QP Partitioning for Radiationless Transitions

by

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Abstract

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This work presents a new implementation of the QP algorithm, a computer method to diagonalize the extremely large matrices arising in multimode vibronic problems. Benchmark calculations are included, showing the accuracy of the program. The QP algorithm is extended to treat multiple electronic surfaces for competitive control and this is demonstrated with an Hamiltonian including three electronic states, a model of the benzene radical cation. Finally, the evolution of zeroth-order states in a simple two electronic states, two dimensional model with a conical intersection is explored, towards building a time-dependent view of overlapping resonances coherent control.
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Chapter 1

Introduction

Photochemistry has been one of the most fruitful areas of chemical physics in the 20th century. Technological advances in optics, spearheaded by the invention of the laser, have greatly deepened our understanding of light-matter interactions and the underlying quantum mechanics. This understanding has in turn opened the door for important technologies, including various forms of spectroscopies, which have dramatically changed the way physical and chemical research are now done.

G. N. Lewis, who coined the term photon, initially conceived of light as a simple reactant that can be added and removed from chemical reactions.\(^1\) Further developments in the quantum theory of radiation and light-matter interactions\(^2\) quickly dispelled this idea and showed the complexity of radiative processes. However, the idea of using photons as a chemical reagent has remained.\(^3\) The development of the ultrafast laser, and important theoretical advances in quantum control, are bringing us ever closer to being able to synthesize molecules from simple components using targeted applications of light.

Several approaches to the quantum control of molecular processes have been explored. Pump and dump consists of using one pulse to prepare the system and one pulse to dump it into a certain channel.\(^4\) Methods using adiabatic passage,\(^5\) popular with atomic
systems, use a slow detuning to push the electronic wavefunction to a final state. Optimal quantum control abstracts the physical details of the system and uses feedback to devise a light pulse that promotes the desired state. Coherent control uses phase coherence to build constructive and destructive interference between different pathways as a way to steer processes and is the focus of this work.

Coherent control of a superposition of states requires those states to simultaneously overlap with one or several energy eigenstates, as shown in section 1.4. This condition was first proposed by Frishman and Shapiro, in the control of the spontaneous emission of excited states. The system was coupled to a continuum of modes of the radiation field, as is customary in the quantum theory of radiation. Christopher et al. later showed that the same concept is applicable to states coupled to another subspace of bound states as is common in intramolecular processes. In particular, if that subspace has a very high density of states, the states obtained are similar to those of a continuum, albeit with a much more complicated spectral structure. This form of control was termed overlapping resonances coherent control and is the impetus for this work.

Coherent control has several advantages over other approaches. It is, for example, applicable to complex systems where methods based on adiabatic passage and the quantum Zeno effect fail, and knowledge of the system at hand helps avoiding local minima which affect optimal control theory. Most importantly, coherent control is based in the physics of light-matter interactions and yield an enlightening physical picture of the target system.

Although there are a few available wavepacket propagation methods for molecular systems, they return time-dependent results and not spectra. They are ways to get approximate spectra from those methods, such as filter diagonalization, but calculating phase effects in the propagations to formulate a coherent control strategy would require very long wavepacket propagations, a major reason why optimal control theory is seen as a more feasible alternative.
The QP algorithm\textsuperscript{15} is a highly efficient computer methodology to calculate the resonance spectra of systems with large numbers of degrees of freedom. The use of a quasicontinuum approximation permits the diagonalization of matrices beyond the reach of any standard numerical methods. Such a technique is of great use in the application of overlapping resonances coherent control to realistic models. We have recently completed a new implementation of the QP algorithm, with the goal of extending its application to new systems. Chapter 2 describes the implementation in detail, including benchmark calculations.

In Chapter 3, we present novel results on using the QP algorithm to treat systems with more than two electronic surfaces. The extension is used to treat the benzene radical cation Hamiltonian of D"oscher et al.\textsuperscript{16} This is only the second system ever solved using the QP algorithm and the results acts as a confirmation of the power of the technique.

Finally, Chapter 4 presents some early results on a time dependent view of the theory of overlapping resonances coherent control. A simple model was used to investigate the effect of a conical intersection on eigenstates of a diabat and the wavefunctions produced by phase control. A qualitative study of the resulting wavepackets was undertaken.

The rest of this introduction will cover the basics of the theory of non-adiabatic transitions, overlapping resonances and the QP algorithm. The QP partitioning arose in the study of continuum system, and we cover this in section 1.2. Section 1.3 gives a detailed introduction to the QP algorithm. Finally, overlapping resonances coherent control is introduced in section 1.4.

\section{1.1 Nonadiabatic effects in photochemistry}

The Born-Oppenheimer approximation, the separation of the slow nuclear degrees of freedom from the fast motions of the electrons, makes calculating the electronic structure
of small molecules computationally feasible. It is usually warranted but breakdowns of
the Born-Oppenheimer approximation give rise to ubiquitous processes, such as internal
conversion and intersystem crossing.\textsuperscript{17} The formal Hamiltonian describing a molecule is
written as

\[ \hat{H}(R, r) = \hat{T}_n(R) + \hat{T}_e(r) + \hat{U}(R, r) \] (1.1)

where \( \hat{T}_n \) and \( \hat{T}_e \) are the kinetic operators for the nuclei and electrons and \( \hat{U} \) is the
potential energy caused by the nucleus-nucleus, the electron-electron and the nucleus-
-electron forces. This equation is usually separated into electronic and nuclear parts,

\[ \hat{H}(R, r) = \hat{T}(R) + \hat{H}_{el}(R, r) \] (1.2)

where the electronic Hamiltonian depends parametrically on the nuclear coordinates.
Solving the electronic Hamiltonian \( \hat{H}_{el} \) first,

\[ \hat{H}_{el}\Phi_{el}(R, r) = E(R)\Phi_{el}(R, r) \] (1.3)

shows that the eigenvalue equation for the electronic degrees of freedom creates a potential
\( E(R) \) for the nuclear degrees of freedom. The exact wavefunction is written in the Born
representation as

\[ \Psi(R, r) = \sum_i \chi_i(R)\phi_i(r, R) \] (1.4)

where \( \chi_i(R) \) are nuclear wavefunctions. This expansion is formally exact but not very
useful: the system is still fully coupled and solving it requires solving both the nuclear
and electronic parts at the same time. Using eq. 1.4 with the Hamiltonian given by
eq 1.1, multiplying by the electronic eigenfunction \( \phi_j \) and integrating over electronic
coordinates gives us the following Schrödinger equation for the nuclear motion,

$$i\hbar \frac{\partial \chi_j}{\partial t} = \left( \hat{T}_n + E_j(R) \right) \chi_j - \sum_i \hat{\Lambda}_{ji} \chi_i$$  \hspace{1cm} (1.5)$$

where the $\hat{\Lambda}$ is the non-adiabatic coupling operator, defined by

$$\hat{\Lambda}_{ji} = \hat{T}_n \delta_{ji} - \langle \phi_j | \hat{T}_n | \phi_i \rangle .$$  \hspace{1cm} (1.6)$$

In atomic units,

$$\hat{T}_n = -\frac{1}{2M} \nabla_n^2,$$  \hspace{1cm} (1.7)$$

is the nuclear kinetic energy operator, where the subscript $n$ denotes nuclear degrees of freedom. The non-adiabatic coupling operator is written as the sum of a scalar potential coupling $G$ and a derivative coupling $F \cdot \nabla$,

$$\hat{\Lambda}_{ij} = \frac{1}{2M} (F_{ij} \cdot \nabla + G_{ij})$$  \hspace{1cm} (1.8)$$

$$F_{ij} = \langle \phi_i | \nabla \phi_j \rangle$$  \hspace{1cm} (1.9)$$

$$G_{ij} = \langle \phi_i | \nabla^2 \phi_j \rangle .$$  \hspace{1cm} (1.10)$$

In the Born-Oppenheimer approximation, $\hat{\Lambda}$ is zero. In the adiabatic approximation, only off-diagonal elements of $\hat{\Lambda}$ are dropped which blocks the system from moving from one surface to another but includes the effects of having multiple surfaces.

Applying neither approximation leads to the following nuclear Schrödinger equation,

$$-\frac{1}{2M} (\nabla + F)^2 \chi + V\chi = i\hbar \frac{\partial \chi}{\partial t}$$  \hspace{1cm} (1.11)$$
where the identity,

\[
G = \nabla \cdot F + F \cdot F \tag{1.12}
\]

is used. This is a gauge equation, similar to what appears in the quantum theory of particles in magnetic fields.\(^\text{18}\) The derivative coupling term \(F\) is, for example, responsible for breaking time-reversal invariance and introducing the Berry phase, a geometric phase closely related to Aharonov-Bohm effect.\(^\text{19}\) The influence of the geometric phase on vibronic wavepackets leads to many interesting effects, including spontaneous symmetry breaking.\(^\text{20}\)

Note that for \(i \neq j\), the derivative coupling is given by

\[
F_{ij} = \langle \phi_i | \nabla \phi_j \rangle \tag{1.13}
\]

\[
= \frac{\langle \phi_i | \nabla \hat{H}_{el} | \phi_j \rangle}{V_j - V_i} \tag{1.14}
\]

which has a discontinuity where the potentials \(V_i\) and \(V_j\) meet. If the coupling potential \(\nabla H_{el}\) is a linear function of the nuclear coordinates, the two potentials will intersect conically.\(^\text{21}\) Conical intersections are a common feature of molecular wavefunctions and are vital to our understanding of ultrafast non-radiative processes.\(^\text{22}\) The discontinuity forms a small region of intense coupling, a molecular “funnel” through which the vibrational wavefunction can effectively transit to another electronic surface.\(^\text{23}\)

Conical intersections create discontinuities in the derivative coupling and are therefore numerically troublesome. Recent work\(^\text{24}\) attest to their importance and they cannot be simply eliminated. Diagonalization becomes a lot simpler if a transformation can be found such that the derivative couplings become standard potential couplings, or

\[
-\frac{1}{2M} (\nabla + F)^2 \chi + V \chi \rightarrow -\frac{1}{2M} \nabla^2 \chi + W \chi. \tag{1.15}
\]
This is the diabatic transformation and the new potential surfaces due to $W$ are termed diabats. The diabatic surfaces are usually much smoother\cite{25} which makes the diagonalization of the individual surface Hamiltonians easier.

Formally, the diabatic Hamiltonian is obtained by a local change of gauge of eq. 1.11. In a truncated system, where only a finite number of electronic states are used, this transformation is only exact for diatomic models.\cite{26} However, an approximate diabatic transformation can be made if the coupling between electronic diabatic states is important only over a comparatively small region of space, as is the case for a conical intersection. Numerical diabatization, pioneered by Köppel, Domcke and Cederbaum,\cite{27} allows fitting the adiabatic potential energy surfaces to approximate diabats with potential couplings. The model Hamiltonians used in this work are diabatic Hamiltonians, of the form

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}$$

(1.16)

where the coupling $\hat{H}_{12}$ depends only on the nuclear coordinates and $\hat{H}_1, \hat{H}_2$ are the individual electronic surface Hamiltonians. This form naturally leads to a physically meaningful partitioning, similar to the Feshbach partitioning of continuum problems. This partitioning is vital to the QP algorithm, an extension of Feshbach partitioning to intramolecular processes.

