An Eulerian surface hopping method for the Schrödinger equation with conical crossings

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Abstract

In a nucleonic propagation through conical crossings of electronic energy levels, the codimension two conical crossings are the simplest energy level crossings, which affect the Born-Oppenheimer approximation in the zeroth order term. The purpose of this paper is to develop the surface hopping method for the Schrödinger equation with conical crossings in the Eulerian formulation. The approach is based on the semiclassical approximation governed by the Liouville equations, which are valid away from the conical crossing manifold. At the crossing manifold, electrons hop to another energy level with the probability determined by the Landau-Zener formula. This hopping mechanics is formulated as an interface condition, which is then built into the numerical flux for solving the underlying Liouville equation for each energy level. While a Lagrangian particle method requires the increase in time of the particle numbers, or a large number of statistical samples in a Monte Carlo setting, the advantage of an Eulerian method is that it relies on fixed number of partial differential equations with a uniform in time computational accuracy. We prove the positivity and l^1-stability and illustrate by several numerical examples the validity and accuracy of the proposed method.

Keyword:—Surface hopping method, Conical crossings, Liouville equation, Landau-Zener formula, Interface condition, High resolution scheme.

1 Introduction

The quantum mechanical description of molecular dynamics is given by the time-dependent Schrödinger equation,

$$i\hbar\partial_t\Phi(t,\mathbf{x},\mathbf{y}) = H\Phi(t,\mathbf{x},\mathbf{y}), \tag{1}$$

$$\Phi(0,\mathbf{x},\mathbf{y}) = \Phi_0(\mathbf{x},\mathbf{y}). \tag{2}$$

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Here $\hbar$ is the reduced Planck constant and $\Phi(t, \mathbf{x}, \mathbf{y})$ is the total wave function. The vector $\mathbf{x} \in \mathbb{R}^N$ and $\mathbf{y} \in \mathbb{R}^n$ denote the positions of N nuclei and n electrons, respectively. The molecular Hamiltonian operator H consists of two parts, the kinetic energy operator of the nuclei and the electronic Hamiltonian for fixed nucleonic configuration,

$$H = -\sum_{j=1}^{N} \frac{\hbar^2}{2M_j} \Delta_{x_j} + H_e(\mathbf{y}, \mathbf{x}),$$

with,

$$H_e(\mathbf{y}, \mathbf{x}) = -\sum_{j=1}^{n} \frac{\hbar^2}{2m_j} \Delta_{y_j} + \sum_{j<k} \frac{1}{|y_j - y_k|} + \sum_{j<k} \frac{Z_j Z_k}{|x_j - x_k|} - \sum_{k=1}^{N} \sum_{j=1}^{n} \frac{Z_j}{|x_j - y_k|}.$$

Here m_j denotes mass of the j-th electron, and M_j, Z_j denote mass and charge of the j-th nucleus. The electronic Hamiltonian H_e consists of the kinetic energy of the electrons as well as the inter-electronic repulsion potential, inter-nuclear repulsion potential and the electronic-nuclear attraction potential.

The time-dependent Schrödinger equation (1) mathematically describes the fundamental behavior of the matter at the molecular scale. In principle, it is possible to describe all chemical systems by solving this equation. However, due to the high dimensionality of the molecular configuration space $\mathbb{R}^{N+n}$, numerical simulation of the Schrödinger equation (1) is a formidable challenge. For common molecules like carbon dioxide CO_2, which consists of 3 nuclei and 22 electrons, the full time-dependent Schrödinger equation is cursed by the high dimensionality of the molecular configuration space $\mathbb{R}^{75}$. The Born-Oppenheimer approximation is a commonly used approach in quantum chemistry to reduce the degrees of freedom.

This approximation was proposed in the early days of quantum mechanics by Born and Oppenheimer [2] and is still indispensable in quantum chemistry. It is built upon from the mass discrepancy between the light electrons m and the heavy nuclei M in molecules. Due to the mass difference, the motions of the particles are in different time scales. The electrons move relatively fast, which are treated quantum mechanically, while the nuclei move relatively slowly, which can be considered as classical particles. This allows the wave function of a molecule to be split into its electronic and nuclear components.

Assume L is the typical length, T the typical time scale, Ω the typical mass scale, $m_j = m$, and $M_j = M$, $\forall j$. Then one can nondimensionalize the Schrodinger equation (1) by introducing

$$\tilde{t} = \frac{t}{T}, \quad \tilde{\mathbf{x}} = \frac{\mathbf{x}}{L}, \quad \tilde{\mathbf{y}} = \frac{\mathbf{y}}{L}, \quad \tilde{m} = \frac{m}{\Omega}, \quad \tilde{M} = \frac{M}{\Omega},$$

$$\tilde{H}_e(\tilde{\mathbf{y}}, \tilde{\mathbf{x}}) = \frac{\tilde{m} T^2}{\Omega \hbar^2 L^2} H_e(\mathbf{y}, \mathbf{x}), \quad \tilde{\Phi}(\tilde{t}, \tilde{\mathbf{x}}, \tilde{\mathbf{y}}) = \Phi(t, \mathbf{x}, \mathbf{y}),$$

and obtain

$$i\delta \tilde{m} \partial_{\tilde{t}} \tilde{\Phi}(\tilde{t}, \tilde{\mathbf{x}}, \tilde{\mathbf{y}}) = -\sum_{j=1}^{N} \frac{\delta^2}{2} \frac{\tilde{m}}{\tilde{M}} \Delta_{\tilde{x}_j} \tilde{\Phi}(\tilde{t}, \tilde{\mathbf{x}}, \tilde{\mathbf{y}}) + \tilde{H}_e(\tilde{\mathbf{y}}, \tilde{\mathbf{x}}) \tilde{\Phi}(\tilde{t}, \tilde{\mathbf{x}}, \tilde{\mathbf{y}}), \tag{3}$$

where $\delta = \frac{\hbar T}{\Omega L^2}$ is a dimensionless number. We let $\delta = 1$, $\hat{t} = \frac{\tilde{t}}{\sqrt{\tilde{m}\tilde{M}}}$, $\hat{\Phi}(\hat{t}, \tilde{\mathbf{x}}, \tilde{\mathbf{y}}) = \tilde{\Phi}(\tilde{t}, \tilde{\mathbf{x}}, \tilde{\mathbf{y}})$ and $\varepsilon = \sqrt{\frac{\tilde{m}}{\tilde{M}}}$, then (3) becomes

$$i\varepsilon \partial_{\hat{t}} \hat{\Phi}(\hat{t}, \tilde{\mathbf{x}}, \tilde{\mathbf{y}}) = -\sum_{j=1}^{N} \frac{\varepsilon^2}{2} \Delta_{\tilde{x}_j} \hat{\Phi}(\hat{t}, \tilde{\mathbf{x}}, \tilde{\mathbf{y}}) + \tilde{H}_e(\mathbf{y}, \mathbf{x}) \hat{\Phi}(\hat{t}, \tilde{\mathbf{x}}, \tilde{\mathbf{y}}). \tag{4}$$

For convenience, in the following, we still use t, x, y and H_e to stand for $\hat{t}$, $\tilde{x}$, $\tilde{y}$ and $\tilde{H}_e$ respectively. The time-dependent Schrödinger equation (1) then becomes

$$i\varepsilon \partial_t \Phi(t, \mathbf{x}, \mathbf{y}) = -\sum_{j=1}^{N} \frac{\varepsilon^2}{2} \Delta_{x_j} \Phi(t, \mathbf{x}, \mathbf{y}) + H_e(\mathbf{y}, \mathbf{x}) \Phi(t, \mathbf{x}, \mathbf{y}). \tag{5}$$

In the Born-Oppenheimer approximation, one first solves the following time-independent *electronic* eigenvalue problems,

$$H_e(\mathbf{y}, \mathbf{x}) \varphi_k(\mathbf{y}; \mathbf{x}) = E_k(\mathbf{x}) \varphi_k(\mathbf{y}; \mathbf{x}), \quad \forall \mathbf{x} \in \mathbb{R}^N, \ k = 1, 2, \cdots. \tag{6}$$

Here one assumes that the spectrum of H_e is discrete with a complete set of orthonormal eigenfunctions $\{\varphi_k(\mathbf{y}; \mathbf{x})\}$ called the *adiabatic* basis, over the electronic coordinates for every fixed nucleus coordinates, i.e.,

$$\int_{-\infty}^{\infty} \varphi_i^*(\mathbf{y}; \mathbf{x}) \varphi_j(\mathbf{y}; \mathbf{x}) d\mathbf{y} \equiv \langle \varphi_i(\mathbf{y}; \mathbf{x}) | \varphi_j(\mathbf{y}; \mathbf{x}) \rangle_{\mathbf{y}} = \delta_{ij}, \quad \sum_k |\varphi_k >< \varphi_k| = \mathbf{1},$$

where δ_{ij} is the Kronecker delta and $\mathbf{1}$ is the identity operator. The electronic energy eigenvalue $E_k(\mathbf{x})$, called the *potential energy surface*, depends on the positions of the nuclei. They can be obtained as a continuous function of $\mathbf{x}$ by varying $\mathbf{x}$ in small steps and repeatedly solving the eigenvalue problem (6).

Next the total wave function $\Phi(t, \mathbf{x}, \mathbf{y})$ is expanded in terms of the eigenfunctions $\{\varphi_k\}$:

$$\Phi(t, \mathbf{x}, \mathbf{y}) = \sum_k \chi_k(t, \mathbf{x}) \varphi_k(\mathbf{y}; \mathbf{x}). \tag{7}$$

Insert ansatz (7) into the time-dependent Schrödinger equation (5), multiply all the terms from the left by $\varphi_k^*(\mathbf{y}; \mathbf{x})$, integrate with respect to $\mathbf{y}$, and then one obtains a set of coupled differential equations:

$$i\varepsilon \frac{\partial}{\partial t} \chi_k(t, \mathbf{x}) = \left[-\sum_{j=1}^{N} \frac{\varepsilon^2}{2} \Delta_{x_j} + E_k(\mathbf{x}) \right] \chi_k(t, \mathbf{x}) + \sum_l C_{kl} \chi_l(t, \mathbf{x}), \tag{8}$$

where the coupling operator C_{kl} is defined by

$$C_{kl} \equiv \left\langle \varphi_k \left| -\sum_{j=1}^{N} \frac{\varepsilon^2}{2} \Delta_{x_j} \right| \varphi_l \right\rangle - \sum_{j=1}^{N} \varepsilon^2 \langle \varphi_k | \nabla_{x_j} | \varphi_l \rangle \nabla_{x_j}. \tag{9}$$

As long as the potential energy surfaces $\{E_k(\mathbf{x})\}$ are well separated, all the coupling operators C_{kl} are negligible. By ignoring C_{kl} in (8), one obtains a set of decoupled Schrödinger equations

$$i\varepsilon\frac{\partial}{\partial t}\chi_k(t,\mathbf{x}) = \left[-\sum_{j=1}^{N}\frac{\varepsilon^2}{2}\Delta_{x_j} + E_k(\mathbf{x})\right]\chi_k(t,\mathbf{x}), \quad (t,\mathbf{x}) \in \mathbb{R}^+ \times \mathbb{R}^N. \tag{10}$$

This means that the nuclear motion proceeds without the transitions between electronic states. This is the essence of the *Born-Oppenheimer approximation* or *adiabatic approximation*. This kind of representation is called *adiabatic representation*.

