), $E_0$, so that the $|\psi_0\rangle$ component of the wavepacket does not oscillate. Dynamics are shown for the first 600 fs, which corresponds to a half-period of the dominant nonadiabatic motions. Panel (b) shows propagation under an adiabatic Hamiltonian, starting from the same initial conditions, with $E_0$ set as the zero of energy. Panel (c) shows the initial wavepacket at time zero; the dashed line shows the ground state $v=0$ vibrational density distribution colored according to the laser polarization in the $xy$ plane, which dictates the electronic superposition excited. Dark purple shows the population density excited to the lower adiabatic surface and red shows the population density on the upper adiabatic surface. Panel (d) shows $\langle q(T) \rangle = \langle \Psi(T)|\hat{q}|\Psi(T)\rangle$ for nonadiabatic propagation in red and adiabatic propagation in black. Oscillations arise from the displacement of the adiabatic curves with respect to the ground state curve. Panel (e) shows $\left|\langle A|\Psi\rangle\right|^2 = \int_{-\infty}^{\infty} \Phi_y dq_-$, the integrated projection onto pigment $A$. The adiabatic curve shows a weak oscillation due to the coordinate dependence of the mixing angle $\theta'(q_-)$. Nonadiabatic effects cause an interference which leads to maximum excitonic oscillation from 400 – 600 fs in the red curve. Panel (f) shows the projection of the wavepackets onto the lower adiabatic surface, $\left|\langle -|\Psi\rangle\right|^2 = \int_{-\infty}^{\infty} \Phi^2 dq_-$.
superpositions, $|\psi_0\rangle \leftrightarrow |\psi_1\rangle$ and $|\psi_0\rangle \leftrightarrow |\psi_2\rangle$, with weak electronic oscillations growing in for 600 fs before decaying away again. Figure 5.6 emphasizes that the lowest basis state, which is almost $|\alpha\rangle|0\rangle$ or $|\beta\rangle|0\rangle$, is hardly affected by the nonadiabatic coupling in this model.

Figure 5.7 shows wavepacket dynamics after excitation polarized at $90^\circ - \theta^d$, which maximally excited the upper diabatic excitonic surface. In panel (c) we see very little (can barely be seen on this scale) population density created in the lower surface. Panel (a) shows the exact nonadiabatic propagation, with rapid color oscillations which begin as blue-red oscillations indicating the phase evolution of the nominally $|+\rangle|0\rangle$ state but become green-purple oscillations of a nominally $|\rangle|1\rangle$ state. On the same time scale the vibrational probability density converts from a $v=0$ state to one which resembles a $v=1$ state. These dynamics are caused by the superposition between $|\psi_1\rangle$ and $|\psi_2\rangle$, which are dominantly the anti-symmetric and symmetric linear combinations of $|+\rangle|0\rangle$ and $|\rangle|1\rangle$. Both the laser polarization and a small Franck-Condon factor make $|\rangle|1\rangle$ a dark state for these excitation conditions. Panel (b) shows the adiabatic propagation; there is a side-to-side oscillation caused by a $\Delta v = 1$ superposition on the $|+\rangle$ potential energy curve, but little other motion.