### 1.2 Feshbach partitioning for continuum problems

Feshbach partitioning\cite{28} is a method to calculate the eigenvalues and eigenfunctions of systems of bound states coupled to a continuum of energy eigenstates. In the original formulation, the bound states (or zeroth order states) are the eigenstates of an electron around an atom and the continuum is composed of the states of the unbound electron.
Because the QP algorithm is a direct descendant of Feshbach partitioning, I present here a short introduction to the theory of Feshbach resonances.\textsuperscript{29}

Consider an Hamiltonian $\hat{H}$ composed of bound states $|\kappa\rangle$ and a continuum of states $|E\rangle$. Let $\hat{Q}$ and $\hat{P}$ be partitioning projectors such that

\begin{align}
\hat{Q} + \hat{P} &= 1 \\
\hat{Q}^2 &= \hat{Q} \\
\hat{P}^2 &= \hat{P}.
\end{align}

Any Hamiltonian can be expressed as a partitioned Hamiltonian,

\begin{align}
\hat{H} &= \left(\hat{P} + \hat{Q}\right) \hat{H} \left(\hat{P} + \hat{Q}\right) \\
&= \hat{Q}\hat{H}\hat{Q} + \hat{Q}\hat{H}\hat{P} + \hat{P}\hat{H}\hat{Q} + \hat{P}\hat{H}\hat{P}.
\end{align}

This is always true but not necessarily useful. It can be made useful by a judicious choice of the $Q$ and $P$ spaces. Define $\hat{Q}$ and $\hat{P}$ such that the individual partitions are diagonal in the bases of the bound and continuum states,

\begin{align}
\hat{Q}\hat{H}\hat{Q} |\kappa\rangle &= E_\kappa |\kappa\rangle \\
\hat{P}\hat{H}\hat{P} |E\rangle &= E |E\rangle.
\end{align}

Note that these are not the eigenstates of the full Hamiltonian,

\begin{equation}
\hat{H} |\gamma\rangle = E_\gamma |\gamma\rangle.
\end{equation}

Using $\hat{Q} + \hat{P} = 1$ and multiplying this equation on the left with $\hat{Q}$ or $\hat{P}$ gives the following
two equations,
\[
\begin{align*}
\left( \varepsilon_{\gamma} - \hat{Q}\hat{H}\hat{Q} \right) \hat{Q} \left| \gamma \right\rangle &= \hat{Q}\hat{H}\hat{\hat{P}} \left| \gamma \right\rangle \\
\left( \varepsilon_{\gamma} - \hat{\hat{P}}\hat{H}\hat{\hat{P}} \right) \hat{\hat{P}} \left| \gamma \right\rangle &= \hat{\hat{P}}\hat{H}\hat{\hat{Q}} \left| \gamma \right\rangle.
\end{align*}
\] (1.25) (1.26)

Solving eq. 1.26 for \( \hat{\hat{P}} \left| \gamma \right\rangle \) yields the following,
\[
\hat{\hat{P}} \left| \gamma \right\rangle = \left( \varepsilon_{\gamma} - \hat{\hat{P}}\hat{H}\hat{\hat{P}} \right)^{-1} \hat{\hat{P}}\hat{H}\hat{\hat{Q}} \left| \gamma \right\rangle
\] (1.27)

which is then used in eq. 1.25 to obtain
\[
\varepsilon_{\gamma}\hat{Q} \left| \gamma \right\rangle = \left( \hat{Q}\hat{H}\hat{Q} + \hat{Q}\hat{H}\hat{\hat{P}} \left[ \varepsilon_{\gamma} - \hat{\hat{P}}\hat{H}\hat{\hat{P}} \right]^{-1} \hat{\hat{P}}\hat{H}\hat{\hat{Q}} \right) \hat{Q} \left| \gamma \right\rangle,
\] (1.28)

an eigenvalue equation for the \( Q \) part of the eigenstates \( \left| \gamma \right\rangle \). The term in parentheses is the Feshbach effective Hamiltonian, denoted \( \tilde{H}(\varepsilon_{\gamma}) \). Solving this equation for various atomic decay processes is not at all trivial\(^{29,30}\) but there is interesting physics even in the simplest analytical case.

Given a set of bound states \( (Q) \) coupled to a continuum of states in \( P \),\(^{31}\) the effective Hamiltonian is
\[
\tilde{H}(\varepsilon_{\gamma}) = \lim_{\epsilon \to 0} \tilde{H}(\varepsilon_{\gamma} + i\epsilon) = \hat{Q}\hat{H}\hat{Q} + \hat{Q}\hat{H}\hat{\hat{P}} \left[ \varepsilon_{\gamma} + i\epsilon - \hat{\hat{P}}\hat{H}\hat{\hat{P}} \right]^{-1} \hat{\hat{P}}\hat{H}\hat{\hat{Q}}
\] (1.29)

where the energy is endowed with an imaginary infinitesimal \( i\epsilon > 0 \) to denote outgoing
boundary conditions. Using the Sokhotskyi-Plemelj formula,

$$\lim_{\epsilon \to 0} \left[ E_\gamma + i\epsilon - \hat{P}\hat{H}\hat{P} \right]^{-1} = P_\nu \left[ E_\gamma - \hat{P}\hat{H}\hat{P} \right]^{-1} + i\pi \delta \left( E_\gamma - \hat{P}\hat{H}\hat{P} \right)$$

(1.31)

where $P_\nu$ denotes the Cauchy principal value integral,

$$P_\nu \int_a^b dE' \frac{f(E')}{E - E'} = \lim_{\epsilon \to 0^+} \left( \int_a^{E-\epsilon} dE' \frac{f(E')}{E - E'} + \int_{E+\epsilon}^b dE' \frac{f(E')}{E - E'} \right).$$

(1.32)

The effective Hamiltonian is then expanded as

$$\tilde{H}(E_\gamma) = \hat{Q}\hat{H}\hat{Q} + \hat{Q}\hat{H}\hat{P} P_\nu \left[ E_\gamma - \hat{P}\hat{H}\hat{P} \right]^{-1} \hat{P}\hat{H}\hat{Q} + i\pi \hat{Q}\hat{H}\hat{P}\delta(E_\gamma - \hat{P}\hat{H}\hat{P})\hat{P}\hat{H}\hat{Q}$$

(1.33)

and its matrix elements are directly obtainable,

$$\langle \kappa | \tilde{H}(E_\gamma) | \kappa' \rangle = \epsilon_\kappa \delta_{\kappa,\kappa'} + \Delta_{\kappa,\kappa'} + \frac{i}{2} \Gamma_{\kappa,\kappa'}$$

(1.34)

where the shift and the line width are defined as

$$\Delta_{\kappa,\kappa'} = \frac{1}{2\pi} P_\nu \int dE' \frac{\Gamma_{\kappa,\kappa'}}{E_\gamma - E'}$$

(1.35)

$$\Gamma_{\kappa,\kappa'} = 2\pi \int dE \langle \kappa | \hat{V} | E \rangle \langle E | \hat{V} | \kappa' \rangle \delta(E_\gamma - E)$$

$$= 2\pi \langle \kappa | \hat{V} | E_\gamma \rangle \langle E_\gamma | \hat{V} | \kappa' \rangle$$

(1.36)

---

aGiven a state $|\psi(t)\rangle$, its projection on any given eigenstate at time $t$ is

$$| \langle E | \psi(t) \rangle |^2 = e^{-2\epsilon t/\hbar}.$$

(1.30)

This means that any bound state component of $|\psi\rangle$ will vanish at $t \to \infty$ on a timescale proportional to $1/\epsilon$. This boundary condition ensures that the state will spread outward through space, as is physical. It is required by the non-normalizability of the continuum states.\(^2\)

bNote that the boundaries of the integral in $\Delta_{\kappa,\kappa'}$ need to be definite if the shift is to be finite. This is identical to the renormalization required in the quantum electrodynamics of bound states coupled to a continuum of modes of radiation.\(^2\)
and $\hat{V}$ is the coupling potential between the states $|\kappa\rangle$ in $Q$ and the states $|E_\gamma\rangle$ in $P$.

In the quantum mechanics of continua, a resonance state is an eigenstate of the non-Hermitian Hamiltonian (such as the effective Hamiltonian of eq. 1.34) obtained by integrating out the continuous degrees of freedom. The resonance is the spectrum of this state given its overlap with the continuous eigenstates of $\hat{H}$,

$$F_\kappa(E_\gamma) = \langle \kappa | \gamma \rangle \langle \gamma | \kappa \rangle$$

where $|\gamma\rangle$ are the eigenstates of the full Hamiltonian, not to be confused with the $P$ eigenstates at $E_\gamma$, $|E_\gamma\rangle$. From eq. 1.28,

$$E_\gamma \sum_\kappa | \kappa \rangle \langle \gamma | \kappa \rangle = \hat{H}(E_\gamma) \sum_\kappa | \kappa \rangle \langle \kappa | \gamma \rangle$$

where the projector $\hat{Q}$ is expanded explicitly in the bound states $|\kappa\rangle$. Projecting on the left with $\langle \kappa |$,

$$E_\gamma \langle \kappa | \gamma \rangle = \left( \epsilon_\kappa + \Delta_{\kappa,\kappa} + \frac{i}{2} \Gamma_{\kappa,\kappa} \right) \langle \kappa | \gamma \rangle + \sum_{\kappa' \neq \kappa} \left( \Delta_{\kappa,\kappa'} + \frac{i}{2} \Gamma_{\kappa,\kappa'} \right) \langle \kappa' | \gamma \rangle.$$  

The second term is due to the interplay between the zeroth-order states. Assuming it is finite and denoting it $A(E_\gamma)$, elementary algebra yields

$$F_\kappa(E_\gamma) = \frac{|A(E_\gamma)|^2}{(E_\gamma - [\epsilon_\kappa + \Delta_{\kappa,\kappa}])^2 + \Gamma_{\kappa,\kappa}^2/4}$$

which is the Fano line shape. Far away from other resonances states, where $A(E_\gamma)$ varies slowly with $E_\gamma$, it is a Lorentzian centered at the shifted energy of $|\kappa\rangle$ with a width of $\Gamma$. Close to other resonances, the problem becomes more complicated and the resonances lose their simple Fano shapes. In particular, overlapping resonances create a structured spectrum even if their individual widths are larger than the spacing between...
the resonances: the interference effects preclude analyzing the system as a simple sum of non-interacting zeroth-order states. In the case of a space of bound states coupled to another space of bound states, the resonances become very complicated entities (see fig. 2.6 for an example) which account for the varied nature of intramolecular processes.

1.3 The QP algorithm is a Feshbach partitioning for bound states

Feshbach partitioning gives an intuitive view of scattering processes and provides an efficient method to calculate the effect of continua on bound states. This kind of partitioning can also be applied to intramolecular processes, as was shown successfully by Christopher et al.\textsuperscript{9} for a simplified, four modes model of the pyrazine molecule. The QP algorithm, a computational method to efficiently diagonalize large systems using this partitioning, was developed shortly after\textsuperscript{15} and applied to a realistic model of pyrazine, with all 24 modes.\textsuperscript{34} This section reviews the extension of Feshbach partitioning to systems of bound states and introduces the QP algorithm as an efficient computational mean of diagonalizing large Hamiltonians.

Consider a system consisting of bound states $|\kappa\rangle$ and $|\beta\rangle$. Define partitioning operators $\hat{P}$ and $\hat{Q}$ such that $\hat{Q}$ selects the $|\kappa\rangle$ states and $\hat{P}$ the $|\beta\rangle$,

\begin{equation}
\hat{Q} = \sum_{\kappa} |\kappa\rangle \langle \kappa| \tag{1.41}
\end{equation}

\begin{equation}
\hat{P} = \sum_{\beta} |\beta\rangle \langle \beta| . \tag{1.42}
\end{equation}

Additionally, let the states $|\kappa\rangle$ and $|\beta\rangle$ diagonalize the $Q$ and $P$ parts of the Hamiltonian,
such that

\[ \hat{Q} \hat{H} \hat{Q} |\kappa\rangle = \epsilon_\kappa |\kappa\rangle \]  
\[ \hat{P} \hat{H} \hat{P} |\beta\rangle = \epsilon_\beta |\beta\rangle . \]  

(1.43)  
(1.44)

The partitioning presented in sec. 1.2 did not use the properties of continuum states until the effective Hamiltonian is defined explicitly in eq. 1.34. Therefore, the derivation of the effective Hamiltonian \( \tilde{H}(E_\gamma) \), eq. 1.17 to 1.28, holds for bound states. The eigenvalue equation for \( \hat{Q}|\gamma\rangle \) in the bound state case is

\[ E_\gamma \hat{Q}|\gamma\rangle = \tilde{H}(E_\gamma) \hat{Q}|\gamma\rangle \]  
\[ [\tilde{H}(E_\gamma)]_{\kappa,\kappa'} = \epsilon_\kappa \delta_{\kappa,\kappa'} + \sum_\beta \frac{V_{\kappa,\beta} V_{\kappa,\beta}^\dagger}{E_\gamma - E_\beta} \]  

(1.45)  
(1.46)

where the effective Hamiltonian matrix elements are explicitly written and \( \hat{Q}\hat{H}\hat{P} = \hat{V}_{\kappa,\beta} \), the coupling operator.

