TOPLOGICAL ORIGINS OF BOUND STATES IN THE CONTINUUM FOR SYSTEMS WITH CONICAL INTERSECTIONS

by

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Abstract

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Bound states in the continuum (BSCs) were reported in a linear vibronic coupling model with a conical intersection [Cederbaum et al. Phys. Rev. Lett. 2003, 90, 013001]. It was also found that these states are destroyed within the Born-Oppenheimer approximation. We investigate whether a nontrivial topological or geometric phase associated with the conical intersection is responsible for BSCs. To address this question we explore modifications of the original 2D two-state linear vibronic coupling model supporting BSCs. These modifications either add geometric phase effects after the Born-Oppenheimer approximation or remove the geometric phase within a two-state problem. Using the stabilization graph technique we have shown that the geometric phase is crucial for emergence of BSCs.
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Chapter 1

Introduction

A normalizable ($L^2$-integrable) eigenstate of the system Hamiltonian that has no interaction with the continuum states is said to be localized and is called a bound state. The first to discover potentials that support these bound states with energies embedded in the continuum were von Neumann and Wigner.\[34\] An example can be seen in Fig. 1.1.\[8\] Experimentalists as well as theoreticians have observed systems with these von Neumann-Wigner potentials.\[3, 5, 30\] Bound states in the continuum (BSCs) have spurred a lot of enthusiasm across physical sciences, because they can be found in photonic crystal slabs,\[29\] patterned dielectric slabs,\[11\] and produce lasing action from BSCs cavities.\[14\] It was suggested that semiconductor superlattices can support BSCs.\[10, 31\]

Figure 1.1: A von Neumann-Wigner potential supporting bound states in the continuum.\[8\]
BSCs are attractive due to their minimal dissipation of energy, allowing for promising applications involving light-matter interaction. The dissipation is tunable by changing certain parameters in the system exploited in on-chip photonics. BSCs are responsible for efficient light transfer, useful in optical devices. They also generate high order vector beams that can be implemented in optical imaging, optical trapping, and laser machining.

We will consider BSCs in the context of the molecular problem. In 2003, Cederbaum et al. found a potential in the diabatic representation, left of Fig. 1.2, that supports a bound state embedded in the continuum using a model with coupled electronic states. Switching to the adiabatic representation reveals a conical intersection (CI) that introduces a phase factor, called geometric phase (GP). Applying the Born-Oppenheimer approximation (BOA) only the lower state is considered and the state becomes a state that has interaction with the continuum and a finite lifetime, known as a resonance state. A resonance state is not a physically realizable state, but its energy is of value.

![Figure 1.2: The diabatic (left) and BOA (right) potentials (solid curves) calculated by Cederbaum et al. [4], with the bound and resonance state densities (dashed curves), respectively.](image)

This particular potential is the simplest model for nonadiabatic dissociation reactions and similar potentials can be found in the excited states of phenol, as seen in Fig. 1.3. The tunnelling dynamics in the photodissociation of phenol were studied both experimentally and theoretically. The theory agrees with the experiments only if GP is included. The phenol potential does not have BSCs, however, the inclusion of GP tremendously slows down the tunnelling but it never stops completely.

It has been previously shown that GP causes localization into one well of a 2D double-well problem. A cross section of that potential can be seen in Fig. 1.4. If that second well was changed to an unbound potential, would GP have the same effect? This potential describes the model used
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by Cederbaum *et al.* [4] and will be used to explore the change in state behaviour in the different representations. The main focus will be on the role of GP. Along the way, we will address questions such as how to find a resonance state, how GP is introduced into our model, and why the density of states is important when referring to resonance states.

This thesis continues in the following order. Chapter 2 gives the background related to the problem in question. Chapter 3 describes the different models and the approach for the determination of state behaviour. Chapter 4 discusses the results, as well as demonstrates the decay of the resonance phenomenon. Chapter 5 sums up the work.

Figure 1.3: 1D potentials for the photodissociation of phenol. [41]

Figure 1.4: A cross section of the double-well potential (black) with probability density of the bound state (dashed blue).
Chapter 2

Theory

2.1 Bound States

Observable quantities are associated with the eigenvalues of a quantum mechanical operator that has a discrete or continuous spectrum. An example of a potential for a Hamiltonian with a discrete spectrum is the harmonic oscillator potential, Fig. 2.1, where the eigenstates are bound states. This means the probability density is localized inside the potential, and decreases outside, eventually reaching zero. The momentum operator is an example of observables whose spectrum is continuous. Eigenfunctions corresponding to states of a discrete spectrum are normalizable, and generally eigenfunctions in a continuous spectrum are not normalizable, and are therefore not physically realizable states. The word “generally” is used here because there can exist normalizable bound states that are embedded in a continuum.

![Figure 2.1: Harmonic oscillator potential (black) with probability densities of the bound states (blue).](image)
The hydrogen molecule is an example of a system where both bound and unbound (continuum) eigenstates exist, Fig. 2.2. Low energy BO nuclear states for the ground electronic potential are bound and nuclear BO states with energy higher than dissociation energy are unbound (continuum). If we consider energies below the dissociation energy (zero in this case), in the ground electronic state the spectrum is discrete with bound nuclear states. The triplet excited electronic state of hydrogen (red) is unbound, decaying to zero as the two H atoms are separated. This unbound potential supports a continuum. In this example, bound states and unbound states are separate in energy.