The effect of the nonadiabatic coupling on energy transfer is clearly seen in figure 5.7 panels (e) and (f), which show the projections onto $|A\rangle$ and $|\rangle$ respectively. The $|\psi_1\rangle \leftrightarrow |\psi_2\rangle$ superposition drives a 30 cm$^{-1}$ large-amplitude oscillation from mostly $|B\rangle$-like to mostly $|A\rangle$-like. The projection onto $|\rangle$ reaches a maximum of 0.98 at 580 fs.
Figure (5.7) Wavepacket dynamics following excitation with laser polarization parallel to the transition dipole to the upper diabatic excitonic surface
Figure (5.7) Wavepacket dynamics following excitation with laser polarization parallel to the transition dipole to the upper diabatic excitonic surface. Panel (a) shows the full wavepacket propagation, with amplitude representing vibrational probability density and color indicating electronic composition of the real part of the wavefunction, using the color wheel of figure 5.2(c). The zero of energy has been set to the lowest eigenvalue of Hamiltonian (5.19), \( E_0 \), so that the \( |\psi_0\rangle \) component of the wavepacket does not oscillate. Dynamics are shown for the first 600 fs, which corresponds to a half-period of the dominant nonadiabatic motions. Vibrational probability density changes and color variations arise from the superposition of \( |\psi_1\rangle \) and \( |\psi_2\rangle \). Panel (b) shows propagation under an adiabatic Hamiltonian, starting from the same initial conditions, with \( E_a^0 \) set as the zero of energy. Weak vibrational motions appear from the superposition of \( |+\rangle|0\rangle \) and \( |+\rangle|1\rangle \), but completely fail to describe dynamics after \( \sim 100 \) fs. Panel (c) shows the initial wavepacket at time zero; the dashed line shows the ground state \( v=0 \) vibrational density distribution colored according to the laser polarization in the \( xy \) plane, which dictates the electronic superposition excited. Dark purple shows the population density excited to the lower adiabatic surface and red shows the population density on the upper adiabatic surface. Panel (d) shows \( \langle q(T) \rangle = \langle \Psi(T)|\hat{q}|\Psi(T)\rangle \) for nonadiabatic propagation in red and adiabatic propagation in black. The red nonadiabatic curve shows a shift from initially oscillating about the minima of the \( + \) surface to oscillating about the minima of the \( - \) surface at 600 fs. Panel (e) shows \( \langle A|\Psi\rangle^2 = \int_{-\infty}^{\infty} \Phi_A^2 dq_- \), the integrated projection onto pigment \( A \). The adiabatic curve shows weak oscillations due to the coordinate dependence of \( \theta^a(q_-) \), while the nonadiabatic curve shows a large population transfer to the \( |A\rangle \) pigment arising from the \( |\psi_1\rangle \) and \( |\psi_2\rangle \) superposition. Panel (f) shows the projection of the wavepackets onto the lower adiabatic surface, \( \langle \Psi|\Psi\rangle^2 = \int_{-\infty}^{\infty} \Phi_-^2 dq_- \). For nonadiabatic dynamics, the time dependence of the projection onto the lower adiabatic state is dominated by an oscillation at the superposition frequency between \( |\psi_1\rangle \) and \( |\psi_2\rangle \).
before decreasing, showing almost complete transfer to the lower adiabatic surface. The near-completeness of the transfer stems from the near-degeneracy of the adiabatic basis states $|+\rangle|0\rangle$ and $|−\rangle|1\rangle$.

Figure 5.8 shows wavepacket dynamics following excitation with a laser polarization parallel to the pigment $B$ transition dipole. Panel (a) shows the wavepacket motion under the exact nonadiabatic Hamiltonian; little happens in the vibrational distribution for about 100 fs; early dynamics are dominated by a color change from orange to green, which is the wave-like excitonic motion of the system (similar to that discussed for figure 5.5(e)). After about 200 fs, a rich dynamics makes itself apparent with fast side-to-side oscillations and mixed $v=0$ and $v=1$ character. Panel (b) shows that the bulk of the dynamics are missed under an adiabatic approximation.