This decomposition is exact but an efficient method to solve the above eigenvalue equation is still required. Equation 1.45 shows that if the total Hamiltonian \( \hat{H} \) as an eigenvalue \( E_\gamma \) then the effective Hamiltonian evaluated at \( E_\gamma \) must also have an eigenvalue equal to \( E_\gamma \). Let the function \( \tilde{\epsilon}_i(E) \) be the \( i \)-th eigenvalue of \( \tilde{H} \) evaluated at \( E \).\(^a\) Then, finding all the eigenvalues of the full Hamiltonian entails finding all the roots of the following \( N_Q \) equations,

\[ \tilde{\epsilon}_i(E) = E. \]  

(1.47)

This is not a trivial task and is discussed further in section 2.2.5. The eigenvector corresponding to the eigenvalue \( E_\gamma \) gives the \( Q \) space part of \( |\gamma\rangle \). However, the \( P \) part

\(^a\)The ordering of the eigenvalues is constant here. Numerically, that is not the case but the ordering is enforceable, as discussed in sec. 2.2.5.
of the eigenvector is trivially recoverable from eq. 1.27.

### 1.3.1 Computational efficiency

The computational efficiency of the QP algorithm was compared to the efficiency of straight diagonalization in Christopher et al.\textsuperscript{15} The run time of the QP algorithm scales as

\[ O = (N_Q + N_P)N_E \left(C_1N_Q^3 + C_2N_Q^2N_P\right) \]  

(1.48)

where \(N_Q\) and \(N_P\) are the size of the \(Q\) and \(P\) spaces, \(N_E\) is the number of diagonalizations of \(\tilde{H}\) required to find an eigenvalue within some tolerance and \(C_1, C_2\) are some constants. This represents the effort required to build the effective Hamiltonian \((N_Q^2N_P)\), diagonalize it \((N_Q^3)\) and refine the \(N_Q + N_P\) eigenvalues of the Hamiltonian. The scaling of a straight forward diagonalization of a matrix of size \(N_T = N_Q + N_P\) is roughly \(25N_T^3\). The QP algorithm becomes advantageous when \(N_Q \ll N_P\). If that is the case, the run time will scale roughly as \(N_P^2\).

The QP method demands a small \(Q\) space to be efficient. Most systems of interest in non-adiabatic processes have a large number of vibrational states on all of their electronic manifolds. To use the QP algorithm, a way is needed to select the states \(|\kappa\rangle\) such that the \(Q\) space can be brought to a manageable size. This is explained in more details in sec. 2.2.3.

Although the QP algorithm is a valid matrix diagonalization technique, the many diagonalizations of \(\tilde{H}(E)\) required to obtain the eigenvalues to sufficient numerical precision means that the scaling prefactor is very large. As such, the range of systems it is useful for is rather limited compared to general diagonalization algorithms.
However, the possibility of coarse-graining the $P$ space makes it an invaluable tool for problems with sizes larger than what other algorithms can do, as it will be seen below. The coarse-graining makes the running time dependent on the number of bins, not on the number of $P$ states. This makes the QP algorithm with coarse-graining independent of the number of degrees of freedom, even though the dimensionality of the matrices grow exponentially.

### 1.3.2 Coarse-graining the $P$ space

The previous section has described the efficiency of the QP algorithm as an exact diagonalization method. However, systems with many degrees of freedom have much higher dimensionalities than diagonalizable with any exact methods, including the QP algorithm. The power of the QP algorithm lies in the ability to coarse-grain the $P$ space. Consider the effective Hamiltonian previously described,

$$[\tilde{H}(E_\gamma)]_{\kappa,\kappa'} = \epsilon_\kappa \delta_{\kappa,\kappa'} + \sum_{\beta} V_{\kappa,\beta} V_{\kappa,\beta}^\dagger.$$  \hspace{1cm} (1.49)

The influence of the states $|\beta\rangle$ comes in through the sum. This allows reducing the effective size of the problem by binning several states together,

$$[\tilde{H}(E_\gamma)]_{\kappa,\kappa'} \approx \epsilon_\kappa \delta_{\kappa,\kappa'} + \sum_m \frac{1}{E_{\gamma} - E_m} \sum_{\beta \in A_m} V_{\kappa,\beta} V_{\kappa,\beta}^\dagger.$$  \hspace{1cm} (1.50)

where the first sum is over the bins $m$ and the second sum is over the states $|\beta\rangle$ in the $m$-th bin. Since the binning is done prior to the QP diagonalization, this greatly reduces the effort required to build the effective Hamiltonian for each energy evaluation. Clearly, if the bins were of infinitesimal size, this would be exact. However, this approach works well even for relatively large bins if the $P$ space is a quasicontinuum. This is true of
molecular systems, where the large number of modes means the spectrum is extremely dense.

The coarse-graining approximation, examined further below, allows the QP algorithm to become truly effective. For example, in the full-dimensional (24 modes) pyrazine model, there are roughly $10^{11}$ states in $S_1$ with non-negligible contribution to the resonances. This is a system beyond the reach of any exact diagonalization methods, even if only a few eigenvalues are desired. However, it is clear from previous studies that the sheer quantity of states is important for the dynamics and quantum control in pyrazine. They cannot be simply neglected.

Coarse-graining the QP Hamiltonian greatly reduces the effective size of the full Hamiltonian. However, it must be noted that it does not reduce the actual size of the full Hamiltonian nearly as much. In fact, the QP solution for pyrazine with 400 bins and 200 states in $Q$ gives roughly 70,000 eigenstates, even though the effective dimension is $N_Q + N_P = 600$. This was not discussed in the original exposition of the QP algorithm. The binning is the result of the following transformation

$$\sum_\beta \frac{1}{E_\gamma - E_\beta} V_{\kappa,\beta} V_{\kappa,\beta}^\dagger \rightarrow \sum_m \frac{1}{E_\gamma - E_m} \sum_{\beta \in A_m} V_{\kappa,\beta} V_{\kappa,\beta}^\dagger. \tag{1.51}$$

The coarsening in the QP algorithm consists of taking all the states in bin $A_m$ and making them degenerate, with energy $E_m$, or

$$\{E_\beta\} \forall \beta \in A_m \rightarrow \{E_m\} \forall \beta \in A_m. \tag{1.52}$$

This is similar to the common energy denominator approximation used in calculating electron exchange potentials. If there was only one bin, this would be a system of dimension $N_Q$ with $N_Q$ eigenvalues. If there are $N_Q$ eigenvalues per bin then the Hamiltonian would have $N_Q \times N_P$ eigenvalues in total. Empirically, we find that this is roughly
correct, if the bins are picked such that they contain a large number of \( P \) states. In systems where the number of \( P \) states is limited, such as the two-dimensional model of pyrazine used in sec. 2.3, the coarse-graining is both unnecessary and incorrect.

Can this transformation be justified? Clearly, at the level of the bin width, the eigenspectrum of the exact Hamiltonian will look significantly different from the spectrum of the coarse-grained Hamiltonian. However, if an energy range several times a bin width is considered, the approximation is a good one. In the time domain, this means the result is going to be correct on a time scale of

\[
\Delta t \approx \frac{\hbar}{\Delta_m}
\]

where \( \Delta_m \) is the bin width. This gives a rough estimate of how many bins we should use for a given problem.

\subsection*{1.3.3 Time propagation of QP results}

Once the eigenvalues have been obtained, the propagator can be calculated for arbitrary times by simply projecting onto the energy eigenvectors,

\[
|\psi(t)\rangle = \sum_{\gamma} e^{-iE_{\gamma}t/\hbar} |\gamma\rangle \langle \gamma|\psi\rangle
\]

in the Schrodinger picture. However, in the coarse-grained case, the \( P \) space resolution of the eigenstates is lost. This means the coarse-grained QP algorithm requires that the initial state lies fully in \( Q \) such that it can be properly described by the resonances obtained.

Because the number of \( Q \) states is small, it is convenient to calculate the explicit
propagator for any state in $Q$. In matrix form, this is given by

$$[M(t)]_{\kappa, \kappa'} = \sum_{\gamma} e^{-iE_\gamma t/\hbar} \langle \kappa | \gamma \rangle \langle \gamma | \kappa' \rangle$$

(1.55)

where

$$|\psi(t)\rangle = \hat{M}(t) |\psi(t=0)\rangle$$

(1.56)

From the propagator, various quantities related to coherent control, such as $f_{\kappa, \kappa'}$ from sec. 1.4, are easily calculated. Wavepacket propagations require in this scheme a negligible computational effort.

We mention here a closely related technique due to Thanopulos et al.\textsuperscript{11} that apply the QP partitioning idea. The time-dependent QP algorithm, which is also compatible with coarse-graining, solves the integrodifferential equations that underlies the dynamics directly, bypassing the QP diagonalization. This permits the inclusion of time-dependent fields. However, the time-dependent QP does not calculate the resonance spectrum of the individual states and is, as such, not well suited to the purposes of this work.

### 1.4 Overlapping resonances and coherent control

The resonance state is not as well defined a concept for systems of bound states as it is for continua. Consider a partitioned Hamiltonian

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_{AB}$$

(1.57)

where the subspaces $A$ and $B$ are two electronic surfaces. The “zeroth-order” eigenstates are the eigenstates of the Hamiltonians $\hat{H}_A$ and $\hat{H}_B$. The resonance of a state $|\kappa\rangle$ is given
by its overlap with the energy eigenstates $|\gamma\rangle$,

$$F_{\kappa,\gamma} = a_{\kappa,\gamma}^* a_{\kappa,\gamma} = \langle \kappa | \gamma \rangle \langle \gamma | \kappa \rangle$$

(1.58)

by analogy with the line shapes of the resonance state in continuum systems (sec. 1.2). Although the zeroth-order states are no longer eigenstates of an effective Hamiltonian, the apparition of dense eigenspectra, similar to those of true resonance states, motivate the use of the term.$^3$ The complex vector $a_{\kappa,\gamma}$ is termed a resonance amplitude.