![Figure 2.2: The ground (blue) and excited (red) electronic states of the hydrogen molecule. The ground electronic state has a discrete spectrum below the dissociation energy (0 a.u. in this case) whereas the excited electronic state has a continuous spectrum. The probability density of the nuclear wavefunctions (dashed black) is given for the discrete and continuous parts of the spectrum.](image)

### 2.2 Resonance States

In Hermitian quantum mechanics, a resonance can be seen as a phenomenon associated with a collection of eigenstates for the system, called a wavepacket.[21] The largest contributors to the resonance wavepacket are states having localization in the interaction region with a tail outside not having $L^2$-integrability, called resonance states. Because of the superposition of eigenstates and the existence of these eigenstates beyond the interaction region, the resonance wavepacket decays in the interaction region over time. This resonance behaviour will be demonstrated in this section using the Hermitian and non-Hermitian formalism. We will start with the time-independent Schrödinger equation defined as
Chapter 2. Theory

follows

$$H |\phi_n\rangle = E_n |\phi_n\rangle$$  \hspace{1cm} (2.1)$$

where \(\{|\phi_n\rangle\}_{n=1}^{\infty}\) form a complete orthonormal set and \(H\) is the system Hamiltonian that has unbound (continuum) states. The stationary states of the time-dependent Schrödinger equation are

$$|\phi_n(t)\rangle = e^{-iE_n t} |\phi_n\rangle.$$  \hspace{1cm} (2.2)$$

A non-stationary solution can be constructed by a linear combination of stationary states. From this definition of non-stationary states, the resonance wavepacket is a non-stationary solution in the Hermitian formalism. Let \(|\Psi(0)\rangle\) be some initial state prepared in the interaction region that is not an eigenstate of \(H\). Since \(\{|\phi_n\rangle\}_{n=1}^{\infty}\) is a complete set, any state can be written as a linear combination of the eigenstates. Applying the resolution of identity to the initial state, we get

$$|\Psi(0)\rangle = \int dn |\phi_n\rangle \langle \phi_n | \Psi(0) \rangle = \int dn c_n |\phi_n\rangle.$$  \hspace{1cm} (2.3)$$

Here, we took the integral over all \(n\) states, assuming a summation over the discrete states and integration over the continuum states. To look at the dynamics of \(|\Psi(0)\rangle\), the time-dependent wavefunction is given by

$$|\Psi(t)\rangle = e^{-iHt} |\Psi(0)\rangle = \int dn c_n |\phi_n\rangle e^{-iE_n t}.$$  \hspace{1cm} (2.4)$$

The probability of finding \(|\Psi(t)\rangle\) in the initial state is

$$|\langle \Psi(0) | \Psi(t) \rangle|^2 = \left| \int dn c_n^* \int dk c_k \langle \phi_n | \phi_k \rangle e^{-iE_k t} \right|^2 = \left| \int dn |c_n|^2 e^{-iE_n t} \right|^2.$$  \hspace{1cm} (2.5)$$
which is known as the autocorrelation function. For cases where $E_n$’s span a dense manifold of different values, the autocorrelation function decays exponentially,

$$\left| \int dn |c_n|^2 e^{-iE_nt} \right|^2 \sim e^{-\Gamma t}.$$ (2.6)

Clearly, $|\Psi(t)\rangle$ is non-stationary and the probability of finding the particle in the initial state decays with a lifetime inversely proportional to $\Gamma$. This decay is related to the probability density in the interaction region, however, the norm of $|\Psi(t)\rangle$ is conserved because we are using the formalism of Hermitian quantum mechanics.

It is difficult to practically obtain the decay because the expansion in Eq. 2.4 has an infinite number of terms that do not have an analytical form. One can evolve the state explicitly using the split operator method [7] without the expansion over eigenstates, but the dynamics can be quite time consuming. There are other methods based on scattering theory to estimate the energy and lifetime without a time-dependent approach. The Scattering matrix (S-matrix) is a transformation from incoming to outgoing wavefunctions for a particular potential. These wavefunctions are free particle states, giving rise to transmission and reflection coefficients. The S-matrix is constructed from the transmission and reflection coefficients.[32] Poles of the S-matrix appear when the amplitude of the incoming wave vanishes. These poles, if imaginary, give the energies and lifetimes of the resonance wavepacket $E^{\text{res}}_\alpha = E_\alpha - i/2\Gamma_\alpha$. The lifetime is inversely proportional to the imaginary component, $\Gamma_\alpha$. This method is challenging because the S-matrix can be rather difficult to construct.[21]

A different approach to describing the resonance wavepacket was developed by creating a fictitious state with complex energy as an eigenstate of the Hamiltonian. One way to embody the resonance wavepacket into an eigenstate with imaginary energy would be by imposing outgoing boundary conditions on the solutions of the time-independent Schrödinger equation.[21] Forcing these outgoing boundary conditions changes the formalism of the problem to the non-Hermitian domain, resulting in the possibility of non-real eigenvalues. These wavefunctions diverge spatially. The complex scaling method was developed such that the resonance states are normalizable eigenstates of the non-Hermitian Hamiltonian.[20]

It is easy to show that the resonance state decays exponentially in the non-Hermitian formalism. Taking the resonance state $|\phi_\alpha\rangle$, that is a solution of the time-independent Schrödinger equation, to be
the initial wavefunction for the time-dependent problem, we end up with

\[ |\phi_\alpha(t)\rangle = e^{-iHt} |\phi_\alpha\rangle = e^{-iE_\alpha t} |\phi_\alpha\rangle = e^{-iE_\alpha t} e^{-\frac{1}{2}\Gamma_\alpha t} |\phi_\alpha\rangle. \]  

(2.7)

This is a non-stationary state because the second exponential is real. The autocorrelation function of \( |\phi_\alpha(t)\rangle \) is

\[ |\langle \phi_\alpha(0)|\phi_\alpha(t)\rangle|^2 = \left|\langle \phi_\alpha(0)|e^{-iE_\alpha t} e^{-\frac{1}{2}\Gamma_\alpha t} \phi_\alpha(0)\rangle\right|^2 = e^{-\Gamma_\alpha t}, \]

(2.8)

clearly showing that this system decays exponentially in time.