The time-dependence of the vibrational coordinate expectation value (figure 5.8(d)) looks quite similar to what was seen in figure 5.5 following excitation along the $A$-pigment transition dipole; a roughly 200 cm$^{-1}$ oscillation which initially matches the adiabatic approximation moves the wavepacket from side to side. The adiabatic calculation moves strictly to one side of $q=0$ as the wavepacket oscillates on the displaced upper adiabatic potential curve. The nonadiabatic calculation develops a large oscillation to both sides of $q=0$ and these oscillations grow in and fade away at the difference frequency between the $|\psi_0\rangle \leftrightarrow |\psi_1\rangle$ and $|\psi_0\rangle \leftrightarrow |\psi_2\rangle$ superpositions. Initially the oscillation in the nonadiabatic calculation matches the adiabatic approximation, and is centered around the minima of the upper adiabatic curve; near 600 fs (when the vibrational oscillation is largest) the oscillation is roughly centered around the minima of the lower adiabatic curve.
Figure (5.8) Wavepacket dynamics following excitation with laser polarization parallel to the transition dipole of pigment B.
Figure (5.8) Wavepacket dynamics following excitation with laser polarization parallel to the transition dipole of pigment B. Panel (a) shows the full wavepacket propagation, with amplitude representing vibrational probability density and color indicating electronic composition of the real part of the wavefunction, using the color wheel of figure 5.2(c). The zero of energy has been set to the lowest eigenvalue of Hamiltonian (5.19), $E_0$, so that the $|\psi_0\rangle$ component of the wavepacket does not oscillate. Dynamics are shown for the first 600 fs, which corresponds to a half-period of the dominant nonadiabatic motions. Vibrational oscillations and color variations arise from the superposition of $|\psi_0\rangle$, $|\psi_1\rangle$ and $|\psi_2\rangle$. Panel (b) shows propagation under an adiabatic Hamiltonian, starting from the same initial conditions, with $E^a_0$ set as the zero of energy. The adiabatic approximation completely fails to describe dynamics after $\sim$100 fs. Panel (c) shows the initial wavepacket at time zero; the dashed line shows the ground state $v=0$ vibrational density distribution colored according to the laser polarization in the $xy$ plane, which dictates the electronic superposition excited. Dark purple shows the population density excited to the lower adiabatic surface and red shows the population density on the upper adiabatic surface. Panel (d) shows $\langle q(T) \rangle = \langle \Psi(T)|q|\Psi(T)\rangle$ for nonadiabatic propagation in red and adiabatic propagation in black. The red nonadiabatic curve shows significantly larger oscillations than the adiabatic. Panel (e) shows $\left|\langle A|\Psi\rangle\right|^2 = \int_{-\infty}^{\infty} \Phi^2 dq_-$, the integrated projection onto pigment $A$. Both the nonadiabatic and the adiabatic curves show deep excitonic oscillations occurring at about 200 cm$^{-1}$. Nonadiabatic effects cause a slow oscillation toward an overall $|A\rangle$-like character and an interference which damps the excitonic oscillation from 400 – 600 fs. Panel (f) shows the projection of the wavepackets onto the lower adiabatic surface, $\left|\langle -|\Psi\rangle\right|^2 = \int_{-\infty}^{\infty} \Phi^2 dq_-$. The time dependence of the projection onto the lower adiabatic state is dominated by an oscillation at the superposition frequency between $|\psi_1\rangle$ and $|\psi_2\rangle$. 
Figure 5.8(e) shows the projection onto $|A\rangle$. The adiabatic calculation shows the same sort of excitonic oscillation seen in figure 5.5 following excitation along the $A$-pigment transition dipole. The exact nonadiabatic calculation oscillates similarly to the adiabatic approximation for about 100 fs; then the $|\psi_1\rangle \leftrightarrow |\psi_2\rangle$ superposition begins to increase the overall $|A\rangle$ character (this can also be seen in panel (f) as an increase in overall $|\dot{\cdot}\rangle$ character). At the same time that the $|\psi_1\rangle \leftrightarrow |\psi_2\rangle$ superposition increases the overall $|A\rangle$ character, the beating between the two superpositions, $|\psi_0\rangle \leftrightarrow |\psi_1\rangle$ and $|\psi_0\rangle \leftrightarrow |\psi_2\rangle$ damps out the excitonic oscillations. This gives us a situation where the $|A\rangle$ character reaches a maximum with respect to its slow oscillations precisely when the fast oscillations temporarily die out, giving a window of time from 400 fs to 600 fs when there is little change in electronic character.

5.5 Discussion

Hamiltonian (5.3) describes a pigment dimer system in the limit that $J >> \lambda$. Apart from an exact nonadiabatic calculation, stationary states are best described in an excitonic basis, in the sense that exact wavefunctions can be expressed as a linear combination of a small number of simple basis functions. In this basis, the stabilization energy $\lambda$ from each pigment projects onto an anti-correlated vibration $q_\pi$, which contributes to both excitonic stabilization and coupling between excitonic surfaces. The coupling between excitonic surfaces is unavoidable – if there is any vibrational displacement upon excitation of the individual pigments, there will be a coordinate-dependent coupling between excitonic surfaces, which will then resemble a pseudo-Jahn-
Teller nonadiabatic coupling problem. It is possible for the component of $q_-$ which becomes an excitonic stabilization to vanish; inspection of equation (5.6) shows that $d_s = 0$ if the site electronic energy gap $\delta = 0$, i.e. in the usual homo-dimer problem. In that case, the vibrational displacement of individual pigments projects onto a $q_+$ coordinate which does not affect energy transfer, and the $q_-$ coordinate becomes purely a coupling coordinate in the excitonic basis.