Given a state in some superposition of zeroth-order eigenstates $|\kappa\rangle$ at time 0,

$$|\Psi(t = 0)\rangle = \sum_\kappa c_\kappa |\kappa\rangle$$

(1.59)

the state at time $t$ is given by

$$|\Psi(t)\rangle = \sum_{\kappa,\gamma} c_\kappa a_{\gamma,\kappa} e^{-iE_\gamma t/\hbar} |\gamma\rangle$$

(1.60)

where the states $|\gamma\rangle$ are eigenstates of the full Hamiltonian $\hat{H}$ with energy $E_\gamma$. Two important quantities in this equation are the preparation coefficients,

$$c_\kappa = \langle \kappa | \Psi(t = 0) \rangle$$

(1.61)

and the resonance amplitudes,

$$a_{\kappa,\gamma} = \langle \gamma | \kappa \rangle.$$ 

(1.62)

For quantum control, it is assumed that the system can be prepared by populating the zeroth order eigenstates through modulated light, i.e. that the preparation vector $c_\kappa$ can be arbitrarily chosen. The resonance amplitudes $a_{\gamma,\kappa}$ are the result of coupling the zeroth order eigenstates in $A$ and $B$: for any time $t$ there is a matrix $M(t)$ that, once applied
onto our preparation vector, gives us the state at $t$. This overlap matrix is defined by

$$M_{\kappa,\kappa'}(t) = \sum_{\gamma} a_{\kappa,\gamma}^* a_{\kappa',\gamma} e^{-iE_\gamma t/\hbar}. \quad (1.63)$$

where

$$|\Psi(t)\rangle = \hat{M}(t) |\Psi(t = 0)\rangle \quad (1.64)$$

and is a propagator between the states $\kappa$ and $\kappa'$ at time $t$. Although the formalism can be extended to other problems,\textsuperscript{37} we are primarily interested in population decay from one electronic state to another. If the states $|\kappa\rangle$ are limited to the states of $H_A$, the population in the $A$ space at time $t$ after excitation is given by

$$P(t) = c\dagger \hat{M}(t) \hat{M}(t) c \quad (1.65)$$

for a preparation vector $c$. Coherent control is a function of the phase of the coefficients $c_\kappa$ and the population is written as a sum of phase-controllable terms and terms independent of phase,

$$P(t) = \sum_\kappa |c_\kappa|^2 g_\kappa(t) + \sum_{\kappa' \neq \kappa} c_{\kappa'}^* c_\kappa f_{\kappa',\kappa}(t) \quad (1.66)$$

where

$$g_\kappa(t) = \sum_{\kappa'} |M_{\kappa,\kappa'}(t)|^2 \quad (1.67)$$

$$f_{\kappa,\kappa'}(t) = \sum_{\kappa''} M_{\kappa,\kappa''}^*(t) M_{\kappa'',\kappa'}(t) \quad (1.68)$$

$$= \sum_{\kappa'',\gamma,\gamma'} \langle \kappa' | \gamma \rangle \langle \gamma | \kappa'' \rangle \langle \kappa'' | \gamma' \rangle \langle \gamma' | \kappa \rangle e^{-i(E_\gamma - E_{\gamma'}) t/\hbar}. \quad (1.69)$$

The overlapping resonance condition makes its appearance here: phase control depends
on the term

\[ \sum_{\kappa'', \gamma, \gamma'} \langle \kappa' | \gamma \rangle \langle \gamma | \kappa'' \rangle \langle \kappa'' | \gamma' \rangle \langle \gamma' | \kappa \rangle \]  

(1.70)

which is significant only if two or more zeroth order states overlap with the same eigenstate \( |\gamma\rangle \). This is resonance overlap, a necessary but not sufficient condition for control at a given time \( t \). The formulation of a theory giving the resonance overlap at a given time \( t \) is the topic of Chapter 4.
Chapter 2

A new implementation

The original QP program, written by P. S. Christopher\textsuperscript{15} was developed alongside the algorithm to compute resonances for pyrazine. Although the program works, it is more of a proof of concept than an usable tool. Several prior attempts were made by others to modify it or apply it to new systems but such efforts failed as the program lacked documentation, was hard coded for pyrazine and compiled for a special purpose machine that is no longer maintained.

To study resonances and their overlaps, a method is needed to calculate them. Although there are ways to obtain resonances for small systems or to extract them from wavepacket propagation methods, they suffer from significant drawbacks which preclude their application to control scenarios. To extend overlapping resonances coherent control to a wider range of systems, we had no choice but to rewrite and restructure the QP program.

This new implementation was built from the ground up to be accessible and extensible, both for my own work and for the work of others. Performance-critical parts were written in Fortran 90 but most of the code is written in Python, a modern programming language
with a wide range of libraries for scientific computing. Message passing is built in for
greater performance on modern clusters and multiprocessor systems.

In this chapter, we will cover in details the new implementation. The first section
(2.1) reviews the product bases that form the core of the QP algorithm as applied to
vibronic problems. Section 2.2 describes the new program. Section 2.3 compares the QP
algorithm with more or less exact numerical methods. The last section (2.4) uses the
pyrazine molecule to benchmark the new implementation.

### 2.1 Product bases and vibronic problems

We are interested in vibronic problems, where the vibrational states on one or multiple
electronic surfaces are coupled to one another. The trial basis functions can be succinctly
written as product of individual modes,

\[
|\Psi\rangle = |\text{el}\rangle |n_1\rangle |n_2\rangle |n_3\rangle \cdots |n_N\rangle \\
= |\text{el}\rangle \prod_{i=1}^{N} |n_i\rangle
\] (2.1)

where $|\text{el}\rangle$ is the electronic degree of freedom and $|n_i\rangle$ represents a state on mode $i$. In
the diabatic representation, the Hamiltonian is composed of two parts,

\[
\hat{H} = \sum_{\text{el}} \left( \hat{T} + \hat{V}_{\text{el}} \right) |\text{el}\rangle \langle \text{el}| + \sum_{\text{el}_1, \text{el}_2 \geq \text{el}_1} \hat{V}_{\text{el}_1, \text{el}_2} |\text{el}_1\rangle \langle \text{el}_2|
\] (2.3)

where the first sum represents the potential energy surfaces of the various electronic
states and the second sum contains the non-adiabatic couplings. The QP program solves
for the states of one electronic surface after coupling to other surfaces. Therefore, the
partitioning operators are of the form

\[ \hat{Q} = \hat{U}_0 |el = 0\rangle \langle el = 0| \quad (2.4) \]
\[ \hat{P}_i = \hat{U}_i |el = i\rangle \langle el = i|. \quad (2.5) \]

The unitary projection operators \( \hat{U} \) diagonalize the Hamiltonians of the individual electronic states,

\[ \hat{U}^\dagger \langle el| \hat{H}| el \rangle \hat{U} = \sum \epsilon_{\phi} |\phi\rangle \langle \phi| \quad (2.6) \]

where the state \( |\phi\rangle \) is a combination of vibrational excitations on electronic state \( |el\rangle \) with an energy of \( \epsilon_{\phi} \). For simplicity, we now focus on the case of one \( Q \) space and one \( P \) space and refer the reader to Chapter 3 for an extension to multiple \( P \) spaces. The QP algorithm requires diagonalized \( Q \) and \( P \) spaces. For a system with a large number of modes of vibrations, this is in general a hard problem. However, it can be made tractable using symmetry.

Normal mode analysis works well because few modes of a molecule are strongly coupled to one another. These modes can be grouped together into low-dimensional component bases and diagonalized individually. The true size of the system only appears when taking a product of those components. The Hamiltonian corresponding to one of the surfaces can be written as

\[ \langle el| \hat{H}| el \rangle = \hat{H}_1 + \hat{H}_2 + \cdots + \hat{H}_K \quad (2.7) \]

\[ \hat{H}_i = \sum_{n \in \text{set } i} \hat{T}_n + \hat{V}_n + \sum_{n,m \in \text{set } i} \hat{V}_{n,m} \quad (2.8) \]

where \( K \) is the number of such sets. In molecular systems, one would use the irreducible representations of the point group symmetry or any group of modes that are coupled only to one another. In this decomposition, a general state on an individual electronic
surface will have the form,

$$|\psi\rangle = \prod_{i=1}^{K} \left( \prod_{j \notin \text{set } i} |n_j\rangle \right).$$  \hfill (2.9)

The individual components are diagonalized to obtain their eigenstates $|\eta\rangle$ such that

$$\left( \sum_{n \in \text{set } i} \hat{T}_n + \hat{V}_n + \sum_{n,m \in \text{set } i} \hat{V}_{n,m} \right) |i,\eta\rangle = \epsilon_{i,\eta} |i,\eta\rangle$$  \hfill (2.10)

$$|i,\eta\rangle = \sum_{n} c_n \prod_{j \in \text{set } i} |n_j\rangle$$  \hfill (2.11)

where the index $n$ runs over all combinations of excitations in the component basis $i$. The diagonal surface states $|\phi\rangle$ from eq. 2.6 can now be written as products of diagonalized states $|\eta\rangle$,

$$|\phi\rangle = \prod_{i=1}^{K} |i,\eta\rangle$$  \hfill (2.12)

with energy

$$\epsilon_{\phi} = \sum_{i=1}^{K} \epsilon_{i,\eta}.$$  \hfill (2.13)

In this new basis, the number of states $|\phi\rangle$ will be equal to the product of the number of states in each component basis. In a sufficiently symmetric system, the number of states required to properly describe the components and converge their energies is relatively small. However, the product basis of all the components can rapidly grow to huge sizes. This is where the QP algorithm becomes significant: diagonalizing the subspaces is numerically easy but diagonalizing the full Hamiltonian with non-adiabatic couplings is hard, as the product form lead to an exponential number of states.

Finally, it is customary to represent the diagonal states on the $Q$ surface by $|\kappa\rangle$ and
the diagonal states on the $P$ surface by $|\beta\rangle$, for convenience. Additionally, note that the matrix elements of the coupling potential $\hat{V}$ are calculated using,

$$V_{\kappa,\beta} = \langle \kappa | \hat{V} | \beta \rangle$$

$$= \left( \langle \text{el} = 0 | \prod_{i=1}^{K} \langle i, \eta_\kappa \rangle | \text{el} = 0 \rangle \right) \hat{V} \left( \langle \text{el} = 1 | \prod_{i=1}^{K} | i, \eta_\beta \rangle | \text{el} = 1 \rangle \right)$$

$$= \prod_{i=1}^{K} \langle i, \eta_\kappa | \hat{V}_i | i, \eta_\beta \rangle$$

where the potential operator $\hat{V}$ has been decomposed into its individual components.

### 2.2 The QP workflow

The previous section showed how the eigenbasis that diagonalizes the $Q$ and $P$ spaces is calculated. This demonstration was done in the order that the QP program takes. In this section, we will walk through a typical use case and explain the various parts of the QP workflow, shown in Figure 2.1. Each steps is described in further details later below.

Solving a vibronic problem with the QP program is straightforward. The steps, for any molecule, will be the following:

1. For each set of coupled states on each surface, the user defines the kinetic energy and potential energy operators and basis, including the number of basis states to be used. This is done in **Subspace** and **Bases**. The component Hamiltonians are built and diagonalized.

2. The components are loaded in **QPVibron**. The user then defines the coupling potentials. The decomposition of $V_{\kappa,\beta}$, shown in eq. 2.16, is built. This requires the calculation of vibrational overlap integrals between the two surfaces.
3. The user loads the parameters that will be used for the rest of the workflow in a parameter file through the interface given by QPMain. The decomposition of $V_{\kappa,\beta}$ and the $Q$ and $P$ energies are loaded automatically.

4. The user uses one of the purification routine to reduce the $Q$ space to a manageable size, given an optimization target such as overlap with the Franck-Condon point. This selects the $|\kappa\rangle$ states and optionally builds the bins for the coarse-graining.

   (a) If coarse-graining is not used, the purification routine is run for the $P$ space. A typical optimization would be to include all states up to some energy cut-off.

5. The user runs `make_coupling_cg` or `make_coupling` depending whether the coarse-graining is used or not. This builds the coupling matrices $V_{\kappa,\beta}V_{\beta,\kappa}$ from their individual parts by calculating the product basis.

6. `qp.solve` is run. This finds the eigenvalues $E_\gamma$ and eigenvectors $Q|\gamma\rangle$ up to a precision given by the user. The results can be analyzed using the helper objects `QPAnalyse` and `QPControl`. Additionally, the Fortran program `timeprop` can be run to generate the propagator matrices $U_{\kappa,\kappa'}(t)$ for arbitrary times.

The rest of this section will cover the technical details of each of those parts, in that order.