The non-Hermitian formalism can be difficult to work with. To stay in the time-independent Hermitian formalism, the stabilization method is used.\[16\] This method takes advantage of the high density of states around the resonance state to extract the energy and lifetime of the resonance state. The density of states near resonance can be constructed directly using the \( S \)-matrix. The construction of the density of states near resonance states is based on the poles of the \( S \)-matrix. This derivation gives

\[ \rho(E) = \frac{1}{\pi} \frac{\Gamma_\alpha/2}{(E - E_\alpha)^2 + \Gamma_\alpha/4}. \]  

(2.9)

In the stabilization method, a stabilization parameter is varied, and the variation in energy is analyzed. This approach will be discussed further in Chapter 3.3.

### 2.3 Born-Oppenheimer Approximation

Several problems in chemical physics require knowledge of the energy spectrum of molecules. The latter can be obtained from the molecular time-independent Schrödinger equation. When describing a chemical system, both the molecular Hamiltonian and the total wavefunction describe the electrons and nuclei. The molecular time-independent Schrödinger equation is given by

\[ H_{\text{mol}} \Psi(r, R) = E \Psi(r, R). \]  

(2.10)
The molecular Hamiltonian is given by

\[ H_{\text{mol}} = T_N + T_e + V_{e-e} + V_{e-N} + V_{N-N} \]  

(2.11)

where \( T_N \) and \( T_e \) are the nuclear and electronic kinetic energy operators. The potential operators are given by \( V_{e-e}, V_{e-N} \) and \( V_{N-N} \), corresponding to the electron-electron repulsion, electron-nucleus attraction, and nucleus-nucleus repulsion. The molecular wavefunction \( \Psi(r, R) \) depends on electronic coordinates \( r \) and nuclear coordinates \( R \). Note that \( r \) and \( R \) are vectors, describing any number of electrons/nuclei. Excluding the kinetic energy of the nuclei in \( H_{\text{mol}} \) results in the electronic Hamiltonian

\[ H_e = T_e + V_{e-e} + V_{e-N} + V_{N-N}. \]  

(2.12)

The electronic Hamiltonian, \( H_e \), depends on the electronic coordinates and parametrically depends on nuclear coordinates. The eigenfunctions of this electronic Hamiltonian are \( \phi_i(r; R) \) such that

\[ H_e \phi_i(r; R) = \epsilon_i(R) \phi_i(r; R) \]  

(2.13)

where \( \epsilon_i(R) \), which form surfaces in the \( R \)-space, are therefore called potential energy surfaces (PESs). The electronic eigenfunctions \( \phi_i(r; R) \) form a complete set in \( r \) for every fixed \( R \). The molecular wavefunction can then be written as a product of electronic \( \phi_i(r; R) \) and nuclear \( \chi_i(R) \) wavefunctions, given by

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

(2.14)

known as the Born-Huang expansion.[2] Applying \( H_{\text{mol}} \) to the Born-Huang expansion, we get

\[ H_{\text{mol}} \Psi(r, R) = (T_N + H_e) \Psi(r, R) \]

\[ = (T_N + H_e) \sum_i \phi_i(r; R) \chi_i(R) \]

\[ = \sum_i T_N \phi_i(r; R) \chi_i(R) + \sum_i \epsilon_i \phi_i(r; R) \chi_i(R). \]  

(2.15)
By multiplying it on the left by $\phi_j^*(r; R)$ and integrating out all electronic coordinates, we obtain

$$\int dr \phi_j^*(r; R) H_{\text{mol}} \psi(r, R) = \int dr \phi_j^*(r; R) \sum_i \left( T_N \phi_i(r; R) \chi_i(R) + \epsilon_i \phi_i(r; R) \chi_i(R) \right)$$

$$= \sum_i \int dr \phi_j^*(r; R) T_N \phi_i(r; R) \chi_i(R) + \sum_i \delta_{ji} \epsilon_i \chi_i(R). \quad (2.16)$$

The kinetic energy operator for the nuclei is given in atomic units and working in mass-weighted Cartesian nuclear coordinates by $T_N = -\frac{1}{2} \nabla_R^2$. Since the electronic wavefunctions are parametrically dependent on nuclear degrees of freedom, the action of the nuclear kinetic energy operator on them yields

$$\sum_i \int dr \phi_j^*(r; R) T_N \phi_i(r; R) \chi_i(R) = -\frac{1}{2} \sum_i \int dr \phi_j^*(r; R) \nabla_R^2 (\phi_i(r; R) \chi_i(R))$$

$$= -\frac{1}{2} \sum_i \left[ \int dr \phi_j^*(r; R) \phi_i(r; R) \nabla_R^2 \chi_i(R) \right.$$

$$+ 2 \int dr \phi_j^*(r; R) \nabla_R \phi_i(r; R) \nabla_R \chi_i(R)$$

$$+ \left. \int dr \phi_j^*(r; R) \nabla_R^2 \phi_i(r; R) \chi_i(R) \right]. \quad (2.17)$$