In the limit that $J >> \lambda$, the nonadiabatic coupling operates through the coupling term $\omega d_+ q_-$ and depends on the quality of the diabatic excitonic states as quasi-stationary electronic states. If this basis is a poor basis, for example if the fluctuations between pigment site energies are large enough and fast enough that delocalized stationary states do not develop, then the coupling as viewed from the diabatic excitonic basis becomes meaningless. In particular, the $\hat{q}_-$ operator which enters into diagonal elements of Hamiltonian (5.6) is the same as the one which enters off-diagonal, and if adiabatic motion can be said to occur on electronically delocalized potential energy surfaces then nonadiabatic coupling must also be present.

Within this model Hamiltonian, which has a near-degeneracy between $\nu=0$ on one adiabatic surface and $\nu=1$ on the lower surface, the nonadiabatic coupling modifies the usual picture of excitonic, coherent energy transfer in two essential ways. Most importantly, panels (f) of figures 5.5-5.8 show that there is always efficient transfer to the lower adiabatic electronic state. Under any laser polarization, nonadiabatic coupling directs population transfer to the lower adiabatic surface. The necessary conditions for this to occur are for the site energy gap to roughly match a vibrational quantum [chapter 4 of this thesis], and, surprisingly, for the nonadiabatic coupling to be weak. This last
condition is a consequence of a need for the optical transition strength to be concentrated in the \( v=0 \) levels of the adiabatic surfaces. [chapter 4 of this thesis] Because this weak-coupling condition creates adiabatic potential energy curves with the low-lying states entirely contained within a lower potential curve, we refer to this as a “nested funnel.”

The other essential modification to the usual coherent energy transfer picture is the influence of the beating phenomena between \( |\psi_0\rangle \leftrightarrow |\psi_1\rangle \) and \( |\psi_0\rangle \leftrightarrow |\psi_2\rangle \) superpositions. As was seen in figures 5.5(d) and 5.8(d), these two superpositions interfere in such a way as to damp out the coherent excitonic oscillations, and do so precisely when the nonadiabatic population transfer is at a maximum. Note that under these weak vibronic coupling conditions, the basis population in \( |\cdot\rangle \) is maximized at about the same time \( |A\rangle \) is maximized. This offers an intriguing possibility relating to dephasing such excitonic oscillations: there is a relatively wide window of opportunity, from about 400 fs to 600 fs with the parameters used here, for the system to dephase and keep essentially all of its energy in the \( A \) pigment (or the lower adiabatic exciton, if the dephasing leaves the electronic energy delocalized).

Coherent energy transfer is an intrinsically oscillatory phenomenon, which at zero-order should not benefit from a coherence that persists through several oscillations. If the decoherence time between pigments were very long compared to the excitonic oscillations, there would be about a 50% chance of decoherence while the energy is localized on either pigment (depending on initial conditions). Alternatively, if decoherence were very short compared to an oscillation, the excitonic surface may effectively not exist, and coherent energy transfer might not occur. Efficient energy transfer, to zero-order, requires a dephasing time that roughly matches a half-period of
the oscillation, so as to trap the energy in one pigment before it has a chance to return.

The interference pattern which appears in these nonadiabatic calculations, however, allows the possibility of an optimal decoherence time which matches the 30 cm\(^{-1}\) beating phenomena, rather than the 200 cm\(^{-1}\) excitonic energy splitting. This feature of the nonadiabatic model appears to be consistent with reports of electronic coherence between excitons lasting 150 to 700 fs,\(^7\) and does not require the longest picosecond timescales to be indicative of electronic coherence.

### 5.6 Conclusion

The change in equilibrium vibration position which occurs on electronic excitation in individual pigment molecules causes a nonadiabatic coupling in the excitonic system if pigment molecules form a complex. This nonadiabatic coupling has been examined using basis states defined by isolated pigments, diabatic basis states including excitonic effects, and adiabatic basis states. Under the conditions of a site splitting which roughly matches a vibrational frequency and a small stabilization energy, nonadiabatic effects cause a sub-picosecond transfer of energy to the lower energy pigment.
5.7 References


Cederbaum Conical Intersections.