In [29], H. Spohn and S. Teufel gave a rigorous analysis of the time-dependent Born-Oppenheimer approximation. They proved that the time-dependent Schrödinger equation (1) without energy level crossing can be approximated by the corresponding Born-Oppenheimer approximation solution with an error of order ε.

When potential energy surfaces $E_k(\mathbf{x})$ approach each other, or even cross, the effect of the coupling operators C_{kl} in (8) becomes nonnegligible and the Born-Oppenheimer approximation breaks down. There will be *non-adiabatic transition* between the adjacent potential energy surfaces $E_k(\mathbf{x})$ and $E_l(\mathbf{x})$. This means that the nuclear motion proceeds with transitions between electronic states and the electronic wave functions can evolve from the reactant electronic configuration to the product electronic configuration, which makes the chemical bonds fission and the chemical reaction like *charge transfer*, *photoisomerization* or *photodissociation* happen. See [3] for more details.

To handle the transitions, one can alternatively consider the so-called *diabatic representation*. Generally, let $U(\mathbf{x})$ denotes a unitary transform matrix. We can see a unitary transformation in the vector space of electronic states does not change the total wave function (7),

$$\Phi = \sum_k \chi_k\varphi_k = \chi^+\varphi = \chi^+U^+U\varphi = (U\chi)^+(U\varphi) \equiv \tilde{\chi}^+\tilde{\varphi}.$$

where we denote U's conjugate transpose by U^+, $\tilde{\varphi} = U\varphi$ and $\tilde{\chi} = U\chi$. If we can find the transformation $U(\mathbf{x})$ by which the the coupling operators C_{kl} vanish, the basis $\{\tilde{\varphi}_k(\mathbf{y};\mathbf{x})\}$ is called *diabatic* basis. Multiplying (10) from the left by U^+ gives

$$i\varepsilon\frac{\partial}{\partial t}\tilde{\chi}(t,\mathbf{x}) = \left[-\sum_{j=1}^{N}\frac{\varepsilon^2}{2}\Delta_{x_j} + V(\mathbf{x})\right]\tilde{\chi}(t,\mathbf{x}), \quad (t,\mathbf{x}) \in \mathbb{R}^+ \times \mathbb{R}^N. \tag{11}$$

Here the potential $V(\mathbf{x}) = U^+\mathtt{diag}(E_1(\mathbf{x}), E_2(\mathbf{x}), E_3(\mathbf{x}), \cdots)U$ is *not* a diagonal matrix any more. From equation (11) one can see that the coupling operators which have disappeared in (8) are reflected in the non-diagonal elements of the potential matrix $V(\mathbf{x})$. As U is a unitary matrix, all expectation values of observables remain the same under the diabatic transformation. However, it should be pointed out that the diabatic transformation can only be found for $1d$ problems by solving a differential equation. In other cases, it is not possible to find a diabatic basis. Thus, people turn to find the so-called *quasi-diabatic* basis, which can minimize the coupling operators C_{kl}. The quasi-diabatic basis is commonly used and efficient. In our paper, we assume in some basis, the coupling operators C_{kl} can be neglected. See [34] for more details about the diabatic representation.

For polyatomic molecules, which consist of more than two nuclei, the potential energy surface crossings can be very complicated. Hagedorn in [7] rigorously derived and classified eleven possible types of eigenvalue crossings of minimal multiplicity in molecular dynamics, and pointed out that the crossing manifold S can be of codimension one, two, three, or five in the nucleonic configuration space.

One of the widely used approaches to simulate the non-adiabatic dynamics is the *surface hopping method*, first proposed by Tully and Preston in 1971 [31], and well developed since then [32, 33, 27]. The basic idea is to combine the classical transports of the system on individual potential energy surfaces with instantaneous transitions from one energy surface to another. Different hopping criteria result in many variants of this method. For example, in [32], an algorithm with "fewest" hoppings was developed. The hoppings in that paper were performaced in a Monte Carlo procedure based on the transition rates. For a review of surface hopping methods see [4].

In recent years, Schütte *et al.* adopted the partial Wigner transform to reduce a full quantum dynamics into the quantum-classical Liouville equation, and then used the surface hopping approach to evolve the Gaussian phase space packets. For the single avoided crossing cases, they demonstrated that the convergence towards full quantum mechanical dynamics of their method was faster than Tully's methods [10]. Kammerer, Lasser, Teufel *et al.* analyzed the propagation through conical surface crossings using the Wigner transform and Wigner measures [24, 18] and proposed a rigorous surface hopping method based on the semiclassical limit of the time-dependent Born-Oppenheimer approximation. They used the particle method to solve the Liouville equation [23, 20]. Each classical trajectory was subject to a deterministic branching process. Branching occurrs whenever a trajectory attains one of its local minimal gaps between the eigenvalue surfaces. The new branches are reweighted according to the Landau-Zener formula for conical crossings.

These classical Lagrangian surface hopping methods are very simple to implement, and in particular, very efficient in high space dimension. However, they require either many statistical samples in a Monte-Carlo framework, or the increase of particle numbers whenever hopping occurs. In addition, in a typical Lagrangian type methods, when the particle trajectories diverge, a complicated numerical re-interpolation procedure is needed to maintain a uniform accuracy in time.

In this paper, we propose an Eulerian surface hopping method for a two-level Schrödinger equations with conical crossing. This method is based on the semiclassical limit of the Born-Oppenheimer approximation, namely, the system of linear Liouville equations. These Liouville equations for different energy levels are decoupled unless near the hopping zone, where the transition process, determined by the Landau-Zener formula, is modeled by an interface condition. This interface condition can be incorporated into the numerical flux of the Liouville solver, in the same way as was done for partial transmission and reflection of high frequency waves across an interface or barrier [16, 15, 12, 11]. The advantage of this Eulerian method is that, regardless of the number of times hopping occurs, the number of equations to be solved remain the same. This PDE based Eulerian numerical method also allows a uniform discretization accuracy.

This paper is organized as follows. In Sec. 2, we recall the Wigner transform approach to get the semiclassical limit of the two-level Schrödinger equation and present the Landau-Zener formula for the transition rate at conical crossing between different energy level surfaces. In Sec. 3, we present our Eulerian setup for surface hopping,

the interface condition that models the Landau-Zener transition, and the numerical discretization. The positivity and l_1-stability of the scheme are proved. Numerical examples are given in Sec. 4 to verify the convergence and accuracy of the proposed method. We make some concluding remarks in Sec. 5.

2 The surface hopping method

2.1 A two-level Schrödinger equation

Consider a typical case, `i.e.` the time-dependent two-level Schrödinger equation in configuration space,

$$i\varepsilon\partial_t\psi^\epsilon(t,\mathbf{x}) = \left(-\frac{\varepsilon^2}{2}\Delta_{\mathbf{x}} + V(\mathbf{x})\right)\psi^\varepsilon(t,\mathbf{x}), \quad (t,\mathbf{x}) \in \mathbb{R}^+ \times \mathbb{R}^2, \tag{12}$$

$$\psi^\varepsilon(0,\mathbf{x}) = \psi_0^\varepsilon(\mathbf{x}) \in \mathbf{L}^2(\mathbb{R}^2,\mathbb{C}^2). \tag{13}$$

Here $\psi^\varepsilon(t,\mathbf{x}) \in \mathbb{C}^2$ is the vector wave equation, $\Delta_{\mathbf{x}} = \mathtt{diag}(\Delta_{x_1}+\Delta_{x_2}, \Delta_{x_1}+\Delta_{x_2})$ and $V(\mathbf{x})$ is the real symmetric potential matrix,

$$V(\mathbf{x}) = \frac{1}{2}\mathrm{tr}V(\mathbf{x}) + \begin{pmatrix} v_1(\mathbf{x}) & v_2(\mathbf{x}) \\ v_2(\mathbf{x}) & -v_1(\mathbf{x}) \end{pmatrix}. \tag{14}$$

The Hamiltonian is given by $H = -\frac{\varepsilon^2}{2}\Delta_{\mathbf{x}} + V(\mathbf{x})$. The dimensionless semiclassical parameter $\varepsilon > 0$ is given by $\varepsilon = \sqrt{\frac{m}{M}}$, where m and M are the masses of an electron and a nucleus respectively. Then, all oscillations are roughly characterized by the frequency $1/\varepsilon$, which typically ranges between one hundred and one thousand. Hereafter, we will treat ε as a small parameter and discuss the semiclassical limit of the Schrödinger equations (12)-(13).

The potential $V(\mathbf{x})$ has eigenvalues $\lambda^{(\pm)} = \mathrm{tr}V(\mathbf{x}) \pm \sqrt{v_1(\mathbf{x})^2 + v_2(\mathbf{x})^2}$. Two energy levels are called *crossing at a point* $\mathbf{x}_* \in \mathbb{R}^2$ if $\lambda^+(\mathbf{x}_*) = \lambda^-(\mathbf{x}_*)$. Such a crossing is called *conical* if the vectors $\nabla_{\mathbf{x}} v_1(\mathbf{x}_*)$ and $\nabla_{\mathbf{x}} v_2(\mathbf{x}_*)$ are linearly independent. If all the crossings are conical, the crossing set $S = \{\mathbf{x} \in \mathbb{R}^2 | \lambda^+(\mathbf{x}) = \lambda^-(\mathbf{x})\}$ is a submanifold of *codimension two* in $\mathbb{R}^2$.