This is known as the adiabatic representation. In the last two terms, derivatives are performed on the electronic wavefunction with respect to nuclear coordinates. The last summation is known as the diagonal Born-Oppenheimer correction (DBOC) terms, and the second summation is the nonadiabatic couplings (NACs). The BOA presumes these terms to be negligible and Eq. 2.16 then becomes

$$\int dr \phi_j^*(r; R) H_{\text{mol}} \psi(r, R) \approx \sum_i \left( -\frac{1}{2} \int dr \phi_j^*(r; R) \phi_i(r; R) \nabla_R^2 \chi_i(R) + \delta_{ji} \epsilon_i \chi_i(R) \right)$$

$$= \sum_i \left( -\frac{1}{2} \delta_{ji} \nabla_R^2 \chi_i(R) + \delta_{ji} \epsilon_i \chi_i(R) \right)$$

$$= (T_N + \epsilon_j) \chi_j(R). \quad (2.18)$$

From Eqs. 2.10 and 2.18

$$\sum_i \int dr \phi_j^*(r; R) E \phi_i(r; R) \chi_i(R) = (T_N + \epsilon_j) \chi_j(R) \quad (2.19)$$

$$E \chi_j(r; R) = (T_N + \epsilon_j) \chi_j(R).$$
There are limitations to the BOA. By taking the derivative with respect to nuclear coordinates of \( \int dr \phi_j^* (r; R) H \phi_i (r; R) \) we end up with

\[
\int dr \phi_j^* (r; R) \nabla_R \phi_i (r; R) = \frac{\int dr \phi_j^* (r; R) \nabla_R H \phi_i (r; R)}{\epsilon_i (R) - \epsilon_j (R)}.
\] (2.20)

As \( \epsilon_i (R) \) and \( \epsilon_j (R) \) get close in energy, the derivative coupling increases significantly. When they are equal, the BOA breaks down. The derivative coupling terms are found in the NACs and can be difficult to calculate. To avoid these terms, a different representation of the electronic wavefunctions can be used.

### 2.4 Diabatic and Adiabatic Representations

In the adiabatic representation, electronic states parametrically depend on the nuclei. As a result, we get NACs and DBOC terms, which couple the PES formed from \( \epsilon_i (R) \)'s to one another. What we want to do is change the basis of our electronic states such that the NACs and DBOC do not appear. These states can be obtained from the adiabatic states by a unitary rotation that zeros the NACs and DBOC. These new states are called diabatic states. Such a rotation cannot be done in general (one can only try to minimize NACs) for a finite number of electronic states involved in the rotation.[19] The diabatic states cannot be obtained from the adiabatic representation exactly, however the opposite is possible. This is why we will start with the diabatic representation.

The diabatic representation of a Hamiltonian with two electronic states has the following form:

\[
H_{\text{dia}} = \begin{pmatrix} T_N & 0 \\ 0 & T_N \end{pmatrix} + \begin{pmatrix} V_{11} & V_{12} \\ V_{12} & V_{22} \end{pmatrix}.
\] (2.21)

Here \( V_{11} \) and \( V_{22} \) are diabatic potentials coupled by \( V_{12} \). Notice that the kinetic energy operator matrix is diagonal.

In chemical systems, the electronic states are ordered in terms of energy. These are known as adiabatic states (or BO states) that form PESs. To get to the adiabatic representation, a transformation is applied to the diabatic Hamiltonian using the unitary matrix

\[
U = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix}
\] (2.22)
that diagonalizes the potential matrix $V$. The diagonal form of $V$ is defined as $W$ such that

$$W = U^{-1} V U$$

$$= \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} V_{11} & V_{12} \\ V_{12} & V_{22} \end{pmatrix} \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix}. \quad (2.23)$$

If we concentrate on the matrix elements that go to zero, for example the top right element, we can solve for $\theta$:

$$0 = \sin \theta \cos \theta V_{11} - \sin \theta \cos \theta V_{22} + \cos^2 \theta V_{12} - \sin^2 \theta V_{12}$$

$$0 = \frac{1}{2} \sin(2\theta) (V_{11} - V_{22}) + \cos(2\theta) V_{12}$$

$$\tan(2\theta) = \frac{2V_{12}}{V_{22} - V_{11}}$$

$$\theta = \frac{1}{2} \arctan \left( \frac{2V_{12}}{V_{22} - V_{11}} \right),$$

where $\theta$ goes from $0$ to $\pi$ since $\arctan \left( \frac{2V_{12}}{V_{22} - V_{11}} \right)$ goes from $0$ to $2\pi$.

The eigenvalues of $V$ are the electronic states that make the PESs. With a two state model, there is an upper state $W_+$ and a lower state $W_-$:

$$W = \begin{pmatrix} W_- & 0 \\ 0 & W_+ \end{pmatrix} \quad (2.25)$$

where

$$W_\pm = \frac{1}{2} (V_{11} + V_{22}) \pm \frac{1}{2} \sqrt{(V_{11} - V_{22})^2 + 4V_{12}^2}. \quad (2.26)$$

Applying the unitary transformation to $H_{\text{dia}}$, the result is

$$H_{\text{dia}} = \begin{pmatrix} T_N + \tau_{11} & \tau_{12} \\ \tau_{21} & T_N + \tau_{22} \end{pmatrix} + \begin{pmatrix} W_- & 0 \\ 0 & W_+ \end{pmatrix}, \quad (2.27)$$

where

$$\tau_{11} = \tau_{22} = \frac{1}{2} (\nabla R \theta)^2$$

$$\tau_{12} = -\tau_{21} = \frac{1}{2} \nabla^2 R \theta + \nabla R \theta \nabla R. \quad (2.28)$$
These $\tau_{ij}$ are the NACs and the $\tau_{ii}$ terms are the DBOC terms, as seen in Eq. 2.16. Therefore, under the BOA that neglects DBOC and NACs, the Hamiltonian is reduced to

$$H_{BO} = \begin{pmatrix} T_N & 0 \\ 0 & T_N \end{pmatrix} + \begin{pmatrix} W_- & 0 \\ 0 & W_+ \end{pmatrix}. \tag{2.29}$$

Since this matrix is diagonal, individual states can be considered separately.