### 2.2.1 Building a basis

Given that the Hamiltonian is evaluated numerically, a truncated finite basis must be used to build the matrix. The basis used must be able to efficiently represent the eigenfunctions of the Hamiltonian. We have implemented an arbitrary dimensional harmonic basis for use with the QP program to solve vibrational problems. Note however that the
Figure 2.1: The QP workflow. The complete QP workflow is composed of five programs and several python objects. The python objects are accessed from user-written scripts and serve as glue between the numerically intensive, parallel Fortran programs. Additional helper scripts are used to automate some of this process and are not shown here.
algorithm is itself basis independent and that other bases, such as plane waves for rotational problems, are also implementable.

The basis was implemented using sparse matrices to limit memory usage. Although not required for the problems presented in this thesis, as the product basis form used for pyrazine and benzene allows the use of relatively small bases for the component Hamiltonians, basis dimensions well into the tens of thousands are currently doable.

The Hamiltonian, once built, is diagonalized. This is done either using the dense, full diagonalization methods of the Linear Algebra Package\textsuperscript{39} or using a sparse, implicitly restarted Arnoldi algorithm.\textsuperscript{40} The Arnoldi solver is mostly appropriate for the $Q$ space as the program requires only a small number of basis states. However, for the $P$ space, the dense solver is used if memory allows it to ensure that all the $P$ states that couple strongly to our selected $Q$ states are included.

### 2.2.2 Calculating coupling elements

The next step is to calculate the coupling matrix elements $V_{\kappa,\beta}$ that will be used in building the coupling matrix. Equation 2.16 shows that only the coupling between the product bases is needed. Given a set of potential operators, all the matrix vectors that couple the individual components (denoted by $i$) are built,

$$V_{\kappa,\beta,i} = \langle i, \eta_{\kappa} | \hat{V}_i | i, \eta_{\beta} \rangle$$

(2.17)

toward building the full potential,

$$V_{\kappa,\beta} = \prod_{i=1}^{K} V_{\kappa,\beta,i}.$$  
(2.18)
Starting with the non-diagonal $Q$ harmonic basis, the potential matrix is calculated and projected onto the $P$ harmonic basis. This yields the matrix

$$[\hat{V}]_{\beta,\kappa} = |\beta\rangle \sum_{\kappa'} \langle n_{\beta}|n_{\kappa'}\rangle \langle n_{\kappa'}|\hat{V}|n_{\kappa}\rangle \langle n_{\kappa}|$$  \hspace{1cm} (2.19)

which requires the calculation of the overlap integrals $\langle n_{\beta}|n_{\kappa'}\rangle$. We find that the most convenient method is to use large trial bases centered in the same coordinates for $P$ and $Q$, which reduces the overlaps to the Kronecker delta $\delta_{n_{\beta},n_{\kappa}}$. Smaller bases centered at each of the $P$ and $Q$ ground state geometries could be used but the smaller sizes would not compensate for the long calculation times required for the overlaps, even using analytic formulas.\textsuperscript{41} Note that the overlap matrix is not in general square as the $P$ and $Q$ spaces do not contain the same number of states. This matrix is then projected onto the diagonal $|\eta\rangle$ states,

$$[\hat{V}]_{\beta,\kappa} = U_{\beta}^d [\hat{V}]_{\beta,\kappa} U_{\kappa}$$  \hspace{1cm} (2.20)

where the unitary matrices $U_{\beta}$ and $U_{\kappa}$ that diagonalize the component Hamiltonians were used.

### 2.2.3 Reducing the $Q$ space

The next step is to bring down the number of states in $Q$ to a manageable size. This essential step is dictated by the physics of the system. For both benzene and pyrazine, the overlap with a Franck-Condon excitation from the ground state electronic state was used to select the final $|\kappa\rangle$ states. This is equivalent to picking the $N_Q$ states with the
largest value of

\[ O_\kappa = |\langle \kappa | n = 0 \rangle|^2 \] (2.21)

\[ = \prod_{i=1}^{K} |\langle i, \eta_\kappa | i, n = 0 \rangle|^2, \] (2.22)

where the \( n \) represent the initial harmonic bases chosen and \( i \) is the product index. The states are optimized by sorting the overlap vectors and performing a breadth-first search on the tree represented by those vectors.\(^{42}\) This allows rapidly finding the maximal states without looping over all possible combinations, of which there can be a very large number (\( \approx 10^{10} \) in pyrazine).

The same routine can also be used to optimize the \( P \) space if coarse-graining is not used or to list all combinations of states up to a given energy. However, the sheer amount of states required for the coarse-graining means that an entirely different method must be used to assemble the coupling matrix.

### 2.2.4 Assembling and coarse-graining the product basis

Once the component coupling matrices are built, the product basis must be calculated. However, the large number of states that comprise the final Hamiltonian is a major hindrance. The original QP program picked states in \( P \) by their overlap with the states in \( Q \) but we have found this method to be hard to generalize. In the pyrazine model, for example, there are \( \approx 10^{11} \) states in the system. Even if the \( 10^7 \) states that contribute the most to the potential were successfully selected, the sheer number of remaining state could contribute a lot more. To calculate the binned coupling matrix, a new method has been implemented that allows binning the full extent of the Hamiltonian.

Give two sets of kets \( |\eta_1\rangle \) and \( |\eta_2\rangle \) with dimension \( N_1 \) and \( N_2 \), the direct product of the sets will contain all possible combinations of the kets, with a dimension \( N = N_1 N_2 \).
Once this is done for each component basis, they are binned and some of the energy space structure is lost. The strategy of the new program is to bin them at each pair of component basis in a grid much finer than the output bins and hope that the loss of resolution in energy will be less than that caused by the final binning. The following is done,

- Start with the two first component bases and pick all possible combinations.
- For each combination, add it to one of the intermediate bins.
- Repeat with the intermediate bins and the next component basis.

The result numerically converges when the number of intermediate bins is roughly ten times the number of final bins. This also gives the same result as the original QP program.

Note that the coupling matrix that is calculated is the outer product of the potential matrices,

\[
\Gamma_{\kappa,\kappa',\alpha} = \sum_{\beta \in \alpha} V_{\kappa,\beta}^* V_{\beta,\kappa}.
\] (2.23)

Therefore, if there are more than one potential matrix and the full potential is given by

\[
\hat{V} = \sum_i \hat{V}^{(i)},
\] (2.24)

the cross terms \(V_{\kappa,\beta}^{(i)} V_{\beta,\kappa}^{(j)}\) that arise from taking the product must also be calculated. Additionally, the calculation is done separately for every pair \(\kappa, \kappa'\). The coupling matrix \(\Gamma_{\kappa,\kappa',\alpha}\) is an outer product of vectors \(V_{\kappa,\beta}\) and must be positive semidefinite. The positive semidefiniteness of the matrix can be broken within numerical error. This is important for the solver, as explained in the next section.
2.2.5 The QP solver

As in section 1.3, the roots of the following equation need to be found:

\[ \Delta_\kappa(E_\gamma) = E_\gamma - \tilde{\epsilon}_\kappa \]  \hspace{1cm} (2.25)

where \( \tilde{\epsilon}_\kappa \) are the eigenvalues of the effective Hamiltonian matrix,

\[
[H(E_\gamma)]_{\kappa,\kappa'} = \epsilon_\kappa \delta_{\kappa,\kappa'} + \sum_\beta \frac{V_{\kappa,\beta} V_{\kappa,\beta}^\dagger}{E_\gamma - E_\beta} \]

\[ = \epsilon_\kappa \delta_{\kappa,\kappa'} + \sum_\beta \frac{\Gamma_{\kappa,\kappa',\beta}}{E_\gamma - E_\beta}. \]  \hspace{1cm} (2.27)

This is an \( N_Q \) vector-valued function of \( E_\gamma \) with sharp peaks around the energies \( E_\beta \).

The eigenvectors of \( \tilde{H}(E_\gamma) \), denoted \( |D_\gamma\rangle \), are normalized to unity by the numerical eigensolver but are proportional to \( \hat{Q} |\gamma\rangle \). The final eigenvectors are given by

\[
\hat{Q} |\gamma\rangle = \left( 1 + \sum_\beta \frac{\langle D_\gamma | \Gamma_\beta | D_\gamma \rangle}{(E_\gamma - E_\beta)^2} \right)^{-1} |D_\gamma\rangle. \]  \hspace{1cm} (2.28)

as derived in the original paper.\(^{15}\) Note that eigenvalues very close to the bin centers or \( P \) energies \( E_\alpha \) are almost entirely in \( P \), due to the square dependence on the energy difference. These eigenvalues are “dark”, in that they contribute only slightly to the time-dependent behavior of a state initially in \( Q \). To ensure convergence, an avoidance parameter \( \delta E_\gamma \) is introduced and the program will avoid solving for zeros within \( \delta E_\gamma \) of the bin centers.

The quality metric \( q_{\kappa,\kappa'} \) is defined as

\[
q_{\kappa,\kappa'} = \sum_\gamma \langle \kappa | \gamma \rangle \langle \gamma | \kappa' \rangle. \]  \hspace{1cm} (2.29)
Note that this is equal to the matrix elements of the projector $\hat{Q}$ if the eigenvalues are known exactly,

$$q_{\kappa,\kappa'} = \langle \kappa | \hat{Q} | \kappa' \rangle = \delta_{\kappa,\kappa'} \quad (2.30)$$

The quality metric gives a measure of the completeness of the solution. Obtaining a complete solution imposes an upper bound on the avoidance parameter $\delta E_\gamma$: if it is too large, some eigenvalues will be missing and the diagonal elements of $q$ will be less than one.

Additionally, the positive semidefinite nature of the coupling matrix ensures that

$$\langle D_\gamma | \Gamma_\alpha | D_\gamma \rangle > 0 \quad (2.31)$$

and that the resulting eigenvectors will be orthonormal. If the coupling matrix is not positive semidefinite, diagonal elements of $q$ greater than 1 are seen. This only happens if the solver is too aggressive in its search for eigenvalues and approaches the bin centers closer than the largest magnitude negative eigenvalue of $\Gamma_\alpha$. This imposes a lower bound on the parameter $\delta E_\gamma$.

The parallel solver takes the energy space and splits it into pieces of width $\Delta_w$, avoiding the bin centers. This grid is then distributed to multiple compute nodes and the zeros are found in parallel. The grid width $\Delta_w$ must be selected small enough to resolve closely spaced zeros. This is done by selecting a small width such that most grid intervals contain no zeros and very few contain more than one.

The solver uses the mean value theorem to detect if there is a zero at each grid point. The zeros are then refined down to the machine precision using Brent’s method$^{43}$, a combination of bisection, the secant method and quadratic interpolation. This converges faster than bisection alone, requiring fewer computationally expensive diagonalization
calls. The diagonalizations themselves are done using LAPACK, as the $Q$ space is small.

Finally, it is important to conserve the ordering of the eigenvalues while solving the problem so that all mean-value comparisons in the solver are valid. This is done by reordering the eigenvalues after each diagonalization based on overlap with previous eigenvectors, as explained in the original paper.

### 2.3 Comparison with exact numerical methods

To verify the numerical accuracy of the QP algorithm, we have used it with an oversimplified model for the pyrazine $S_2 \rightarrow S_1$ transition, due to Sukharev and Seideman that is easily diagonalized using standard methods. This model has a low-lying conical intersection and is described in more details in Chapter 4.

The primitive basis used consists of two mode harmonic oscillator eigenfunctions with the harmonic frequencies of the model. States up to 12 eV where selected. The $P$ space contains all of the resulting eigenvalues. The $Q$ space was selected by picking the 150 states in $Q$ with greatest overlap with the ground state of the $S_0$ harmonic oscillator. This gave a total matrix size of $N_Q + N_P = 150 + 2243 \approx 2300$ basis states. This is a small system which does not benefit from the QP algorithm since the number of $Q$ states is only a bit smaller than the number of $P$ states. However, it is easily amenable to direct diagonalization and grid-based propagation methods that can be compared to our QP implementation.