2.2 The semiclassical limit

In this section, we discuss the semiclassical limit of the Schrödinger equations (12)(13). Denote $\mathbf{x} = (x,y) \in \mathbb{R}^2$ and $\mathbf{k} = (\xi,\eta) \in \mathbb{R}^2$. Introduce the Wigner function

$$W^\varepsilon(\psi^\varepsilon)(\mathbf{x},\mathbf{k}) = (2\pi)^{-2}\int_{\mathbb{R}^2} e^{i\mathbf{y}\cdot\mathbf{k}}\psi^\varepsilon(\mathbf{x}-\frac{\varepsilon}{2}\mathbf{y}) \otimes \bar{\psi}^\epsilon(\mathbf{x}+\frac{\varepsilon}{2}\mathbf{y})d\mathbf{y}, \quad (\mathbf{x},\mathbf{k}) \in \mathbb{R}^2_{\mathbf{x}} \times \mathbb{R}^2_{\mathbf{k}}.$$

Note that, although the Winger function W^ε cannot recover the wave function ψ^ε, the moments of W^ε give the physical observables including the position density, flux, and energy. The Wigner function is a convenient tool to study the semiclassical limit of the Schrödinger equation [5, 6, 26]. Let u denote this weak limit,

$$\lim_{\varepsilon\to 0} W^\varepsilon(t,\mathbf{x},\mathbf{k}) \rightharpoonup u(t,\mathbf{x},\mathbf{k}),$$

which is called the *Wigner measure* or *semiclassical measure*. We now precisely describe this limit.

First, for the Schrödinger equation (12), the complex 2×2 matrix-valued symbol is given by

$$P(\mathbf{x}, \mathbf{k}) = \frac{i}{2}|\mathbf{k}|^2 + iV(\mathbf{x}),$$

where $\mathbf{k}$ is the conjugate variable to the position variable $\mathbf{x}$. The two eigenvalues of $-iP(\mathbf{x}, \mathbf{k})$ are

$$\lambda_1(\mathbf{x}, \mathbf{k}) = \frac{|\mathbf{k}|^2}{2} + \mathrm{tr}V(\mathbf{x}) + \sqrt{v_1(\mathbf{x})^2 + v_2(\mathbf{x})^2},$$

and

$$\lambda_2(\mathbf{x}, \mathbf{k}) = \frac{|\mathbf{k}|^2}{2} + \mathrm{tr}V(\mathbf{x}) - \sqrt{v_1(\mathbf{x})^2 + v_2(\mathbf{x})^2}.$$

We assume that the Hamiltonian flow λ_τ leaves invariant the set

$$\Omega = (\mathbb{R}^2_{\mathbf{x}} \times \mathbb{R}^2_{\mathbf{k}}) \backslash S.$$

For $(\mathbf{x}, \mathbf{k}) \in \Omega$, we denote by $\chi_\tau(\mathbf{x}, \mathbf{k})$ the column eigenvector corresponding to the eigenvalue $\lambda_\tau(\mathbf{x}, \mathbf{k})$ and the matrix $\Pi_\tau(\mathbf{x}, \mathbf{k}) = \chi_\tau(\mathbf{x}, \mathbf{k})(\chi_\tau(\mathbf{x}, \mathbf{k}))^T$ is the orthogonal projection onto the eigenspace associated to $\lambda_\tau(\mathbf{x}, \mathbf{k})$.

By Theorem 6.1 of [6], outside the crossing set S, the Wigner measure $u(t, \cdot)$ commutes with the projectors Π_τ and thus can be decomposed as

$$u(t, \cdot) = \Pi_1 u(t, \cdot)\Pi_1 + \Pi_2 u(t, \cdot)\Pi_2.$$

Since the eigenspaces are one-dimensional, the decomposition is simplified to be

$$u(t, \cdot) = u_1(t, \cdot)\Pi_1 + u_2(t, \cdot)\Pi_2,$$

where the scalar function $u_\tau(t, \mathbf{x}, \mathbf{k})$ is determined by projection

$$u_\tau(t, \mathbf{x}, \mathbf{k}) = \mathrm{tr}(\Pi_\tau u(t, \mathbf{x}, \mathbf{k})).$$

Here u_τ are continuously t-dependent positive scalar measures on $\mathbb{R}^2_{\mathbf{x}} \times \mathbb{R}^2_{\mathbf{k}}$ defined by

$$\partial_t u_\tau + \nabla_{\mathbf{k}} \lambda_\tau \cdot \nabla_{\mathbf{x}} u_\tau - \nabla_{\mathbf{x}} \lambda_\tau \cdot \nabla_{\mathbf{k}} u_\tau = 0, \quad (t, \mathbf{x}, \mathbf{k}) \in \mathbb{R}^+ \times \Omega \tag{15}$$

$$u_\tau(0) = \mathrm{tr}(\Pi_\tau \mu_0), \quad (\mathbf{x}, \mathbf{k}) \in \Omega \tag{16}$$

$$u_\tau(t, \mathbf{x}, \mathbf{k}) = 0, \quad t \in \mathbb{R}^+, \quad (\mathbf{x}, \mathbf{k}) \in S, \quad \tau = 1, 2. \tag{17}$$

The scalar functions $u_\tau(t, \mathbf{x}\ \mathbf{k}), \tau = 1, 2$, can be interpreted as the phase space probability density corresponding to the upper and lower energy level, respectively. One can recover the probability densities $U_1(t, \mathbf{x})$ and $U_2(t, \mathbf{x})$ in the configuration space by computing their zeroth moments,

$$U_\tau(t, \mathbf{x}) = \int_{R^2_{\mathbf{k}}} u_\tau(t, \mathbf{x}, \mathbf{k}) d\mathbf{k}, \quad \tau = 1, 2. \tag{18}$$

Therefore, the Liouville equations (15) in phase space give the propagation of the Wigner measures $u_1(t, \cdot)$ and $u_2(t, \cdot)$ on any given time interval, provided that their support do not intersect the eigenvalue crossing set S.

The computational challenge arises when their support set intersects the eigenvalue crossing set S, where the Liouville equations corresponding to $u_1(t, \cdot)$ and $u_2(t, \cdot)$ are coupled due to the non-adiabatic transition between the two energy levels. Hence we need an extra crossing condition at set S to couple them.

2.3 The Landau-Zener formula

In [23], there is a heuristic derivation of the non-adiabatic transition probability between $u_1(t,\cdot)$ and $u_2(t,\cdot)$ at S. The derivation is based on the Hamiltonian system corresponding to the Liouville equations (15)

$$\dot{\mathbf{x}}_\tau(t) = \nabla_{\mathbf{k}}\lambda_\tau(t) = \mathbf{k}_\tau(t), \tag{19}$$

$$\dot{\mathbf{k}}_\tau(t) = -\nabla_{\mathbf{x}}\lambda_\tau(t), \quad \tau = 1, 2, \tag{20}$$

where $\mathbf{x}_\tau(t) = (x_\tau(t), y_\tau(t)) \in \mathbb{R}^2_{\mathbf{x}}$ and $\mathbf{k}_\tau(t) = (\xi_\tau(t), \eta_\tau(t)) \in \mathbb{R}^2_{\mathbf{k}}$ are the position and velocity of u_τ. The basic idea is to insert the trajectories $(\mathbf{x}(t), \mathbf{k}(t))$ of the Hamiltonian systems (19)-(20) into the trace-free part of the potential matrix (14) and obtain an ordinary differential system,

$$i\varepsilon\frac{d}{dt}\psi(t) = \begin{pmatrix} v_1(\mathbf{x}(t)) & v_2(\mathbf{x}(t)) \\ v_2(\mathbf{x}(t)) & -v_1(\mathbf{x}(t)) \end{pmatrix}\psi(t).$$

The non-adiabatic transitions between u_1 and u_2 happen in the region, where the gap between the eigenvalues becomes minimal. The function

$$h(\mathbf{x}(t)) = |\lambda_1(\mathbf{x}(t)) - \lambda_2(\mathbf{x}(t))| = 2|\mathbf{v}(\mathbf{x}(t))|,$$

measures the gap between the eigenvalues in phase space along the classical trajectory $(\mathbf{x}(t), \mathbf{k}(t))$, where $\mathbf{v}(\mathbf{x}) = (v_1(\mathbf{x}), v_2(\mathbf{x}))$ is a vector and $|\cdot|$ is the Euclidean norm. The necessary condition for a trajectory to attain the minimal gap is given by,

$$\frac{d}{dt}|\mathbf{v}(\mathbf{x}(t))|^2 = \mathbf{v}(\mathbf{x}(t)) \cdot \nabla_{\mathbf{x}}\mathbf{v}(\mathbf{x}(t))\mathbf{k}(t) = 0,$$

where $\nabla_{\mathbf{x}}\mathbf{v}(\mathbf{x}(t)$ is the Jacobian matrix of vector $\mathbf{v}(\mathbf{x}(t))$, and $\mathbf{k}(t) = \dot{\mathbf{x}}(t)$. Hence, a crossing manifold in the phase space containing these points of the minimal gaps is

$$S^* = \left\{(\mathbf{x}, \mathbf{k}) \in \mathbb{R}^2_{\mathbf{x}} \times \mathbb{R}^2_{\mathbf{k}} \middle| \mathbf{v}(\mathbf{x}(t)) \cdot \nabla_{\mathbf{x}}\mathbf{v}(\mathbf{x}(t))\mathbf{k}(t) = 0\right\}.$$

The transition probability when one particle hits S^* is obtained as, refer to [23],

$$T(\mathbf{x}_0, \mathbf{k}_0) = \exp\left(-\frac{\pi}{\varepsilon}\frac{(v(\mathbf{x}_0) \wedge \nabla_{\mathbf{x}}v(\mathbf{x}_0) \cdot \mathbf{k}_0)^2}{|\nabla_{\mathbf{x}}v(\mathbf{x}_0) \cdot \mathbf{k}_0|^3}\right), \tag{21}$$

which is the famous *Landau-Zener formula.*

Notice that T decays exponentially in $\mathbf{x}$ and $\mathbf{k}$. When $\varepsilon \to 0$,

$$T \to T_0 = \begin{cases} 1, & (\mathbf{x}, \mathbf{k}) \in S = \{(0,0)\}, \\ 0, & (\mathbf{x}, \mathbf{k}) \notin S, \end{cases}$$

which means when $\varepsilon \to 0$, the hopping only occurs on S. It is consistent with the result in the previous subsections.