### 2.5 Conical Intersections

The two adiabatic surfaces, $W_-$ and $W_+$, intersect when

$$\Delta W = W_+ - W_- = \sqrt{(V_{11} - V_{22})^2 + 4V_{12}^2} = 0. \tag{2.30}$$

This happens when both of the following conditions are satisfied:

$$V_{11} - V_{22} = 0$$

$$V_{12} = 0. \tag{2.31}$$

The most common form of intersections is a CI. When the potential energy surfaces get closer and closer, the derivative couplings in Eq. 2.20 get larger, causing the CI to act as a funnel, allowing radiationless transition between adiabatic states. Generally, CIs not only promote transitions between different electronic states but also introduce Berry phase or GP.[1, 15, 18, 28]

### 2.6 Geometric Phase

Rotating the diabatic electronic states to adiabatic states by $U$, we get

$$\begin{pmatrix} \phi_1^{\text{adia}}(r; R) \\ \phi_2^{\text{adia}}(r; R) \end{pmatrix} = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \phi_1^{\text{dia}}(r; R) \\ \phi_2^{\text{dia}}(r; R) \end{pmatrix}$$

$$= \begin{pmatrix} \cos \theta \phi_1^{\text{dia}}(r; R) - \sin \theta \phi_2^{\text{dia}}(r; R) \\ \sin \theta \phi_1^{\text{dia}}(r; R) + \cos \theta \phi_2^{\text{dia}}(r; R) \end{pmatrix}. \tag{2.32}$$
When the electronic wavefunction, which parametrically depends on nuclear coordinates, is transported around a closed path encircling the CI, $\theta$ from Eq. 2.24 goes from 0 to $\pi$. Both adiabatic electronic wavefunctions change sign. The nuclear wavefunction must also change sign in order to keep the total wavefunction single-valued. The total wavefunction must be single-valued in order to have only one probability density. This sign change is from a phase factor, known as GP. It is important to note that GP is ignored in the BOA, but it is implicitly included in the diabatic representation. To avoid the difficulty of working with double-valued wavefunctions, the Mead and Truhlar projection method [18] can be used. This method introduces a phase factor to the BO Hamiltonian that depends on nuclear coordinates, $e^{i\theta(R)}$. This is done as follows:

\[
H_{BO}^{GP} = e^{-i\theta(R)}H_{BO}e^{i\theta(R)}
\]

\[
= \begin{pmatrix}
e^{-i\theta(R)}T Ne^{i\theta(R)} & 0 \\
0 & e^{-i\theta(R)}T Ne^{i\theta(R)}
\end{pmatrix}
+ \begin{pmatrix}
W_{-} & 0 \\
0 & W_{+}
\end{pmatrix}
\]

\[
= \begin{pmatrix}
T_{N} + \tau_{GP} & 0 \\
0 & T_{N} + \tau_{GP}
\end{pmatrix}
+ \begin{pmatrix}
W_{-} & 0 \\
0 & W_{+}
\end{pmatrix}
\]

where

\[
\tau_{GP} = \frac{(\nabla \theta)^{2}}{2} + i\nabla \theta \nabla + \frac{i}{2} \nabla^{2} \theta.
\]

The $H_{BO}^{GP}$ only differs from $H_{BO}$ in the extra $\tau_{GP}$ term. The real part of $\tau_{GP}$ is the same as DBOC. The imaginary part is what allows for the funneling motion, pulling the wavepacket down to a lower energy state through the CI.
Chapter 3

Methods

3.1 Models

The von Neumann-Wigner long-range potentials were the first potentials discovered to have BSCs.[35] Cederbaum et al. were looking for BSCs in situations where the BOA breaks down. This happens at a CI when the denominator of the NACs goes to zero. They explored potentials with two electronic states that contained a CI to analyze how the nonadiabaticity effects this phenomenon. The symmetry of the electronic states plays an important role because of the destructive interference caused by GP. The simple model used by Cederbaum et al. [4] that falls in this new class of potentials was a diabatic 2D two-state Hamiltonian,

\[ H_{\text{dia}} = T_N 1_2 + \begin{pmatrix} V_b & V_{bc} \\ V_{bc} & V_c \end{pmatrix}, \]

(3.1)

where the nuclear kinetic energy operator is \( T_N = -\frac{1}{2}(\omega_x \partial_x^2 + \omega_y \partial_y^2) \). \( V_b \) is the parabolic potential in both \( x \) and \( y \) and \( V_c \) is decaying exponentially in the \( x \) direction, but parabolic in \( y \), Fig. 3.1, given as follows

\[ V_b = \frac{\omega_x}{2} x^2 + \frac{\omega_y}{2} y^2, \]

(3.2)

\[ V_c = \epsilon e^{-\beta(x+\delta)} + \frac{\omega_y}{2} y^2. \]

(3.3)

The coordinates \( x \) and \( y \) can be thought as mass and frequency weighted normal modes. Such a choice of nuclear coordinates is possible for model Hamiltonians where intersecting bound and continuum states have different electronic symmetries.[4] The other parameters were set to \( \omega_x = 0.015, \omega_y = 0.009, \lambda = 0.01, \)
Figure 3.1: The diabatic potential (left) and the BO potential (left) for the 2D two-state Hamiltonian.

Even though all vibrational states of $V_b$ are coupled to the continuum states of $V_c$, it was discovered that the lowest state of the $V_b$ gives rise to a BSC, Fig. 1.2. A simple way to understand this result is to inspect which continuum states can be coupled to the ground state of $V_b$. Due to the linear dependence of $V_{bc}$ and separable $x$ and $y$ components of $V_c$, all such states can be denoted as $(k,1)$, where $k$ is the quantum number along the $x$-direction and 1 is the vibrational quantum along the $y$-direction. Comparing the energy of the $V_b$ ground state, $(\omega_x + \omega_y)/2 = 0.012$, with the lowest energy of the $(k,1)$ manifold, $3\omega_y/2 = 0.0135$, a gap that makes the bound ground state off-resonance from states of the coupled $(k,1)$ continuum becomes evident. This gap lifts the edge of the coupled continuum above the energy of the bound state and thus effectively breaks the state emergence in the continuum.