In figure 2.2, we compare the QP result to a direct diagonalization using the Intel implementation of LAPACK, the canonical dense diagonalization library. Note that eigenstates that lie entirely in $P$ are not found by the QP program as expected by the
Figure 2.2: Plotted here is the population in $Q$ for eigenstates $|\gamma\rangle$ of the two-dimensional model of pyrazine used in Chapter 4. The eigenstates with large $\langle \hat{Q} \rangle$ are the “extreme states” of Sukharev and Seideman\textsuperscript{44}, which they claim can be used for quantum control. Note that the QP algorithm cannot find states that do not overlap with $Q$ at all.
form of the effective Hamiltonian shown in eq. 1.28. The eigenspectra are otherwise identical.

In figure 2.3, we have compared the result from the QP algorithm to solving the Schrödinger equation on a grid. We used a discrete Fourier basis\textsuperscript{45} for the grid, with an adaptively stepped Runge-Kutta propagator. Additional structure appears in the QP result due to the limited number of $Q$ states but the behavior is very close. Grid-based methods are the gold standard of the field as the approximations made are very well controlled\textsuperscript{38} but the number of grid points required scales as $N^d$ where $d$ is the dimension of the system. They can only be used for very small systems, where the QP algorithm is not required.

\section*{2.4 A benchmark study with 24 modes pyrazine}

To verify the accuracy of the coarse-graining, the 24 dimensional pyrazine Hamiltonian of Raab et al.\textsuperscript{35} was solved as originally done with the first iteration of the QP algorithm.\textsuperscript{34} In figure 2.4, we compare the result of a QP run using 400 bins and 200 $Q$ states with the MCTDH result from Raab et al. The result starts to diverge by about 80 fs, exactly as is expected from eq. 1.53 for a bin width of 0.008 eV. Decreasing the bin width leads to increased accuracy at longer times\textsuperscript{15} but all the processes of interest occur before 80 fs.

The comparison between the photoelectron spectra shown in figure 2.5 shows the major limitation of the QP program: we have to use the eigenstates of the $Q$ space which puts a computational limit on the possible initial conditions. At high energy, where individual states in $Q$ contribute very little to the overlap with the Franck-Condon wavepacket, the spectrum returned by the QP program lacks a significant amount of population. This does not imply an error in the algorithm: the area of the QP spectrum is
Figure 2.3: Evolution of a Franck-Condon wavepacket in the two dimensional model of Sukharev and Seideman.\textsuperscript{44} On the left is the result from a QP run, using 150 $Q$ states. This is compared with the picture on the right, where the propagation is done on a grid using numerical integration. Additional structure appears in the QP run because of the limited number of $Q$ states used to represent the wavepacket.
Figure 2.4: Autocorrelation function $|J(t)| = |\langle \Psi(0) | \Psi(t) \rangle|$ as calculated by the QP algorithm ($N_Q = 200$) and MCTDH.\textsuperscript{35} The autocorrelation function is a sensitive measure of the quality of a solution. This is done using 400 bins spaced by about 0.008 eV.

exactly 70\% that of the MCTDH spectrum, the same as the overlap between the $Q$ states picked and the Franck-Condon wavepacket. Using more $Q$ states gives a fuller spectrum but it is computationally more expensive. However, getting a smooth spectrum required only a very small phenomenological broadening (2 meV) showing the high density of eigenstates in the solution.

The time required to compute the eigenspectrum of pyrazine is fairly short on a modern multicore system. We used an Intel Xeon X5650-based machine and 6 compute cores. The run time is broken down in the following fashion:

- Diagonalizing the individual irreducible representations of pyrazine took 20 minutes using the parallel dense LAPACK, as implemented by Intel.
Figure 2.5: Photoelectron spectrum of the pyrazine $S_2 \rightarrow S_1$ transition as calculated by the QP program and MCTDH. The two simulations, with 100 and 200 $Q$ states, show the slow convergence of the spectrum as more states form a better description of the Franck-Condon wavepacket.
• Purifying the $Q$ space, selecting the states with highest overlap with the Franck-Condon wavepacket took 3 minutes for 200 states. This corresponds to a 70% overlap.

• Building the coarse-grained coupling matrix took 30 minutes.

• Solving the QP problem, the main step, took close to four hours.

• Building the propagators took five minutes.

The total running time is about five hours, four of those are spent finding the eigenvalues using the solver. Although we have not undertook a detailed study of the scaling behavior of the QP program, finding the eigenvalues requires no interprocess communication at all and is expected to scale strongly with the number of compute nodes.

The QP algorithm main’s strength, however, is that time propagations are trivial once we have the full eigenspectrum of a system. In figure 2.6, we show a typical example of overlapping resonances coherent control, using two strongly overlapping zeroth-order states. The control map, which shows the influence of phase on the decay of population of a superposition of zeroth-order states, is the result of 2500 wavepacket propagation, which can be generated in only a few seconds once the eigenvalues have been found. For comparison, the same system was treated with MCTDH in 1999 and one trajectory required 485 hours. Even accounting for a two orders of magnitude growth in computer power since, which is generous, the QP algorithm with coarse-graining still outperforms MCTDH by several orders of magnitude if a large amount of trajectories is required.

2.5 Concluding remarks

We have described the new implementation of the QP program and established its accuracy. The remarkable efficiency of the QP algorithm is due to the product form of the potential, which allows the $Q$ and $P$ subspaces to be diagonalized efficiently.
Figure 2.6: The QP algorithm returns the resonance line shapes of states in $Q$, from which we can do coherent control. Plotted on the left is the resonance line shape ($|\langle \kappa | \gamma \rangle |^2$ of two strongly overlapping eigenstates of $Q$, $|3\rangle$ and $|5\rangle$). Plotted on the right is the population at 15 fs of a combination of given by $\sqrt{\alpha} |3\rangle + e^{i\phi} \sqrt{1 - \alpha} |5\rangle$, showing phase control of the population.
The QP program as it now stands is easily understood and easily extensible. We mentioned in passing that the QP algorithm is basis independent. We want to test this assumption in the future by implementing new basis functions for other problems, including rotational degrees of freedom. Additional extensions to open quantum systems\cite{46} and to the modeling of radiation processes\cite{47} are being investigated.

Technical work we hope to do includes a proper study of the scaling properties of the QP algorithm with respect to the number of compute nodes in large clusters. Additionally, we want to derive optimal values for several parameters, such as the QP grid width $\Delta_w$ and the $P$ energies avoidance width $\delta E_\gamma$, to ensure that the implementation can be easily used by others.
Chapter 3

An extension to multiple electronic surfaces

Coherent control has early on been applied to competitive processes. For example, in the laser distillation of enantiomeric molecules,\textsuperscript{3} a molecule starts with two ground states $L$ and $D$, representing the two enantiomer of the target molecule. It is excited to an upper electronic surface and relaxed back down to one of the two enantiomers. Given an initial mixture of $L$ and $D$ and several cycles of excitation and relaxation, the mixture is purified controllably to one of the two symmetries.

To our knowledge, competitive control of intramolecular processes on more than two electronic surfaces has not been reported. However, the principle is quite similar: given multiple electronic surfaces, can the decay of population be phase controlled to favor a certain surface? To answer this question, the QP algorithm has been extended to treat multiple electronic surfaces, coupled and uncoupled. To test this extension, we have used a model Hamiltonian for the benzene radical cation,\textsuperscript{16,48} one of the few parametrizations of a system of more than two interacting electronic states that is discussed in the literature.
We present here the results obtained by the new QP program for Franck-Condon excitations to the \( \tilde{C} \) and \( \tilde{B} \) surfaces of the benzene radical cation. This serves both to show the power of the method and to introduce an extension to the QP algorithm. The control of competitive processes in this system will be the subject of future study.

In the first section, we derive the equations governing the QP algorithm with multiple coarse-grained \( P \) subspaces. In the second section, we apply those equations to the benzene radical cation Hamiltonian and present population decay curves and spectra.

### 3.1 Uncoupled and coupled electronic surfaces

Consider a general Hamiltonian of the form

\[
\hat{H} = \begin{pmatrix}
\hat{Q}\hat{H}\hat{Q} & \hat{P}_1\hat{H}\hat{Q} & \hat{P}_2\hat{H}\hat{Q} \\
\hat{Q}\hat{H}\hat{P}_1 & \hat{P}_1\hat{H}\hat{P}_1 & \hat{P}_2\hat{H}\hat{P}_1 \\
\hat{Q}\hat{H}\hat{P}_2 & \hat{P}_1\hat{H}\hat{P}_2 & \hat{P}_2\hat{H}\hat{P}_2
\end{pmatrix}
\]  

(3.1)

where the two \( P \) spaces are denoted by \( P_1 \) and \( P_2 \). The following identities apply,

\[
\hat{P}_T = \hat{P}_1 + \hat{P}_2 
\]  

(3.2)

\[
\hat{P}_T^2 = \hat{P}_T 
\]  

(3.3)

\[
\hat{P}_i^2 = \hat{P}_i 
\]  

(3.4)

\[
\hat{Q}\hat{P} = \hat{P}\hat{Q} = 0 
\]  

(3.5)

\[
\hat{P}_1\hat{P}_2 = \hat{P}_2\hat{P}_1 = 0. 
\]  

(3.6)

The full \( P \) space, represented here by \( P_T \), is not diagonal if there is coupling between the \( P_1 \) and \( P_2 \) space.
The formulation for uncoupled $P$ spaces, where
\[
\hat{P}_1 \hat{H} \hat{P}_2 = \hat{P}_2 \hat{H} \hat{P}_1 = 0,
\] (3.7)
is considered first. In this case, $\hat{P}_T = \hat{P}_1 + \hat{P}_2$ is diagonal in the states $|\beta\rangle$ of $P_T$. The derivation proceeds along the lines of section 1.3. The Hamiltonian is written as
\[
\hat{H} |\gamma\rangle = E_\gamma |\gamma\rangle = \hat{H} \left( \hat{P}_1 + \hat{P}_2 + \hat{Q} \right) |\gamma\rangle.
\] (3.8)

Projecting with $\hat{P}_1$, $\hat{P}_2$ and $\hat{Q}$ gives the following three equations,
\[
\left( E_\gamma - \hat{Q} \hat{H} \hat{Q} \right) \hat{Q} |\gamma\rangle = \hat{Q} \hat{H} \left( \hat{P}_1 + \hat{P}_2 \right) |\gamma\rangle \quad (3.9)
\]
\[
\left( E_\gamma - \hat{P}_1 \hat{H} \hat{P}_1 \right) \hat{P}_1 |\gamma\rangle = \hat{P}_1 \hat{H} \hat{Q} |\gamma\rangle \quad (3.10)
\]
\[
\left( E_\gamma - \hat{P}_2 \hat{H} \hat{P}_2 \right) \hat{P}_2 |\gamma\rangle = \hat{P}_2 \hat{H} \hat{Q} |\gamma\rangle. \quad (3.11)
\]

Inverting eq. 3.10, 3.11 and using eq. 3.9 yields
\[
\left( E_\gamma - \hat{Q} \hat{H} \hat{Q} \right) \hat{Q} |\gamma\rangle = \hat{Q} \hat{H} \hat{P}_1 \left( E_\gamma - \hat{P}_1 \hat{H} \hat{P}_1 \right)^{-1} \hat{P}_1 \hat{H} \hat{Q} |\gamma\rangle \quad (3.12)
\]
\[
+ \hat{Q} \hat{H} \hat{P}_2 \left( E_\gamma - \hat{P}_2 \hat{H} \hat{P}_2 \right)^{-1} \hat{P}_2 \hat{H} \hat{Q} |\gamma\rangle,
\]
the eigenvalue equation for $\hat{Q} |\gamma\rangle$ under the influence of $P_1$ and $P_2$. The result is almost identical to the effective Hamiltonian of the standard QP (eq. 1.28) but with two sets of bins and two sets of coupling matrices. This is easily calculated by the QP algorithm: it is entirely equivalent to the standard QP problem, but with more bins.