3 An Eulerian method

3.1 An Eulerian setup

Our Eulerian framework consists of solving the two Liouville equations

$$\partial_t u_\tau + \nabla_{\mathbf{k}}\lambda_\tau \cdot \nabla_{\mathbf{x}} u_\tau - \nabla_{\mathbf{x}}\lambda_\tau \cdot \nabla_{\mathbf{k}} u_\tau = 0, \quad (t,\mathbf{x},\mathbf{k}) \in R^+ \times \Omega, \quad \tau = 1,2\,,$$

with an interface condition that incorporates the Landau-Zener transition. Note that the Schrodinger equation (12) has the conservation of total mass

$$\partial_t \int |\psi^\epsilon|^2 \, d\mathbf{x} = 0, \tag{22}$$

which gives, in the semiclassical limit $\epsilon \to 0$,

$$\partial_t \int (u_1 + u_2)\, d\mathbf{k}\, d\mathbf{x} = 0. \tag{23}$$

For this condition to hold, *the flux needs to be continuous across the hopping surface* S^*. Thus the Landau-Zener transition at S^* should be formulated as a continuity condition for the flux in the normal direction to S^*. Let

$$j_\tau(\mathbf{x},\mathbf{k}) = \nabla_{(\mathbf{x},\mathbf{k})} u_\tau(\mathbf{x},\mathbf{k}),\ \tau = 1,2\,,$$

be the flux, and $\vec{n}$ be the normal direction to S^*. Then the interface condition is

$$\begin{pmatrix} j_1(\mathbf{x}_0^+,\mathbf{k}_0^+)\cdot\vec{n} \\ j_2(\mathbf{x}_0^+,\mathbf{k}_0^+)\cdot\vec{n} \end{pmatrix} = \begin{pmatrix} 1-T(\mathbf{x}_0,\mathbf{k}_0) & T(\mathbf{x}_0,\mathbf{k}_0) \\ T(\mathbf{x}_0,\mathbf{k}_0) & 1-T(\mathbf{x}_0,\mathbf{k}_0) \end{pmatrix} \begin{pmatrix} j_1(\mathbf{x}_0^-,\mathbf{k}_0^-)\cdot\vec{n} \\ j_2(\mathbf{x}_0^-,\mathbf{k}_0^-)\cdot\vec{n} \end{pmatrix}, \tag{24}$$

where $(\mathbf{x}^\pm,\mathbf{k}^\pm)$ are the limits to $(\mathbf{x}_0,\mathbf{k}_0) \in S^*$ along $\vec{n}$.

It should be pointed out that this interface condition only works in the following two cases:

(1) $j_1(\mathbf{x}_0^-,\mathbf{k}_0^-) \neq 0$ and $j_2(\mathbf{x}_0^-,\mathbf{k}_0^-) = 0$,

(2) $j_1(\mathbf{x}_0^-,\mathbf{k}_0^-) = 0$ and $j_2(\mathbf{x}_0^-,\mathbf{k}_0^-) \neq 0\,$.

The interference resulted when two particles from different energy level surfaces arrive at S^* at the same time is not accounted for in this setup. This is a restriction of the method, which will be improved in our future work.

3.2 The numerical fluxes

In this section we describe the finite volume scheme for the 2D Liouville equation

$$\frac{\partial u_\tau}{\partial t} + \xi\frac{\partial u_\tau}{\partial x} + \eta\frac{\partial u_\tau}{\partial y} - \frac{\partial \lambda_\tau}{\partial x}\frac{\partial u_\tau}{\partial \xi} - \frac{\partial \lambda_\tau}{\partial y}\frac{\partial u_\tau}{\partial \eta} = 0, \quad \tau = 1,2. \tag{25}$$

Without loss of generality, we employ the finite volume method with a uniform mesh. Suppose $h_x,\ h_y,\ h_\xi,\ h_\eta > 0$ are mesh sizes. In each direction, the mesh points are at $(x_{i+\frac{1}{2}}, y_{j+\frac{1}{2}}, \xi_{k+\frac{1}{2}}, \eta_{l+\frac{1}{2}})$, satisfying $x_{i+\frac{1}{2}} - x_{i-\frac{1}{2}} = h_x$, $y_{j+\frac{1}{2}} - y_{j-\frac{1}{2}} = h_y$, $\xi_{k+\frac{1}{2}} - \xi_{k-\frac{1}{2}} = h_\xi$, and $\eta_{l+\frac{1}{2}} - \eta_{l-\frac{1}{2}} = h_\eta$. The cells are centered at $(x_i, y_j, \xi_k, \eta_l)$, where $x_i = \frac{1}{2}\left(x_{i-\frac{1}{2}} + x_{i+\frac{1}{2}}\right)$, $y_j = \frac{1}{2}\left(y_{j-\frac{1}{2}} + y_{j+\frac{1}{2}}\right)$, $\xi_k = \frac{1}{2}\left(\xi_{k-\frac{1}{2}} + \xi_{k+\frac{1}{2}}\right)$, $\eta_l =$

$\frac{1}{2}\left(\eta_{l-\frac{1}{2}}+\eta_{l+\frac{1}{2}}\right)$. We do not discrete in time now so that we can choose different schemes, such as Runge-Kutta methods, in time for different accuracy requirements. The cell averages of $(u_\tau)^n_{ijkl}$ are defined by

$$(u_\tau)_{ijkl}=\frac{1}{h_xh_yh_\xi h_\eta}\int_{x_{i-\frac{1}{2}}}^{x_{i+\frac{1}{2}}}\int_{y_{j-\frac{1}{2}}}^{y_{j+\frac{1}{2}}}\int_{\xi_{k-\frac{1}{2}}}^{\xi_{k+\frac{1}{2}}}\int_{\eta_{l-\frac{1}{2}}}^{\eta_{l+\frac{1}{2}}}u_\tau(x,y,\xi,\eta,t)d\eta d\xi dydx,\quad \tau=1,2.$$

The Liouville equations (25) then can be discretized as

$$\begin{aligned}\Big[(u_\tau)_{ijkl}\Big]_t=&-\frac{1}{h_x}\xi_k\left((u_\tau)^-_{i+\frac{1}{2},jkl}-(u_\tau)^+_{i-\frac{1}{2},jkl}\right)\\&-\frac{1}{h_y}\eta_l\left((u_\tau)^-_{i,j+\frac{1}{2},kl}-(u_\tau)^+_{i,j-\frac{1}{2},kl}\right)\\&+\frac{1}{h_\xi}\frac{\partial\lambda_\tau}{\partial x}(x_i,y_j)\left((u_\tau)^-_{ij,k+\frac{1}{2},l}-(u_\tau)^+_{ij,k-\frac{1}{2},l}\right)\\&+\frac{1}{h_\eta}\frac{\partial\lambda_\tau}{\partial y}(x_i,y_j)\left((u_\tau)^-_{ijk,l+\frac{1}{2}}-(u_\tau)^+_{ijk,l-\frac{1}{2}}\right).\end{aligned}\tag{26}$$

For points away from S^*, the numerical flux in (26) is given by the upwind (which is quite diffusive) or its high resolution extension using slope limiters [25] (which offers much better numerical resolution than its first order counterpart). Since no hopping occurs, the fluxes are continuous. For example, at $x=x_{i+\frac{1}{2}}$, we define $(u_\tau)^-_{i+\frac{1}{2},jkl}$=$(u_\tau)^+_{i+\frac{1}{2},jkl}$, $\tau=1,2$. In other directions, the fluxes are defined similarly.

Now we introduce the interface condition for the numerical flux on S^*. Recall that S^* is given by

$$S^*=\left\{(\mathbf{x},\mathbf{k})\in R^2_{\mathbf{x}}\times R^2_{\mathbf{k}}|v(\mathbf{x})\cdot\nabla_{\mathbf{x}}v(\mathbf{x})\mathbf{k}=0\right\},\quad \mathbf{x}=(x,y),\quad \mathbf{k}=(\xi,\eta),$$

which is a curved surface in the phase space $R^2_{\mathbf{x}}\times R^2_{\mathbf{k}}$. In order to design a numerical scheme, we will approximate this curved surface by the closest points on the mesh, similar to what was done in [11]. In [11] the authors used a dimension-by-dimension sweeping to detect the interface. Here we adopt the same approach to approximate S^* in 4D phase space. First of all, we define a function

$$F(x,y,\xi,\eta)=v(\mathbf{x})\cdot\nabla_{\mathbf{x}}v(\mathbf{x})\mathbf{k},\quad \mathbf{x}=(x,y),\quad \mathbf{k}=(\xi,\eta).$$

In the x-direction, we check the sign of $D_{i+\frac{1}{2}}=F(x_i,y_j,\xi_k,\eta_l)F(x_{i+1},y_j,\xi_k,\eta_l)$ for all i. If $D_{i+\frac{1}{2}}\le 0$, we assume there is an interface point at $x=x_{i+\frac{1}{2}}$, This of course introduces an $O(h_x)$ error, but for a Cartesian grid we will tolerate such an error. For other directions, similar sweeping process can determine the approximate location of the S^* in the corresponding direction.

We here just assume u_1 is non-zero and u_2 vanishes, since for the case where u_1 vanishes and u_2 is non-zero, the scheme can be obtained similarly. Suppose the flux u_1 passes through the approximate interface. Part of it will hop to u_2. We approximate the hopping probabilities by the Landau-Zener formula (21), which take values at the cell centers, that is $T_{ijkl}=T(x_i,y_j,\xi_k,\eta_l)$.

In the following, we will explain how to define the numerical fluxes $(u_\tau)^\pm_{i+\frac{1}{2},jkl}$, $(u_\tau)^\pm_{ij,k+\frac{1}{2},l}$, $\tau=1,2$ on the interface. The numerical fluxes $(u_\tau)^\pm_{i,j+\frac{1}{2},kl}$, $(u_\tau)^{n,\pm}_{ijk,l+\frac{1}{2}}$, $\tau=1,2$ are defined similarly.

Numerical fluxes at S^*.