Transforming the problem to the adiabatic representation gives rise to a CI. Considering that the CI’s energy ($E_{CI} \approx 0.015$) is higher than the energy of the ground state of the $V_b$ potential (0.012), one can conclude that the BOA may be quite adequate at least for this state. It turns out that switching to the BOA destroys the bound state and gives rise to a resonance state, Fig. 1.2. This shows that purely energetic consideration is not accurate in this case and a symmetry is broken when the BOA is introduced.

To investigate the role of the GP we considered the time-independent Schrödinger equation for four Hamiltonians. The original diabatic Hamiltonian $H_{\text{dia}}$ [Eq. (3.1)] is used as a reference that includes all contributions: nonadiabatic transitions and GP effects. In contrast, the BO Hamiltonian $H_{BO}$ does not have any of these effects. $H_{BO}^{GP}$ includes only the GP effects but excludes all nonadiabatic transitions. Finally, to obtain a picture where nonadiabatic transitions are preserved but GP effects are removed, we use the diabatic Hamiltonian identical to $H_{\text{dia}}$ but with a modified $V_{bc} = c|y|$. Introducing
the absolute value function in the coupling was shown to remove the GP when the diabatic-to-adiabatic transformation, \( U^{\text{matrix}} \) in Eq. 2.22, is done.[12] We will refer to this Hamiltonian as \( H_{\text{dia}}^{\text{noGP}} \). An alternative to \( H_{\text{dia}}^{\text{noGP}} \) can be a Hamiltonian obtained by transforming \( H_{\text{dia}} \) to the adiabatic representation and ignoring the double-valued boundary conditions introduced by this transformation. The main advantage of \( H_{\text{dia}}^{\text{noGP}} \) is the numerical robustness of the diabatic representation. The four models are:

\[
H_{\text{dia}} = T_N 1_2 + V, \quad (3.4)
\]
\[
H_{BO} = T_N + W_-, \quad (3.5)
\]
\[
H_{BO}^{\text{GP}} = T_N + \tau_{\text{GP}} + W_- \quad (3.6)
\]
\[
H_{\text{dia}}^{\text{noGP}} = T_N 1_2 + \begin{pmatrix} V_b & V_{\text{noGP}}^{\text{bc}} \\ V_{\text{bc}}^{\text{noGP}} & V_c \end{pmatrix}, \quad (3.7)
\]

where \( V_{\text{bc}}^{\text{noGP}} = \lambda |y| \). The eigenenergies of the first two Hamiltonians can be compared to the previously calculated energies that use the complex scaling method.[4] The other two Hamiltonians will allow us to conclude whether is it solely GP that is responsible for the BSCs.

### 3.2 Basis

All Hamiltonians are transformed to matrices using time-independent basis functions. The same product basis of functions in \( x \) and \( y \) directions was used for the two-state diabatic Hamiltonians as well as for the single-state adiabatic Hamiltonians. The nuclear wavefunction is

\[
\chi(x, y) = \sum_n \varphi_n(x) \phi_n(y) \quad (3.8)
\]

where \( \varphi_n(x) \) are Particle in a box (PB) eigenfunctions and \( \phi_n(y) \) are eigenfunctions of the one-dimensional harmonic oscillator with frequency \( \omega_y \).

### 3.3 Resonance Energies and Lifetimes from the Stabilization Method

In Hermitian quantum mechanics, the time-independent Schrödinger equation can be used to distinguish bound states from resonance states. This is done using the stabilization method.[16] In this method,
the energy spectra are analyzed upon variation of a stabilization parameter. The main reason for using PB eigenfunctions is that these functions introduce the length of the box as a natural stabilization parameter. As the length of the box is varied, the energy spectra are investigated. Using a finite basis turns the continuous spectrum to discrete. This truncation is allowed depending on two parameters: box length and number of basis functions. The box length needs to be large enough to model the interaction region. There should be enough basis functions such that the eigenenergies are converged.

![Stabilization diagrams for a) $H_{BO}$ giving rise to a resonance state and b) $H_{dia}$ giving rise to a bound state.](image)

Figure 3.2: Stabilization diagrams for a) $H_{BO}$ giving rise to a resonance state and b) $H_{dia}$ giving rise to a bound state.

The stabilization diagram of a resonance state has a stabilized region (nearly horizontal region) with avoided crossings, as seen in Fig. 3.2a. This stabilization diagram comes from $H_{BO}$. Looking at the probability density of the wavefunction above the stabilized region in Fig. 3.3, the density resembles that of PB eigenfunctions. Travelling along that curve of the stabilization diagram, the density of the wavefunction in the stabilized region is localized in the interaction region of the potential, with a tail outside. Continuing along the curve, the density still resembles that of a PB eigenfunction with an extra maximum from before the stabilized region.

The stabilization method allows us to use normalizable basis functions (and eigenstates) to describe continuum states. This is possible due to the resonance state having little variation with the change in box length, indicated by the stabilized region of the stabilization diagram. As box length is increased, that stabilized region should persist.

The stabilization plot in Fig. 3.2b comes from $H_{dia}$. The horizontal line indicates a bound state exists. At every box length, there is a state that does not change its energy. The probability densities on the curves of the stabilization diagram in Fig. 3.3 are comparable to the resonance state, however, the line representing the bound state is horizontal with no avoided crossings. The density of the wavefunction along this line (for any $L$) is completely localized in the interaction region of the potential.
Chapter 3. Methods

Figure 3.3: Stabilization diagram of a resonance state (center image) with the cross sections of the $H_{BO}$ potential along $x$ (black) as well as the probability density of different wavefunctions along the energy curves (blue).