For coupled $P$ spaces, the situation is more complicated. First, it is assumed that the bottom $2 \times 2$ block of the Hamiltonian matrix can be diagonalized. Then, let $U$ be the
unitary diagonalization matrix, such that

\[
\hat{U}^\dagger \begin{pmatrix}
\hat{P}_1 \hat{H} \hat{P}_1 & \hat{P}_2 \hat{H} \hat{P}_2 \\
\hat{P}_1 \hat{H} \hat{P}_2 & \hat{P}_2 \hat{H} \hat{P}_2 
\end{pmatrix} \hat{U} = \begin{pmatrix}
\hat{P} \hat{H} \hat{P} & 0 \\
0 & \hat{P} \hat{H} \hat{P}
\end{pmatrix}
\]

(3.13)

If this is done, the QP algorithm can diagonalize the full matrix. However, the ability to distinguish between the \( P_1 \) and \( P_2 \) spaces is now lost. Further, time propagations require the evaluation of

\[
\langle \Psi(t) | \hat{P}_i | \Psi(t) \rangle = \langle \Psi | \sum_{\gamma, \gamma'} |\gamma\rangle \langle \gamma | \hat{P}_i | \gamma' \rangle \langle \gamma' | \Psi \rangle \ e^{-i(E_{\gamma'} - E_{\gamma}) t / \hbar}.
\]

(3.14)

This requires all the matrix elements of \( \hat{P}_i \) in the eigenbasis |\( \gamma \rangle \). They can be calculated by using the equation for the \( P \) part of a state |\( \gamma \rangle \), introduced in the introduction (eq. 1.27) and reproduced here,

\[
\hat{P} |\gamma\rangle = \left( E_{\gamma} - \hat{P} \hat{H} \hat{P} \right)^{-1} \hat{P} \hat{H} \hat{Q} |\gamma\rangle.
\]

(3.15)

The matrix elements of \( \hat{P}_i \) are given by

\[
\langle \gamma' | \hat{P}_i | \gamma \rangle = \langle \gamma' | \hat{P}_i \hat{P} | \gamma \rangle
\]

(3.16)

\[
= \langle \gamma' | \hat{Q} \hat{H} \hat{P} \left( E_{\gamma'} - \hat{P} \hat{H} \hat{P} \right)^{-1} \hat{P}_i \left( E_{\gamma'} - \hat{P} \hat{H} \hat{P} \right)^{-1} \hat{P} \hat{H} \hat{Q} |\gamma\rangle
\]

(3.17)

where we have used \( \hat{Q} \hat{P}_i = 0 \) and \( \hat{Q} + \hat{P} = 1 \). If the \( P \) spaces are uncoupled, then \( \hat{P} \hat{P}_i = \hat{P}_i \) and the following is obtained,

\[
\langle \gamma' | \hat{P}_i | \gamma \rangle = \langle \gamma' | \frac{\hat{Q} \hat{H} \hat{P}_i \hat{H} \hat{Q}}{\left( E_{\gamma'} - \hat{P}_i \hat{H} \hat{P}_i \right) \left( E_{\gamma} - \hat{P}_i \hat{H} \hat{P}_i \right)} |\gamma\rangle.
\]

(3.18)

This equation is closely related to the normalization equation (eq. 2.28) for the vectors |\( \gamma \rangle \) and contains the coarse-grained coupling matrix for \( \hat{P}_i \). However, if the \( P \) spaces are
coupled then this expression does not apply. In that case, eq. 3.17 requires calculating elements of the form $\langle \beta | \hat{P} | \beta' \rangle$ where the coupled $P$ eigenstates $| \beta \rangle$ may belong to different bins. We are currently formulating a way to compute those matrix elements.

### 3.2 Diagonalizing the benzene radical cation

In their paper on the dynamics of the benzene radical cation\(^{48}\), Köppel and coworkers simulated a reduced dimensionality system composed of eight normal modes and five electronic states, the benzene $\tilde{X} - \tilde{B} - \tilde{C}$ electronic manifold. The Hamiltonian is reproduced here for clarity,

$$\hat{H} = \hat{T}_0 + \hat{H}_0 + E + \hat{H}_1$$

\[\hat{H}_1 = \begin{pmatrix}
\sum_{i=1}^{2} \kappa_{\tilde{X}} Q_i + \sum_{i=1}^{18} \lambda_{\tilde{X}} Q_{mx} & \sum_{i=1}^{18} \lambda_{\tilde{X}} Q_{my} & 0 & \sum_{i=1}^{2} \lambda_{\tilde{B}} Q_i & 0 \\
\sum_{i=1}^{18} \lambda_{\tilde{X}} Q_{mx} & \sum_{i=1}^{2} \kappa_{\tilde{X}} Q_i - \sum_{i=1}^{18} \lambda_{\tilde{X}} Q_{mx} & -\sum_{i=1}^{2} \lambda_{\tilde{B}} Q_j & \sum_{i=1}^{18} \lambda_{\tilde{B}} Q_{mx} & 0 \\
0 & \sum_{i=1}^{2} \kappa_{\tilde{B}} Q_i + \sum_{i=1}^{18} \lambda_{\tilde{B}} Q_{mx} & \sum_{i=1}^{2} \kappa_{\tilde{B}} Q_i & \sum_{i=1}^{20} \lambda_{\tilde{C}} Q_{nx} & 0 \\
\sum_{i=1}^{2} \lambda_{\tilde{X}} Q_{my} & 0 & \sum_{i=1}^{20} \lambda_{\tilde{C}} Q_{nx} & \sum_{i=1}^{2} \kappa_{\tilde{C}} Q_i & 0 \\
0 & 0 & 0 & \sum_{i=1}^{20} \lambda_{\tilde{C}} Q_{nx} & \sum_{i=1}^{2} \kappa_{\tilde{C}} Q_i
\end{pmatrix}\]

where $\hat{T}_0$ and $\hat{H}_0$ are the harmonic contributions to the Hamiltonian and $\hat{E}$ the energy offsets for the states. Additionally, note that, following Köppel et al.,\(^{48}\) modes $\nu_7$ and $\nu_8$ can be merged to make an effective mode $\nu_{\text{eff}}$, and the modes $\nu_{15}$ and $\nu_{17}$ are dropped as they were shown to have only a negligible effect on the dynamics.

For this demonstration of the QP program, electronic and vibrational degeneracies are neglected. Köppel et al. showed that this is qualitatively correct and that the behavior observed is the same. We are considering doing the full calculation, which we believe is possible.

In this section, the QP program was used to diagonalize the benzene radical cation Hamiltonian presented above. Both the coupled $P$ problem involving an excitation to the $\tilde{C}$ surface and the uncoupled $P$ problem where the excitation is to the $\tilde{B}$ surface
Table 3.1: The decomposition used for solving the benzene radical cation with excitation to the $\tilde{B}$ surface. The total dimensions of the $P$ spaces for $\tilde{X}$ and $\tilde{C}$ are $1.3 \times 10^{13}$ and $6.6 \times 10^{11}$ states, respectively.

3.2.1 Excitation to the $\tilde{B}$ surfaces

Solving the Hamiltonian with $\tilde{B}$ as the $Q$ space is an uncoupled $P$ problem. The Hamiltonian was parametrized at low order: there is no coupling between the modes. As such, it is perfectly suited to the QP algorithm, due to the product form of the eigenstates.

The total Hamiltonian is broken down into four conveniently sized component bases. The breakdown is shown in table 3.1. The small number of modes in each component makes for a swift construction of the product Hamiltonian, requiring seconds on the same machine used with pyrazine in sec. 2.4. To get an overlap of 99% with the Franck-Condon wavepacket required 80 $Q$ states and 2400 bins were used to account properly for both $P$ spaces. This required a run time of five hours. The results are presented in fig. 3.1.

The population curves are well reproduced by the QP program. The noisy nature of the population curves and the spectrum is due to the neglect of vibrational and electronic degeneracies. Quantitative agreement is expected from solving the full system.
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Figure 3.1: Spectrum and populations after an excitation to the $\tilde{B}$ of the benzene radical cation. The $\tilde{C}$ surface, being at a higher energy than the $\tilde{B}$ surface is barely populated and contributes very little to the time dependence. These figures should be compared to figures 6 (a) and 7 (a) of reference 48. The agreement is qualitative, due to the neglect of degeneracies.
3.2.2 Excitation to the \( \tilde{\mathcal{C}} \) surface

Doing the \( \tilde{\mathcal{C}} \) surface introduces an additional complication. The two \( P \) spaces, which are coupled, need to be diagonalized prior to solving with the QP algorithm. This is, in general, a hard problem as having a small \( Q \) space coupled to a large \( P \) space cannot be relied on; the whole diagonalization must be done directly.

Although this system has significantly fewer degrees of freedom than pyrazine, solving the coupled \( P \) Hamiltonian is still computationally intractable, as the number of states required far exceeds the computer memory available. However, an approach similar to what was done for the \( \tilde{\mathcal{B}} \) surface can be applied, and the Hamiltonian can be solved in pieces.

The vibrational modes are split in two groups: modes whose potential energy surfaces depend on the electronic state (\( \nu_{16} \) and \( \nu_{18} \) and the coupling mode \( \nu_{\text{eff}} \)) and modes whose potential surfaces are the same for all the electronic states. This allows building a product basis of the form

\[
|\eta_1\rangle = |\nu_{16}\rangle |\nu_{18}\rangle |\nu_{\text{eff}}\rangle |\text{el}\rangle \tag{3.20}
\]

\[
|\eta_2\rangle = |\nu_2\rangle |\nu_{19}\rangle |\nu_{20}\rangle \tag{3.21}
\]

This is a six degrees of freedom problem and the decomposition used is presented in table 3.2.

The \( \tilde{\mathcal{C}} \) surface of the benzene radical cation is very close to the Franck-Condon point, requiring a small number of \( Q \) states for a full overlap with the Franck-Condon wavepacket. We used 11 \( Q \) states, yielding an overlap of 99%, and 2000 bins spanning a region of size 3.5 eV. Building the product Hamiltonian required approximately forty

\[ a \]

In their analysis, Köppel et al solved the Hamiltonian with only 5 degrees of freedom to obtain a line spectrum. Even this required secular matrices of dimension \( \approx 10^7 \).
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<table>
<thead>
<tr>
<th>Modes of vibration</th>
<th>Basis dimension</th>
<th>X - B</th>
<th>Ĉ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{16}, \nu_{18}, \nu_{\text{eff}}$</td>
<td>11869</td>
<td>440</td>
<td></td>
</tr>
<tr>
<td>$\nu_2, \nu_{19}, \nu_{20}$</td>
<td>7661</td>
<td>901</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: The decomposition used for an excitation to the Ĉ surface. The total dimension of the $P$ space is $9.0 \times 10^7$ states.

minutes. Solving the QP problem required another forty minutes. The results are presented in fig. 3.2. The population of the Ĉ state decays in a similar manner to the MCTDH simulation, albeit to a greater extent: the population curve of reference 48 never quite reaches zero and hovers at around 5%. We attribute this to the addition, in our simulation of mode, $\nu_{20}$, a coupling mode dropped in the MCTDH simulation. The spectrum has more structure, which is attributed to the neglect of degeneracies, leading to a smaller $Q$ space and a low density of interacting states in $P$.

3.3 Concluding remarks

In this chapter we have demonstrated an extension the QP algorithm that allows treating multiple electronic surfaces. This serve as both a confirmation of the power of the program and as a door toward extending overlapping resonances coherent control to competitive processes.

We are currently looking for additional systems that can be amenable to this approach, especially for coherent control. However, the uncoupled condition on the $P$ spaces makes the range of applicable, interesting systems rather limited. Hence, we are also extending this work by developing a methodology to extract the populations of coupled $P$ spaces from the coarse-grained QP results.