If $(x_{i+\frac{1}{2}}, y_j, \xi_k, \eta_l)$ is on the interface, then in the x direction,
for $(u_1)^{\pm}_{i+\frac{1}{2},jkl}$,
1. if $\xi_k \geq 0$,
$(u_1)^{-}_{i+\frac{1}{2},jkl} = (u_1)_{ijkl} + \frac{1}{2}h_x(\sigma_1)_{\underline{i},jkl}, \quad (u_1)^{+}_{i+\frac{1}{2},jkl} = (1 - T_{ijkl})\,(u_1)^{-}_{i+\frac{1}{2},jkl}$,
2. if $\xi_k < 0$,
$(u_1)^{+}_{i+\frac{1}{2},jkl} = (u_1)_{i+1,jkl} - \frac{1}{2}h_x(\sigma_1)_{\underline{i+1},jkl}$, $(u_1)^{-}_{i+\frac{1}{2},jkl} = (1 - T_{ijkl})\,(u_1)^{+}_{i+\frac{1}{2},jkl}$,
for $(u_2)^{\pm}_{i+\frac{1}{2},jkl}$,
1. if $\xi_k \geq 0$,
$(u_2)^{-}_{i+\frac{1}{2},jkl} = (u_2)_{ijkl} + \frac{1}{2}h_x(\sigma_2)_{\underline{i},jkl}$,
$(u_2)^{+}_{i+\frac{1}{2},jkl} = (u_2)^{-}_{i+\frac{1}{2},jkl} + T_{ijkl}\,(u_1)^{-}_{i+\frac{1}{2},jkl}$,
2. if $\xi_k < 0$,
$(u_2)^{+}_{i+\frac{1}{2},jkl} = (u_2)_{i+1,jkl} - \frac{1}{2}h_x(\sigma_2)_{\underline{i+1},jkl}$,
$(u_2)^{-}_{i+\frac{1}{2},jkl} = (u_2)^{+}_{i+\frac{1}{2},jkl} + T_{ijkl}\,(u_1)^{+}_{i+\frac{1}{2},jkl}$.

If $(x_i, y_j, \xi_{k+\frac{1}{2}}, \eta_l)$ is on the interface, then in the ξ direction,
for $(u_1)^{\pm}_{ij,k+\frac{1}{2},l}$,
1. if $-\frac{\partial \lambda_1}{\partial x}(x_i, y_j) \geq 0$,
$(u_1)^{-}_{ij,k+\frac{1}{2},l} = (u_1)_{ijkl} + \frac{1}{2}h_\xi(\sigma_1)_{ij,\underline{k},l}$,
$(u_1)^{+}_{ij,k+\frac{1}{2},l} = (1 - T_{ijkl})\,(u_1)^{-}_{ij,k+\frac{1}{2},l}$,
2. if $-\frac{\partial \lambda_1}{\partial x}(x_i, y_j) < 0$,
$(u_1)^{+}_{ij,k+\frac{1}{2},l} = (u_1)_{ij,k+1,l} - \frac{1}{2}h_\xi(\sigma_1)_{ij,\underline{k+1},l}$,
$(u_1)^{-}_{ij,k+\frac{1}{2},l} = (1 - T_{ijkl})\,(u_1)^{+}_{ij,k+\frac{1}{2},l}$,
for $(u_2)^{\pm}_{ij,k+\frac{1}{2},l}$,
1. if $-\frac{\partial \lambda_2}{\partial x}(x_i, y_j) \geq 0$,
$(u_2)^{-}_{ij,k+\frac{1}{2},l} = (u_2)_{ijkl} + \frac{1}{2}h_\xi(\sigma_2)_{ij,\underline{k},l}$
$(u_2)^{+}_{ij,k+\frac{1}{2},l} = (u_2)^{-}_{ij,k+\frac{1}{2},l} + A_{ijkl}\left|\frac{\partial \lambda_1}{\partial x}/\frac{\partial \lambda_2}{\partial x}\right|$
2. if $-\frac{\partial \lambda_2}{\partial x}(x_i, y_j) < 0$,
$(u_2)^{+}_{ij,k+\frac{1}{2},l} = (u_2)_{ij,k+1,l} - \frac{1}{2}h_\xi(\sigma_2)_{ij,\underline{k+1},l}$
$(u_2)^{-}_{ij,k+\frac{1}{2},l} = (u_2)^{+}_{ij,k+\frac{1}{2},l} + A_{ijkl}\left|\frac{\partial \lambda_1}{\partial x}/\frac{\partial \lambda_2}{\partial x}\right|$
where

$$A_{ijkl} = \begin{cases} T_{ijkl}\,(u_1)^{-}_{ij,k+\frac{1}{2},l}, & \text{when } \frac{\partial \lambda_1}{\partial x}(x_i, y_j) \geq 0, \\ T_{ijkl}\,(u_1)^{+}_{ij,k+\frac{1}{2},l}, & \text{when } \frac{\partial \lambda_1}{\partial x}(x_i, y_j) < 0. \end{cases}$$

Note that in the numerical flux in the direction of ξ, the term $\left|\frac{\partial \lambda_1}{\partial x}/\frac{\partial \lambda_2}{\partial x}\right|$ is to reflect the interface condition (24) in the ξ-direction, namely, the flux in the normal direction to the interface is continuous.

Here $(\sigma_\tau)_{\underline{i}jkl}$ is the slope of u_1 in the cell centered at $(x_i, y_j, \xi_k, \eta_l)$ in x-direction and $(\sigma_\tau)_{ij\underline{k}l}$ in ξ direction. One possible choice is the *monotonized central-difference limiter*, which can be defined by

$$(\sigma_\tau)^n_{\underline{i}jkl} = \text{minmod}(\frac{(u_\tau)^n_{i+1,jkl} - (u_\tau)^n_{i-1,jkl}}{2h_x}, 2\frac{(u_\tau)^n_{i+1,jkl} - (u_\tau)^n_{i,jkl}}{h_x}, 2\frac{(u_\tau)^n_{i,jkl} - (u_\tau)^n_{i-1,jkl}}{h_x}). \tag{27}$$

The definitions of other slopes are similar. In general, one probably needs to modify slope limiter near the interface by using the Hamiltonian preserving principle across the interface, as in [17]. For the numerical examples in the next section, we just use the monotonized central-difference limiter, which works well for our examples, therefore we do not consider this issue here.

The time discretization can be any numerical ODE solver.

Remark 3.1 *In the Hamiltonian-preserving schemes, see [11, 15, 14], when the transmissions happen on the interface, one needs to adjust the momenta in order to conserve the total Hamiltonian. In this paper, since the probability in the Landau-Zener formula (21) decays exponentially, most of the hoppings happen in the neighborhood of the crossing point, where the energy difference between two potential energy surfaces is negligible. Therefore we do not consider the adjustment of momentum here. However, the momentum adjustment is sometimes necessary and it will be addressed in our future work.*

3.3 Positivity and l_1 stability

It is important for the numerical scheme to guarantee the positivity of u_1 and u_2 when solving the Liouville equations (25) with (24), since they represent the densities in phase space.

We consider the scheme for (25) with (24) using the first order numerical flux, and the forward Euler method in time. Let

$$\alpha_{ijkl} = \begin{cases} 0, & (x_i, y_j, \xi_k, \eta_l) \in \mathbb{R}^2_{\mathbf{x}} \times \mathbb{R}^2_{\mathbf{k}} \backslash S, \\ T_{ijkl}, & (x_i, y_j, \xi_k, \eta_l) \in S, \end{cases}$$

be the indicator, which equals the Landau-Zener formula T_{ijkl} on the crossing set S^*, and vanishes away from S^*. For simplicity, we only consider the case $\xi_k > 0$, $\eta_l > 0$, $\frac{\partial \lambda_1}{\partial x}(x_i, y_j) < 0$, $\frac{\partial \lambda_1}{\partial y}(x_i, y_j) < 0$, $\frac{\partial \lambda_2}{\partial x}(x_i, y_j) > 0$ and $\frac{\partial \lambda_2}{\partial y}(x_i, y_j) > 0$. The other cases can be treated similarly with the same conclusion. The scheme (26) for u_1 and u_2 becomes,

$$\begin{aligned} (u_1)^{n+1}_{ijkl} =& (u_1)^n_{ijkl} - \frac{\Delta t}{h_x}\xi_k \left((u_1)^n_{ijkl} - (1 - \alpha_{i-1,jkl}) (u_1)^n_{i-1,jkl} \right) \\ &- \frac{\Delta t}{h_y}\eta_l \left((u_1)^n_{ijkl} - (1 - \alpha_{i,j-1,kl}) (u_1)^n_{i,j-1,kl} \right) \\ &+ \frac{\Delta t}{h_\xi}\frac{\partial \lambda_1}{\partial x}(x_i, y_j) \left((u_1)^n_{ijkl} - (1 - \alpha_{ij,k-1,l}) (u_1)^n_{ij,k-1,l} \right) \\ &+ \frac{\Delta t}{h_\eta}\frac{\partial \lambda_1}{\partial y}(x_i, y_j) \left((u_1)^n_{ijkl} - (1 - \alpha_{ijk,l-1}) (u_1)^n_{ijk,l-1} \right), \end{aligned} \tag{28}$$

$$
\begin{aligned}
(u_2)_{ijkl}^{n+1} = & (u_2)_{ijkl}^{n} - \frac{\Delta t}{h_x}\xi_k \left((u_2)_{ijkl}^{n} - \left(\alpha_{i-1,jkl} \, (u_1)_{i-1,jkl}^{n} + (u_2)_{i-1,jkl}^{n} \right) \right) \\
& - \frac{\Delta t}{h_y}\eta_l \left((u_2)_{ijkl}^{n} - \left(\alpha_{i,j-1,kl} \, (u_1)_{i,j-1,kl}^{n} + (u_2)_{i,j-1,kl}^{n} \right) \right) \\
& + \frac{\Delta t}{h_\xi}\frac{\partial \lambda_2}{\partial x}(x_i, y_j) \left(\alpha_{ij,k+1,l} \, (u_1)_{ij,k+1,l}^{n} + (u_2)_{ij,k+1,l}^{n} - (u_2)_{ijkl}^{n} \right) \\
& + \frac{\Delta t}{h_\eta}\frac{\partial \lambda_2}{\partial y}(x_i, y_j) \left(\alpha_{ijk,l+1} \, (u_1)_{ijk,l+1}^{n} + (u_2)_{ijk,l+1}^{n} - (u_2)_{ijkl}^{n} \right),
\end{aligned} \tag{29}
$$