It has been shown that in the stabilization diagrams, there is a visual difference between a bound state and a resonance state. To quantitatively characterise the resonance state, the density of states needs to be calculated (see Eq. 2.9). Equation 2.9 describes the full density of states for the stabilization region, whereas using PB eigenfunctions we get a density at a particular $L$. We can write the density for a fixed $L$, and therefore discrete levels, as

$$\rho_L(E) = \sum_j \delta(E_j(L) - E) \quad (3.9)$$

where $E_j(L)$ are the curves of the stabilization plot.

Averaging $\rho_L(E)$ over a range of box lengths $\Delta L$, $\langle \rho_L(E) \rangle$, allows us to devise an approximation to the full density of states over all energy levels,

$$\rho(E) \approx \langle \rho_L(E) \rangle = \frac{1}{\Delta L} \int_{L-\Delta L/2}^{L+\Delta L/2} dL \rho_L(E), \quad (3.10)$$

where $\Delta L$ covers the stabilization region. Using the delta function identity, $\int dx \delta(f - f(x)) = \left| \frac{df}{dx} \right|^{-1} |_{f(x)=f'}$.
we obtain

\[
\langle \rho_L(E) \rangle = \frac{1}{\Delta L} \sum_j \left| \frac{dE_j(L')}{dL'} \right|^{-1}_{E_j(L')=E}
\] (3.11)

for \( L' \in \left[ L^{IP}_j - \frac{\Delta L}{2}, L^{IP}_j + \frac{\Delta L}{2} \right] \) where \( L^{IP}_j \) is the inflection point of \( E_j(L) \).

The energy spectra can be split into two parts. The \( Q \) region will describe the states involved in the stabilization region, i.e. the resonance states, and \( P \) will be everything else. The density of states can then be written by

\[
\rho_L(E) = \rho^Q_L(E) + \rho^P_L(E).
\] (3.12)

For a given energy range that contains the states of \( Q \), the number of \( Q \) states does not change as \( L \) increases. However, as \( L \) increases, all eigenenergies of the \( P \) states decrease, resulting in a higher density of states near the resonance. Therefore, for small \( L \) with only the \( Q \) states in the energy range chosen, the density of states in this energy range is attributed to \( \rho^Q_L(E) \), with \( \rho^P_L(E) \) being negligible.

This brings us to the approximation that \( \langle \rho_L(E) \rangle \simeq \rho^Q_L(E) \).

With so few states when \( L \) is small, it can be assumed that the density does not depend on \( L \), and therefore \( \rho^Q_L(E) \simeq \rho^Q(E) \). This density of states near a resonance with small \( L \) is equal to that in
Eq. 2.9, which is a Lorentzian. Therefore, all that needs to be done is to fit Eq. 3.11 by Eq. 2.9 to find
\[ E_{\text{res}} = E_\alpha - \frac{i}{2} \Gamma_\alpha. \] If this is done to a bound state, \( \frac{dE_j(L')}{dL'} = 0 \), and therefore \( \left| \frac{dE_j(L')}{dL'} \right|^{-1} \) would not exist.

To help explain this better, we will consider the stabilization plot in Fig. 3.2a. Let’s consider the energy range from \( 9 \times 10^{-3} - 10 \times 10^{-3} \) a.u. At \( L = 15 \) a.u. or \( L = 25 \) a.u., there is only one state that is part of the \( Q \) region, and the density of states of the \( P \) states is zero. You can see that as \( L \) gets larger, around 30 a.u., two states exist in this region, one \( P \) and one \( Q \). As \( L \) increases, there are many more \( P \) states.

### 3.4 Calculations

The time-independent Schrödinger equation is solved for each Hamiltonian in Eqs. 3.4 - 3.7. The parameters are chosen to be those used by Cederbaum et al. [4] All the Hamiltonians are projected in the working basis from Eq. 3.8 to form the matrix representation of the Hamiltonian in the chosen basis. All Hamiltonians are then diagonalized in order to solve for the eigenenergies of the system in question. The stabilization plots require the energy spectrum for variation in \( L \). Therefore, for each new \( L \), the basis is recalculated in order to reconstruct and diagonalize the matrix Hamiltonian.

The separability of the nuclear basis along with the Hamiltonian made calculations easier in the diabatic representation. All \( x \) components were able to be calculated separately from the \( y \) components. The only integration in \( x \) that was done analytically was the kinetic energy. The integration done analytically in \( y \) was the kinetic energy, and the potential energy including the coupling potential. The analytical integrations in \( y \) were made possible using creation and annihilation operators because of the harmonicity of the eigenfunctions. All other integration was done numerically using the trapezoidal method. All basis functions and potentials done numerically were discretized on an evenly spaced grid starting with 501 points for \( L = 100 \sqrt{\omega_x} \). The grid increased for each increase in \( L \) such that the grid points would remain the same. This needed to be done for stabilization of the bound state.

To capture enough of the bound and continuum parts of the potential in \( x \), the domain chosen for the PB eigenfunctions was \([-4, L]\) (Eqs. (3.2) and (3.3)).