We are also looking into ways of solving the full benzene radical cation Hamiltonian, with electronic and vibrational degeneracies. As the number of modes would be quite
Figure 3.2: Spectrum and population after an excitation to the $\tilde{C}$ of the benzene radical cation. The QP algorithm does not allow us at the present to distinguish between the coupled electronic states that form the $P$ space. They qualitatively agree with figures 3 (b) and 4 (a) of reference 48.
a bit larger, this would be a challenge. However, we believe this is possible on a larger cluster using sparse methods\textsuperscript{40} and a product decomposition of the Hamiltonians.
Chapter 4

Toward a time dependent view of resonances

The resonance approach to non-adiabatic problems has been very useful\textsuperscript{8,49} and provides a intuitive scheme for thinking about radiationless transitions and their control. However, resonances supply an inherently time independent perspective. Processes involving conical intersections can also be analyzed from a time dependent viewpoint, involving concepts like transition rates and population transfer. In this chapter, we describe the work we have begun to understand the relationship between control and overlapping resonances viewed from time dependent and time independent perspectives. We note in advance that this work is still in progress, with the initial steps presented here.

The alternate, more popular, approach to a resonance view of intramolecular processes is wavepacket propagation. Numerous propagation methods are available both for computed potential energy surfaces\textsuperscript{12} and for potentials computed on the fly.\textsuperscript{50} On-the-fly methods are especially popular as they avoid the hard process of fitting potential energy surfaces, which is computationally expensive.\textsuperscript{51} These techniques are inherently time dependent: a new set of initial conditions require recalculating the entire propagation, which can take a fairly long time.
The theory of semiclassical wavepackets with respect to conical intersections has been the subject of numerous studies.\textsuperscript{52,53} The semiclassical approximation requires a fairly localized wavepacket, moving in a ballistic way.\textsuperscript{38} However, the zeroth-order states of coherent control are a completely different entity. The zeroth-order states are often broad and possess considerable structure. Being eigenstates of their own electronic surface, they are unmoving before they start decaying. Theses states have very little in common with semiclassical wavepackets. As such, traditional approaches, using for example Landau-Zener transition rates\textsuperscript{52}, are useless in describing the decay of the wavefunctions of interest.

The time-independent formulation of overlapping resonances coherent control has one major problem: although the resonances can show whether a set of states is controllable, they offer no help in providing a physical picture on how this control relates to the features of the potential energy surface encountered during time evolution.

Through the past year, I have worked toward a time dependent perspective on overlapping resonances coherent control. It is hoped that such a theory could consolidate the wavepacket and resonance views of non-radiative processes. This work is still far from complete but this chapter will present some interesting, early results.

In this chapter, we describe the current efforts made toward developing a such a theory. Using a simple two-dimensional linear vibronic model, the decay of resonance states under the influence of a conical intersection and coherent control is explored.

### 4.1 Resonances and wavepackets

The evolution of Gaussian wavepackets in simple models with vibronic coupling is well studied.\textsuperscript{53,54} The evolution of eigenstates of one of the diabats is not. We are aware of only a few studies related to this work. Although Nikitin et al. demonstrated the evolution of
Table 4.1: Parameters used in the two dimensional pyrazine model, from Sukharev and Seideman.\textsuperscript{44} This model has a conical intersection at \((-4, 0)\) and the \(Q\) surface is centered at \((-2, 0)\). The mode denoted \(x\) is the tuning mode and the mode denoted \(y\) is the coupling mode. These correspond to the \(x\) and \(y\) axes of figures 2.3, 4.1 and 4.2.

The eigenstates\textsuperscript{55}, most of the research was done on time-independent quantities.\textsuperscript{56–60} All used continuum systems, which differ notably from the intramolecular processes of interest. Most significantly, continua break time-reversal invariance\textsuperscript{18} and show exponential decays, not seen in systems of bound states.

To understand the time dependence of overlapping resonances coherent control, we examined the evolution of resonance wavepackets in a simplified two dimensional pyrazine model.\textsuperscript{44} This model consists of two electronic surfaces, modeled as two dimensional harmonic oscillators, coupled through a simple linear coupling. The Hamiltonian for surface \(i\) is given by

\[
\langle i | \hat{H} | i \rangle = E_i + \frac{\omega_x}{2} \left( -\frac{d^2}{dx^2} + x^2 \right) + \kappa_x^{(i)} x + \frac{\omega_y}{2} \left( -\frac{d^2}{dy^2} + y^2 \right) \tag{4.1}
\]

where \(\omega_x, \omega_y\) are the harmonic frequencies of each mode, \(\kappa_x^{(i)}\) is a displacement\textsuperscript{a} of the surface along the tuning mode \(x\) and the ket \(|i\rangle\) selects the \(i\)-th electronic surface. The coupling mode \(y\) couples the two surfaces linearly,

\[
\langle 1 | \hat{H} | 2 \rangle = \langle 2 | \hat{H} | 1 \rangle = \lambda y. \tag{4.2}
\]

This is a linear vibronic model with no rotation, the simplest model of a conical intersection. The parameters used are shown in table 4.1.

Zeroth-order states are generally complicated wavepackets, with nodes and structure.\textsuperscript{a} The \(x\) potential can written as \((x + \kappa_x^{(i)}/2)^2 = x^2 + \kappa_x^{(i)} x + C\) which explains why \(\kappa_x^{(i)}\) is a displacement. The constant energy shift is absorbed in \(E_i\).
Figure 4.1: Two zeroth-order states with a high degree of overlap and optimized superpositions at times 0, 8, 16, 24 and 32 fs. The optimization time is 24 fs. The phase difference and probability amplitudes of the two rightmost states were selected to maximize and minimize decay, respectively. Note the spreading away from the conical intersection at $(-4, 0)$.
Figure 4.1 shows the evolution of two such states and two superpositions. The superpositions were phase controlled for maximal and minimal decay using their high degree of overlap. These two states, highly excited in the tuning mode and lowly excited in the coupling mode, were chosen as a typical example of resonances with high overlap strongly controllable at relatively long times (25 fs).

The Franck-Condon excitation in fig. 2.3 and the zeroth-order states in fig. 4.1 show very different behaviors and should be compared. It should be noted that those states are eigenstates of the upper potential energy surface. As such, if the lower surface was not included, they would be independent of time. Hence, all the time dependence comes from the coupling with the lower surface. The spreading away from the conical intersection, situated at \((-4, 0)\), seen in fig. 4.1 is a general feature of the zeroth-order states. Although the fast decaying controlled state shown there has a higher spatial overlap with the conical intersection region than the slowly decaying superposition, the vast majority of states with weaker control do not exhibit this behavior. Hence, spatial overlap with the conical intersection does not offer a direct route to understanding coherent control via overlapping resonances.

To explore the effect of the phase in control scenarios, the quantum probability current of phase controllable superpositions was also examined. The quantum probability current gives a measure of the velocity of the probability distribution at all points. The quantum probability current is given by

\[
J(r, t) = \frac{\hbar}{2m} \left( \psi^*(r, t) \nabla \psi(r, t) - \psi(r, t) \nabla \psi^*(r, t) \right).
\]  

Note that the probability current is zero if \(\psi(r, t)\) is real everywhere. The \(Q\) eigenstates obey time-reversal invariance and can therefore be made real everywhere,\(^{18}\) guaranteeing that any single \(Q\) eigenstate will have \(J(r, t) = 0\) at time \(t = 0\). However, this is not the
case for superpositions of the form

$$\psi(r, t) = \phi_1(r, t) + e^{i\phi} \phi_2(r, t)$$  \hspace{1cm} (4.4)$$

where the phase $\phi$ imposes a probability current at the points $r$ where $\phi_1(r, t) \neq \phi_2(r, t)$. This relationship between phase and current motivates the use of the probability current to probe phase control. In particular, the velocity field might allow us to formulate a generalized Landau-Zener formula for the decay of controlled superpositions.

In fig. 4.2, the probability current at time $t = 0$ for three optimized pairs of eigenstates of $Q$ with varying magnitudes of phase control, as given by the control metric $f_{\kappa, \kappa'}$ from sec. 1.4, is shown. Strongly controllable states show strong directed motion toward or away from the conical intersection. In states where the control is weaker, there is directed motion in the vicinity of the conical intersection, but not globally.

We explored the probability current with dozens of pairs in the model and found qualitative agreement between the strength of the control $f_{\kappa, \kappa'}$ and the ability for directed motion. We are currently looking for ways to model this relationship mathematically. We believe there is a relation between the velocity at the conical intersection of a controlled superposition and the rate of decay (for a given coupling strength), similar to a Landau-Zener transition. However, the peculiar nature of the zeroth-order states makes the derivation of a transition rate much harder than in corresponding semiclassical systems.\(^{52}\)

\section*{4.2 Concluding remarks}

We have opened a new line of inquiry concerning the decay of resonance states mediated by a conical intersection in systems of bound states. We have proposed an explanation for the coherent control of overlapping zeroth-order states, based on the creation of directed probability current in wavepackets through the influence of phase.
Figure 4.2: Vector plot of the quantum probability current at $t = 0$ for three pairs of eigenstates of $Q$ with no phase control ($f_{61,103} = 0$) and weak ($f_{48,57} = 0.05$) or strong ($f_{40,48} = 0.15$) phase control. The top row are states optimized for minimum decay and the bottom row are states optimized for maximum decay. Coherent control leads to controllable probability current near the conical intersection at $(-4,0)$. 

(a) No control 
(b) Weak control 
(c) Strong control
Although interesting, this qualitative approach still lacks a firm mathematical foundation. This is a main topic of current work and we are investigating possible relationships to similar work done in quantum chaos\textsuperscript{61,62} and the theory of the geometric phase.\textsuperscript{24} Additionally, we are interested in perturbative approaches in the time-dependent $Q$ population operator,

\begin{equation}
\hat{Q}(t) = e^{-i\hat{H}t/\hbar} \hat{Q} e^{i\hat{H}t/\hbar}.
\end{equation}

We believe that such an approach might uncover the influence of the conical intersection on the decay of the $Q$ eigenstates.
Chapter 5

Conclusion

QP partitioning is a useful technique for solving and analyzing intramolecular problems. In this work, we have presented a new implementation of the QP algorithm and extended the treatment to Hamiltonians with multiple partitions. We applied it to the benzene radical cation, were three electronic surfaces were included. Finally, the QP partitioning was used to learn more about the time dependence of zeroth-order states.

The QP algorithm is a highly efficient method to solve molecular problems of realistic dimensions. However, even the behavior of simple models is not well understood. The time evolution of zeroth-order states in low dimensionality models needs to be fully understood in order to gain insight into the wavepacket dynamics. Approaches include perturbative expansions and using the probability current to devise a theory based on the time-of-arrival at the conical intersection.

The coherent control of competitive intramolecular processes is also to be explored. The resonances of a surface with multiple interacting other surfaces will show the contribution from each of the interacting surfaces. Of interest is whether two resonances in $Q$ can overlap with respect to one $P$ space and be non-overlapping with respect to the
other. This would allow for directed control to either $P$ surfaces by optimizing for long or short decay times in the overlapping $P$ space.

The QP program is also uniquely suited for calculations including quantum radiation, for example in induced transparency.\textsuperscript{49} Using a $Q$ subspace consisting of states of matter and vacuum states of the radiation field, coupled to a $P$ space containing number states of the field would permit treating radiation processes directly. The radiation $P$ space could be bound, for cavity QED problems, or continuous, as in the overlapping resonances treatment of Frishman and Shapiro.\textsuperscript{8}

Finally, we want to extend the QP program to treat radically different problems where partitioning is useful, for instance in energy transfer processes.\textsuperscript{63} This would require a very different partitioning, akin to what was used for internal vibrational redistribution.\textsuperscript{37} However, such problems could still be treated within the QP framework.
Bibliography