We can rewrite them into

$$
\begin{aligned}
(u_1)_{ijkl}^{n+1} = & \left(1 - \frac{\Delta t}{h_x}\xi_k - \frac{\Delta t}{h_y}\eta_l + \frac{\Delta t}{h_\xi}\frac{\partial \lambda_1}{\partial x}(x_i, y_j) + \frac{\Delta t}{h_\eta}\frac{\partial \lambda_1}{\partial y}(x_i, y_j) \right) (u_1)_{ijkl}^{n} \\
& + \frac{\Delta t}{h_x}\xi_k (1 - \alpha_{i-1,jkl}) \, (u_1)_{i-1,jkl}^{n} + \frac{\Delta t}{h_y}\eta_l (1 - \alpha_{i,j-1,kl}) \, (u_1)_{i,j-1,kl}^{n} \\
& - \frac{\Delta t}{h_\xi}\frac{\partial \lambda_1}{\partial x}(x_i, y_j)(1 - \alpha_{ij,k-1,l}) \, (u_1)_{ij,k-1,l}^{n} \\
& - \frac{\Delta t}{h_\eta}\frac{\partial \lambda_1}{\partial y}(x_i, y_j)(1 - \alpha_{ijk,l-1}) \, (u_1)_{ijk,l-1}^{n},
\end{aligned} \tag{30}
$$

$$
\begin{aligned}
(u_2)_{ijkl}^{n+1} = & \left(1 - \frac{\Delta t}{h_x}\xi_k - \frac{\Delta t}{h_y}\eta_l - \frac{\Delta t}{h_\xi}\frac{\partial \lambda_2}{\partial x}(x_i, y_j) - \frac{\Delta t}{h_\eta}\frac{\partial \lambda_2}{\partial y}(x_i, y_j) \right) (u_2)_{ijkl}^{n} \\
& + \frac{\Delta t}{h_x}\xi_k \left(\alpha_{i-1,jkl} \, (u_1)_{i-1,jkl}^{n} + (u_2)_{i-1,jkl}^{n} \right) \\
& + \frac{\Delta t}{h_y}\eta_l \left(\alpha_{i,j-1,kl} \, (u_1)_{i,j-1,kl}^{n} + (u_2)_{i,j-1,kl}^{n} \right) \\
& + \frac{\Delta t}{h_\xi}\frac{\partial \lambda_2}{\partial x}(x_i, y_j) \left(\alpha_{ij,k+1,l} \, (u_1)_{ij,k+1,l}^{n} + (u_2)_{ij,k+1,l}^{n} \right) \\
& + \frac{\Delta t}{h_\eta}\frac{\partial \lambda_2}{\partial y}(x_i, y_j) \left(\alpha_{ijk,l+1} \, (u_1)_{ijk,l+1}^{n} + (u_2)_{ijk,l+1}^{n} \right)
\end{aligned} \tag{31}
$$

Now we investigate the positivity of schemes (30) and (31). This is to prove that if $(u_\tau)_{ijkl}^{n} \geq 0, \tau = 1, 2, \forall i, j, k, l$, then it is also true for $(u_\tau)_{ijkl}^{n+1}, \tau = 1, 2$. Clearly, one just needs to show that all coefficients for $(u_\tau)_{ijkl}^{n}, \tau = 1, 2$ are non-negative. For the case we considered here, notice that $\xi_k > 0$, $\eta_l > 0$, $\frac{\partial \lambda_1}{\partial x}(x_i, y_j) < 0$, $\frac{\partial \lambda_1}{\partial y}(x_i, y_j) < 0$, $\frac{\partial \lambda_2}{\partial x}(x_i, y_j) > 0$, $\frac{\partial \lambda_2}{\partial y}(x_i, y_j) > 0$ and $0 \leq \alpha_{ijkl} \leq 1, \forall i, j, k, l$.
If,

$$
\begin{aligned}
& 1 - \frac{\Delta t}{h_x}\xi_k - \frac{\Delta t}{h_y}\eta_l + \frac{\Delta t}{h_\xi}\frac{\partial \lambda_1}{\partial x}(x_i, y_j) + \frac{\Delta t}{h_\eta}\frac{\partial \lambda_1}{\partial y}(x_i, y_j) > 0, \\
& 1 - \frac{\Delta t}{h_x}\xi_k - \frac{\Delta t}{h_y}\eta_l - \frac{\Delta t}{h_\xi}\frac{\partial \lambda_2}{\partial x}(x_i, y_j) - \frac{\Delta t}{h_\eta}\frac{\partial \lambda_2}{\partial y}(x_i, y_j) > 0,
\end{aligned}
$$

more precisely,

$$
\begin{aligned}
& \left(\frac{1}{h_x}\xi_k + \frac{1}{h_y}\eta_l - \frac{1}{h_\xi}\frac{\partial \lambda_1}{\partial x}(x_i, y_j) - \frac{1}{h_\eta}\frac{\partial \lambda_1}{\partial y}(x_i, y_j) \right) \Delta t < 1, \\
& \left(\frac{1}{h_x}\xi_k + \frac{1}{h_y}\eta_l + \frac{1}{h_\xi}\frac{\partial \lambda_2}{\partial x}(x_i, y_j) + \frac{1}{h_\eta}\frac{\partial \lambda_2}{\partial y}(x_i, y_j) \right) \Delta t < 1,
\end{aligned}
$$

then all coefficients for $(u_\tau)^n_{ijkl} \geq 0, \tau = 1, 2$ are non-negative. Generally we must assume

$$\Delta t \max_{i,j,k,l} \left(\frac{1}{h_x}|\xi_k| + \frac{1}{h_y}|\eta_l| + \frac{1}{h_\xi}\left|\frac{\partial \lambda_\tau}{\partial x}(x_i, y_j)\right| + \frac{1}{h_\eta}\left|\frac{\partial \lambda_\tau}{\partial y}(x_i, y_j)\right| \right) < 1, \quad \tau = 1, 2. \tag{32}$$

The scheme (26) is positive when the hyperbolic type CFL condition (32) is satisfied. Since the scheme (26) is flux conservative and positive, the l_1 stability follows easily. We can summarize the result in this section in the following theorem.

Theorem 3.2 *For the Liouville equations (25) with the interface condition (24), when* $(u_\tau)^n_{ijkl} \geq 0, \quad \tau = 1, 2,$ *and the CFL condition (32) is satisfied, the algorithm described in the last subsection, for the first order, preserves the positivity of the solution and has the* l_1 *stability, i.e.*

$$(u_\tau)^n_{ijkl} \geq 0, \quad \tau = 1, 2,$$

$$\sum_{i,j,k,l} \left((u_1)^n_{ijkl} + (u_2)^n_{ijkl} \right) h_x h_y h_\xi h_\eta \leq \sum_{i,j,k,l} \left((u_1)^0_{ijkl} + (u_2)^0_{ijkl} \right) h_x h_y h_\xi h_\eta.$$

4 Numerical examples

In this section we present numerical examples to demonstrate the validity of the surface hopping method proposed in Section 3 and to show the numerical accuracy of the numerical scheme. In the numerical computations the second order upwind shock capture method with the slope limiter (27) is used.

In our numerical experiments we choose the initial data and the potential the same as those in [23], where $u_2(0, \cdot)$, denoting initial value of the probability density for the lower energy level, vanishes. All the u_2, the probability density for the lower level, is generated from u_1, the one for the upper level, when u_1 passes through the crossing set S^*. The potential corresponding to the lower energy level is also designed to be repulsive so that u_2 will never come back after it leaves S^*. This way u_1 and u_2 will not arrive at the same point on the interface at the same time. Thus we do not need to concern the coherence phenomena. More general cases will be considered in our future work.

4.1 Preliminary

We consider the time-evolution of the two-level Schrödinger equations,

$$i\varepsilon \partial_t \psi^\varepsilon(t, \mathbf{x}) = \left(-\frac{\varepsilon^2}{2}\Delta_{\mathbf{x}} + V(\mathbf{x}) \right) \psi^\varepsilon(t, \mathbf{x}), \quad (t, \mathbf{x}) \in \mathbb{R}^+ \times \mathbb{R}^2, \tag{33}$$

$$\psi^\varepsilon(0, \mathbf{x}) = \psi^\varepsilon_0(\mathbf{x}) \in \mathbf{L}^2(\mathbb{R}^2, \mathbb{C}^2). \tag{34}$$

with two different potentials. One is the linear isotropic potential,

$$V_{iso}(\mathbf{x}) = \begin{pmatrix} x & y \\ y & -x \end{pmatrix}, \quad \mathbf{x} = (x, y) \in \mathbb{R}^2, \tag{35}$$

and the other is the linear $E \otimes e$ Jahn-Teller potential [35],

$$V_{JT}(\mathbf{x}) = |\mathbf{x}|^2 + \begin{pmatrix} x & y \\ y & -x \end{pmatrix}, \quad \mathbf{x} = (x, y) \in \mathbb{R}^2, \tag{36}$$

which models the displacement of triatomic molecules from the equilateral triangle configuration [23].

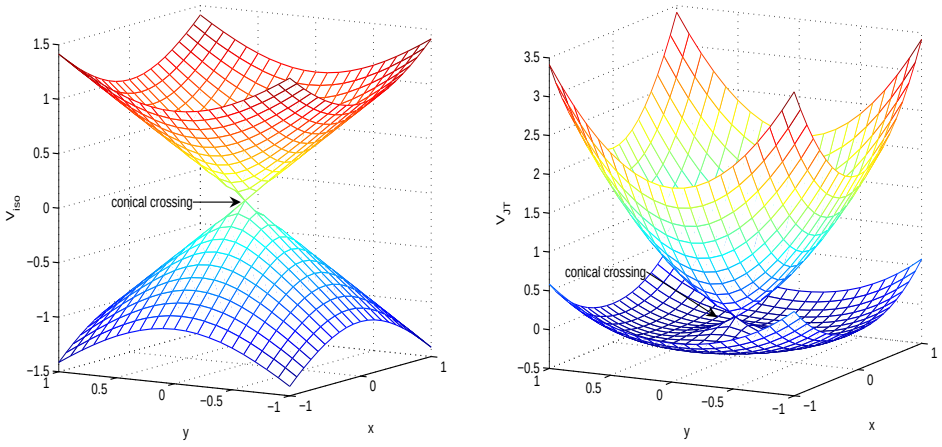

Figure 4.1: The conical crossings for different potentials. The left is for V_{iso}, and the right is for V_{JT}. Here $\epsilon = 0.01$ and the crossing point is (0, 0).

In Figure 4.1, we depict the conical crossings of potentials V_{iso} and V_{JT} versus x and y. One can easily find that the potential energy surfaces of the potentials V_{iso} and V_{JT} have the same conical crossing set $S = (0, 0)$.

Let $\chi_1(\mathbf{x}) = (\cos(\frac{\theta(\mathbf{x})}{2}), \quad \sin(\frac{\theta(\mathbf{x})}{2}))^T$ and $\chi_2(\mathbf{x}) = (-\sin(\frac{\theta(\mathbf{x})}{2}), \quad \cos(\frac{\theta(\mathbf{x})}{2}))^T$ denote the normalized eigenvectors of the potential V_{iso} (or V_{JT}) associated with the upper and lower energy level. Here $\theta(\mathbf{x}) \in (-\pi, \pi)$ is the polar angle of $\mathbf{x} = (x, y) \in \mathbb{R}^2$.