Energy of low lying states for all Hamiltonians converged within \( 10^{-6} \) a.u. with 150 PB and 20 harmonic oscillator eigenfunctions. All programming is done using the Matlab software package.[17]
Chapter 4

Results and Discussion

4.1 Geometric Phase Effects on Bound States in the Continuum

Table 4.1 and Figs. 4.1 and 4.2 summarize results of the stabilization calculations for the lowest localized states of the four Hamiltonians. Looking at the contour plots of the square root of the density of the nuclear wavefunctions, Figs. 4.2, it is easy to see the two contours from the Hamiltonians that do not include GP, $H_{BO}$ and $H_{\text{noGP}}$, exist beyond the interaction region. This is the tunnelling that is part of the continuum. The Hamiltonians accounting for the GP have only real-valued energy up to a numerical error of $10^{-6}$ a.u. Removing the GP leads to a resonance character of the lowest localized state. Thus, the BSCs can be clearly related to the presence of the GP. An intuitive picture of this relation is that in the absence of the GP the nuclear wave-packet can tunnel through a barrier separating the well part of the $W_-$ potential from its asymptotic region, whereas addition of the GP creates destructive interference between the parts of the wave-packet that tunnel through the barrier on different sides of the CI. The absolute overlap of the $H_{\text{dia}}$ and $H_{\text{BO}}^{\text{GP}}$ wavefunctions, $|\langle \Psi_{\text{dia}} | \Psi_{\text{BO}}^{\text{GP}} \rangle |$ is 0.93, which is relatively large considering that the total probability to find the system described by $|\Psi_{\text{dia}}\rangle$ in the ground electronic state is 0.97 (see also Fig. 4.2 (a) and (c)).

A common correction to the $H_{BO}$ Hamiltonian is the DBOC,[27] which for our model can be written as $\left(\nabla \theta\right)^2/2$. The DBOC diverges at the CI and can potentially reduce the lifetime of the

<table>
<thead>
<tr>
<th>$H_{\text{dia}}$</th>
<th>$H_{BO}$</th>
<th>$H_{BO}^{\text{GP}}$</th>
<th>$H_{\text{dia}}^{\text{noGP}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.29</td>
<td>9.23 − i0.10</td>
<td>10.23</td>
<td>10.02 − i0.04</td>
</tr>
</tbody>
</table>
resonance. This is indeed the case, stabilization calculations with $H_{BO} + (\nabla \theta)^2/2$ gives $E = (11.03 + i0.13) \times 10^{-3}$ for the lowest resonance state.

4.2 Resonance Decay

This section discusses a side project that compares the stabilization method to the time-dependent formalism. To analyze the decay of a resonance state in the time-dependent formalism, we used a two-state 1D model with constant coupling:

\[
H_{1D} = \begin{pmatrix} T_N & 0 \\ 0 & T_N \end{pmatrix} + \begin{pmatrix} \frac{\omega x^2}{2} & \lambda \\ \lambda & \epsilon e^{-\beta(x+\delta)} \end{pmatrix},
\]

and PB basis functions. The coordinate $x$ is mass- and frequency-weighted and the parameters used are $\omega = 0.015$, $\lambda = 0.01$, $\epsilon = 0.04$, $\beta = 0.5$, and $\delta = 0.5$. This model does not have a CI and therefore no GP effects because of the constant coupling. This constant coupling does not allow for a bound state to exist. PB eigenfunctions were used as the basis.
Figure 4.2: Contour of the square root of the ground electronic state nuclear probability density of the lowest localized state for different Hamiltonians with box length 20.4 a.u.: a) $H_{\text{dia}}$, b) $H_{\text{BO}}$, c) $H_{\text{GP}}^{\text{BO}}$, and d) $H_{\text{dia}}^{\text{noGP}}$.

To see the dynamics of the system, we used a Gaussian function centered with the parabolic potential as the initial state, $\Psi(x,0)$. This $\Psi(x,0)$ is written as a linear combination of eigenfunctions of $H_{1\text{D}}$. The time-dependent function, $\Psi(x,t)$, was obtained using Eq. 2.4. To avoid using complex absorbing potentials (since we are using a box to model an infinite space) the box length needs to be taken large enough. The larger the box, the more basis functions that need to be used. In this case, the box length was taken to be 370 a.u. using 500 PB eigenfunctions. This was done numerically; the time step was chosen to be 10 a.u. starting from $t = 0$ to $t = 40,000$ a.u. The probability of finding $\Psi(x,t)$ in the initial state from the autocorrelation function $|\int dx\Psi(x,0)\Psi(x,t)|^2$ can be seen in Fig. 4.3.

The autocorrelation function was fit by an exponential, and the result was $e^{-8.8 \times 10^{-5} t}$. The stabilization method for this model gave a resonance energy of $3.7 \times 10^{-3} - \frac{i}{2}8.5 \times 10^{-5}$ a.u. It is clear that the resonance phenomenon causes the state to decay exponentially, consistent with the stabilization calculation. Calculating this probability is time consuming using the parameters listed above, while this is for a single degree of freedom. The stabilization method is much quicker, and is more ideal for...
problems with multiple degrees of freedom. It is easy to see from this example why the time-dependent method is usually avoided, and why in our calculations the stabilization method was used.

Figure 4.3: The autocorrelation function for the dynamics of a Gaussian as the initial state for the $H_{1D}$ model.
Chapter 5

Conclusion

We have unambiguously shown that the nontrivial GP is the reason for the appearance of bound states in the continuum in the considered model problem. This result is yet another illustration that inclusion of the GP can qualitatively change results in nonadiabatic problems and cannot be ignored \textit{a priori}. The observed result is a direct analog of GP-induced localization, obtained in the double-well potential problem.\cite{13, 26} As in the double-well case, one can expect that there is a certain range of parameters of the linear vibronic model that supports BSCs. This expectation is in accord with previous works on GP effects in tunnelling that did not find BSCs for a very similar model with different values of corresponding parameters.\cite{36, 38} Yet, one can hope that it is possible to engineer a molecular system where GP will not only slow down the tunnelling process but will completely freeze it by giving rise to BSCs.

The stabilization method was compared with the time-dependent approach. The decay of the initial state was calculated using the autocorrelation function. This decay was consistent with the stabilization method. For simplicity this was done with a 1D model, clearly illustrating the efficiency of the stabilization method over the time-dependent approach.

This work has shown that the inclusion of GP is necessary to obtain accurate results. Whether the system gives rise to a bound state or a resonance state, GP changes the dynamics of the system. We can use the knowledge that GP changes the decay of the system to modify transition state theory.
Bibliography