The initial value for the two-level Schrödinger problem (33)(34) is given by,

$$\psi_0^\varepsilon(\mathbf{x}) = g^\varepsilon(\mathbf{x})\chi_1(\mathbf{x}),$$

where $g_0^\varepsilon(\mathbf{x})$ is an ε-scaled Gaussian wave packet,

$$g_0^\varepsilon(\mathbf{x}) = \frac{1}{\sqrt{\pi\varepsilon}} \exp\left\{-\frac{1}{2\varepsilon}|\mathbf{x} - \mathbf{x}_0^\varepsilon|^2 + \frac{i}{\varepsilon}\mathbf{k}_0 \cdot (\mathbf{x} - \mathbf{x}_0^\epsilon)\right\},$$

which is centered in $(\mathbf{x}_0^\varepsilon, \mathbf{k}_0) \in R_{\mathbf{x}}^2 \times R_{\mathbf{k}}^2$ with $||g_0^\varepsilon(\mathbf{x})||_{L^2} = 1$, see [23, 27, 9].

The Gaussian wave packets associated with the upper eigenvalue are a simple model for a molecule excited by light or a laser-pulse. First, an initial wave packet is excited from the lower level (ground state) potential by a short laser pulse in the femto or nanosecond regime. This excited wave packet then evolves under the influence of the upper level (excited state) potential. Non-adiabatic transitions between adjacent potential energy surfaces will happen when this wave packet moves close to the crossing regions, see [19, 30].

The standard operator splitting spectral method is used for the Schödinger solver, see [23, 1]. We refer to the appendix for a brief review of this method.

Figure 4.2 depicts the contours of energy populations for the propagation of a Gaussian wave packet through the conical crossing with V_{iso}. The solution was obtained

by the Schrödinger solver, with $\varepsilon = 0.01$ and $h = \frac{1}{400}$. Initially the wave packet is only on the upper energy level. At time $t = 2\sqrt{\varepsilon}$, the Gaussian wave packet is still away from the crossing point, therefore the lower energy level is still empty. Around time $t = 4\sqrt{\varepsilon}$, the wave packet on the upper level moves near the crossing point, then part of it will hop to the lower energy level. Finally at time $t = 6\sqrt{\varepsilon}$ the hopping process finishes and the wave packets in both energy levels will move away from the crossing point.

According to the discussion in the previous section, for the surface hopping method, the crossing manifold S^* can be described by

$$S^* = \{(\mathbf{x}, \mathbf{k}) |\ \mathbf{x} \cdot \mathbf{k} = 0\ \},$$

or more precisely,

$$S^* = \{(x, y, \xi, \eta) |\ x\xi + y\eta = 0\ \}.$$

This crossing manifold is a curved interface in 4D phase space and will be approximated by the adjacent interfaces using the approach discussed in Section 3.2. For those potentials, V_{iso} and V_{JT}, the Landau-Zener formula (21) can be written in a explicit form,

$$T(\mathbf{x}, \mathbf{k}) = T(x, y, \xi, \eta) = \exp\left\{ -\frac{\pi}{\varepsilon} \frac{(x\eta - y\xi)^2}{\sqrt[3]{\xi^2 + \eta^2}} \right\}.$$

The initial values of the corresponding Liouville equation (16) are given by,

$$u_1(0, \mathbf{x}, \mathbf{k}) = \frac{1}{(\pi\varepsilon)^2} \exp\left(-\frac{1}{\varepsilon}|\mathbf{x} - \mathbf{x}_0^\varepsilon|^2 - \frac{1}{\varepsilon}|\mathbf{k} - \mathbf{k}_0|^2 \right), \tag{37}$$

$$u_2(0, \mathbf{x}, \mathbf{k}) = 0, \tag{38}$$

where $u_1(0, \mathbf{x}, \mathbf{k})$ is a Gaussian given by the Wigner transform of an ε-scaled Gaussian wavepacket $\psi_0^\varepsilon(\mathbf{x})$.

In the numerical experiments, the semiclassical parameter is chosen as $\varepsilon = 10^{-k}, k = 2, 3, 4$.

The center of the initial Gaussian wave packet is chosen as, refer to [23],

$$\mathbf{x}_0^\varepsilon = (5\sqrt{\varepsilon}, \frac{1}{2}\sqrt{\varepsilon}), \quad \mathbf{k}_0 = (-1, 0), \tag{39}$$

such that the overlap of the initial Gaussian's support set with the neighborhood of the crossing point $\mathbf{x} = (0, 0)$ is negligible.

The computational time is $[t_i, t_f] = [0, 10\sqrt{\varepsilon}]$. During this time, the Gaussian wave packet $\psi^\varepsilon(t, \mathbf{x})$ moves towards the crossing set. Then part of the population density will hop to the lower energy level according to the Landau-Zener formula and the other part will remain in the upper energy level. Finally the population density on both energy levels will move away from the crossing set.

Let $|\Pi^\tau \psi^\varepsilon(t, \mathbf{x})|^2$, $\tau = 1, 2$ denote the position densities of the projected wave function, where $\Pi^\tau = \chi_\tau(\mathbf{x})(\chi_\tau(\mathbf{x}))^T$, $\tau = 1, 2$ is the orthogonal projection matrix. The total population on the upper (or lower) energy level at any time t is defined by

$$P_{sch}^\tau(t) = \int_{R_\mathbf{x}^2} |\Pi^\tau \psi^\varepsilon(t, \mathbf{x})|^2 d\mathbf{x}, \quad \tau = 1, 2.$$

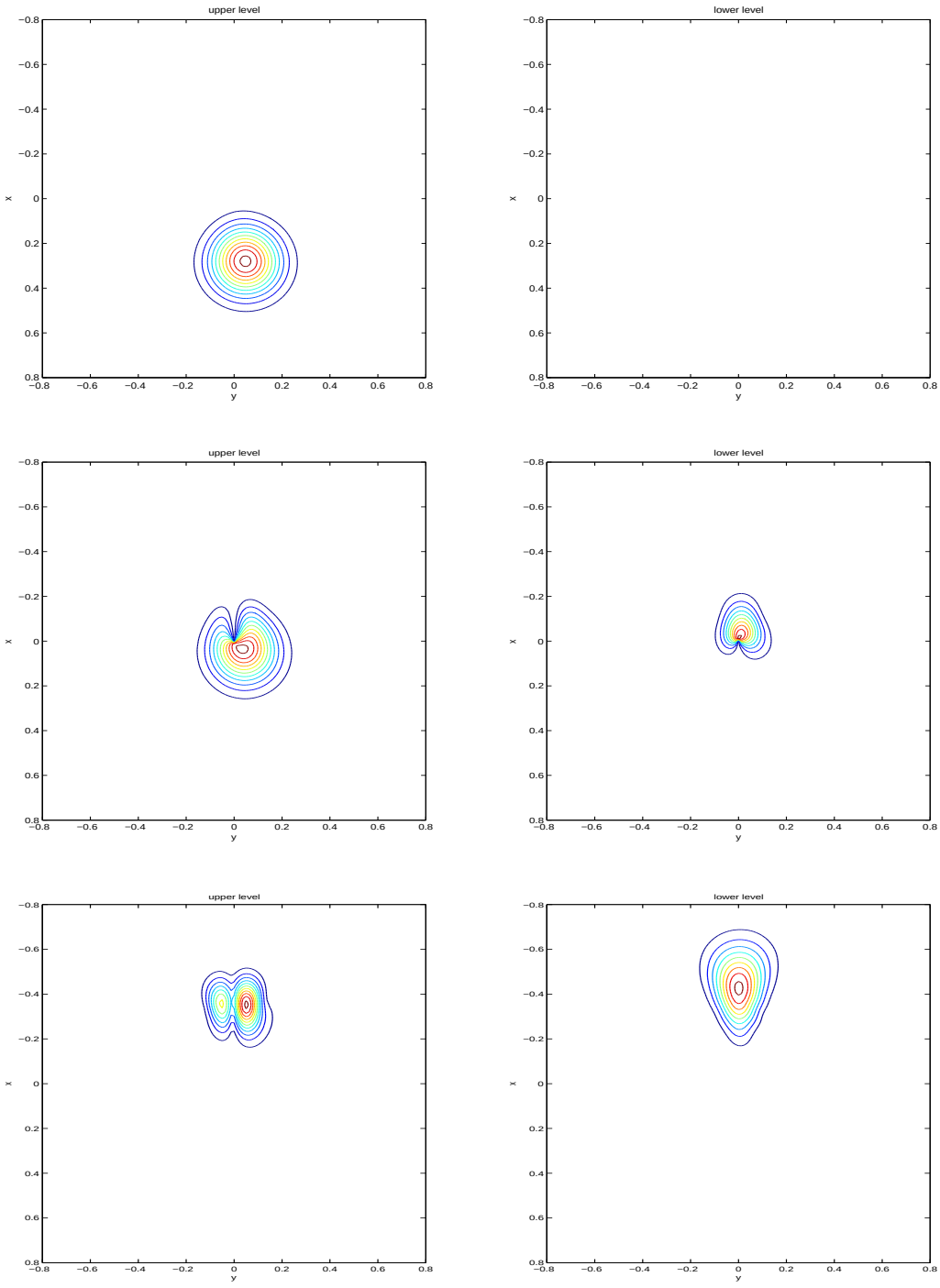

Figure 4.2: The plots show the energy populations for the propagation of a Gaussian wave packet through the conical crossing with V_{iso}. The solution was obtained by the Schrödinger solver, with $\varepsilon = 0.01$ and $h = \frac{1}{400}$. From top to bottom, we plot $|\Pi^\tau \psi^\varepsilon(t, \mathbf{x})|^2$, $\tau = 1, 2$, $t = 2\sqrt{\varepsilon}$, $4\sqrt{\varepsilon}$ and $6\sqrt{\varepsilon}$, which correspond to pre-, during and after hopping periods. The left column corresponds to the upper level, and the right column corresponds to the lower level.

Similarly we can define the total population on the upper (or lower) energy level at any time t obtained by our Eulerian surface hopping method, that is,

$$P^{\tau}_{liou}(t) = \int_{R^2_{\mathbf{k}}} \int_{R^2_{\mathbf{x}}} u_\tau(t, \mathbf{x}, \mathbf{k}) d\mathbf{k} d\mathbf{x}, \quad \tau = 1, 2.$$

In the quantum dynamic simulation it is of interest to determine the final populations $P^\tau(t_f), \tau = 1, 2$ after the non-adiabatic transition, which gives the probability of finding the system in one of the two eigenspaces at time $t = t_f$. It is also of interest to get the population of the upper (or lower) level at all time, which gives the information of the whole surface hopping process. We will compare the results by solving the Schrödinger equation and the surface hopping method in the next subsection. Further more, the long time behavior of surface hopping process will also be tested.

Since the total populations are conserved, i.e.

$$P^1_{sch}(t) + P^2_{sch}(t) = 1, \quad P^1_{liou}(t) + P^2_{liou}(t) = 1, \quad \forall t > 0,$$

we only compare the upper energy level populations $P^1_{liou}(t)$ and $P^1_{sch}(t)$ in our numerical experiments. For simplicity we omit the superscript in next subsection.

4.2 Numerical results

In this section, we will consider the following two examples for the proposed numerical scheme.

Example 4.1 *The propagation equations of the Wigner measures corresponding to the solution to the Schrödinger equations (33) with the linear isotropic potential V_{iso} can be written as the following Liouville equations,*

$$\frac{\partial u_1}{\partial t} + \xi \frac{\partial u_1}{\partial x} + \eta \frac{\partial u_1}{\partial y} - \frac{x}{\sqrt{x^2+y^2}} \frac{\partial u_1}{\partial \xi} - \frac{y}{\sqrt{x^2+y^2}} \frac{\partial u_1}{\partial \eta} = 0, \tag{40}$$

$$\frac{\partial u_2}{\partial t} + \xi \frac{\partial u_2}{\partial x} + \eta \frac{\partial u_2}{\partial y} + \frac{x}{\sqrt{x^2+y^2}} \frac{\partial u_2}{\partial \xi} + \frac{y}{\sqrt{x^2+y^2}} \frac{\partial u_2}{\partial \eta} = 0, \tag{41}$$

with the initial values of u_1 and u_2 chosen as (37)-(39). We test the convergence between the original Schrödinger equation (33) and the Liouville equations (40)(41) by varying the semiclassical parameter as $\varepsilon = 10^{-2}$, 10^{-3}, 10^{-4}.

The computational domain for the Liouville equations (40)(41) is chosen to be $[x, y, \xi, \eta] = [-10\sqrt{\varepsilon}, 10\sqrt{\varepsilon}] \times [-5\sqrt{\varepsilon}, 5\sqrt{\varepsilon}] \times [-1 - 10\sqrt{\varepsilon}, -1 + 10\sqrt{\varepsilon}] \times [-10\sqrt{\varepsilon}, 10\sqrt{\varepsilon}]$. For simplicity, we choose the uniform mesh size $h = h_x = h_y = h_\xi = h_\eta$ and the time step $\tau = \frac{h}{4}$.

Example 4.2 *The propagation equations of the Wigner measures corresponding to the solution to the Schrödinger equations (33) with the linear $E \otimes e$ Jahn-Teller potential V_{JT} can be written as the following Liouville equations,*

$$\frac{\partial u_1}{\partial t} + \xi \frac{\partial u_1}{\partial x} + \eta \frac{\partial u_1}{\partial y} - (2x + \frac{x}{\sqrt{x^2+y^2}}) \frac{\partial u_1}{\partial \xi} - (2y + \frac{y}{\sqrt{x^2+y^2}}) \frac{\partial u_1}{\partial \eta} = 0, \tag{42}$$

$$\frac{\partial u_2}{\partial t} + \xi \frac{\partial u_2}{\partial x} + \eta \frac{\partial u_2}{\partial y} - (2x - \frac{x}{\sqrt{x^2+y^2}}) \frac{\partial u_2}{\partial \xi} - (2y - \frac{y}{\sqrt{x^2+y^2}}) \frac{\partial u_2}{\partial \eta} = 0, \tag{43}$$

with the initial values of u_1 and u_2 chosen as (37)-(39). We test the convergence between the original Schrödinger equation (33) and the Liouville equations (42)(43) by varying the semiclassical parameter as $\varepsilon = 10^{-2}$, 10^{-3}, 10^{-4}.

The computational domain for the Liouville equations (42)-(43) is chosen to be $[x, y, \xi, \eta] = [-12\sqrt{\varepsilon}, 12\sqrt{\varepsilon}] \times [-6\sqrt{\varepsilon}, 6\sqrt{\varepsilon}] \times [-1 - 12\sqrt{\varepsilon}, -1 + 12\sqrt{\varepsilon}] \times [-12\sqrt{\varepsilon}, 12\sqrt{\varepsilon}]$. For simplicity, we choose the uniform mesh size $h = h_x = h_y = h_\xi = h_\eta$ and the time step $\tau = \frac{h}{8}$.

Let

$$E^\varepsilon(t) = |P^\varepsilon_{sch}(t) - P^\varepsilon_{liou}(t)|$$

denote the absolute error of the upper level population during the hopping process for every fixed ε. The comparison of the model errors at $t = t_f$ between the Liouville solver and the Schrödinger solver, i.e. $E^\varepsilon(t_f)$, was done in [23]. Figure 4.3 shows that when we vary the semiclassical parameter as $\varepsilon = 0.01, 0.001, 0.0001$, the error of the upper energy level populations convergence in the order of $O(\sqrt{\varepsilon})$.

The probability density in the configuration space can be recovered by computing the zeroth moment,

$$(U_1)^n_{ij} = (U_1)(t^n, x_i, y_j) = \sum_{kl} (u_1)^n_{ijkl} h_\xi h_\eta.$$

For every fixed ε, we evaluate the accuracy of the high resolution finite volume scheme using the error of the population for the upper level defined by,

$$E_{pop} = \sum_{i,j} U^{num}_{ij} h_x h_y - \sum_{i,j} U^{exc}_{ij} h_x h_y,$$

where the reference solution U^{exc} is approximated by the result obtained on a very fine mesh.

We also use the l_1 norm error defined by,

$$E_{l_1} = \sum_{i,j} |U^{num}_{ij} - U^{exc}_{ij}| h_x h_y.$$

Figures 4.4 and 4.5 shows the E_{pop} and E_{l_1} for the upper level probability density for the linear isotropic potential V_{iso} and the linear $E \otimes e$ Jahn-Teller potential V_{JT} with different ε's. They are computed on different meshes in the phase space at $t = t_f$. One can see that our high resolution scheme converge to the reference solution, which is obtained on a very fine mesh, in nearly second order. Since both potentials have similar conical crossings, our Eulerian surface hopping method has similar performances.

Figure 4.6 plots the evolution of the upper energy level population obtained by different schemes and meshes for the potential V_{iso}. One can see that compared with the second order scheme, the first order one is very diffusive even on a very fine mesh. The second order one gives better agreements with the "exact" solution obtained by the Schrödinger solver. After the hopping process, i.e. after time $t = 0.5$, the offset is due to the model error. For the potential V_{JT}, the result is similar. Therefore we omit it here.

Figure 4.7 shows the long time performance of our surface hopping method with V_{iso}. From time $t = 0.3$ to $t = 0.55$, it undergoes the first hopping process. Between the first ($t = 0.55$) and second ($t = 2.8$) hoppings the particles on the upper level will move in the original directions and the velocities will decrease, until the velocities become zero. Then they will turn back and accelerate toward the crossing point again. The second hopping process takes place between $t = 2.8$ and $t = 3.5$. One can see that our semiclassical method captures the population density quite accurately after the hoppings even by using a very coarse mesh.

Figure 4.8 gives a similar result as figure 4.7, except that the potential V_{JT} is very steep so that three hopping processes occur during this time interval.

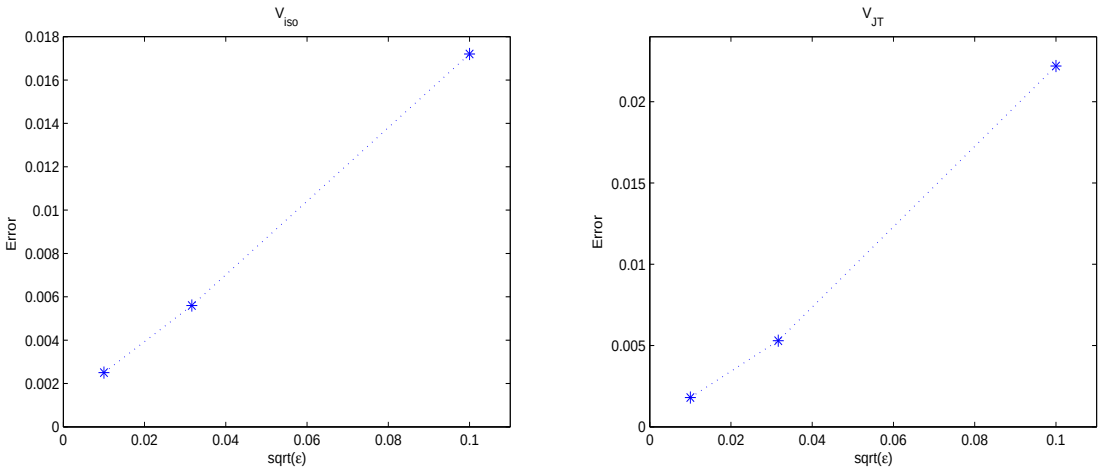

Figure 4.3: The error of the upper energy level populations as a function of $\sqrt{\varepsilon}$, when varying the semiclassical parameter $\epsilon = 0.0001, 0.001, 0.01$. The left is for the linear isotropic potential V_{iso} and the right is for the linear $E \otimes e$ Jahn-Teller potential V_{JT}.

5 Conclusion

In this paper, we constructed a surface hopping method for the Schrödinger equation with conical crossings in the *Eulerian* formulation. The method is based on the semiclassical approximation governed by the Liouville equations, which are valid away from the conical crossing manifold. At the crossing manifold, electrons hop to the other bond energy level with the probability determined by the Landau-Zener formula. This hopping mechanics is formulated as an interface condition, which is then built into the numerical flux for solving the underlying Liouville equation for each energy level. We studied the positivity, l_1 stability of the first order scheme, and conducted numerical experiments to study the accuracy and convergence rate of the proposed scheme. We also test the long time behavior of the surface hopping process.

The diagonal terms of the Wigner function give the semiclassical limit of the Schrödinger equation with conical crossings, however one loses the phase information of the wave function contained in the off-diagonal terms of the Wigner function, which are highly oscillatory and vanish when averaged over time. Therefore this algorithm

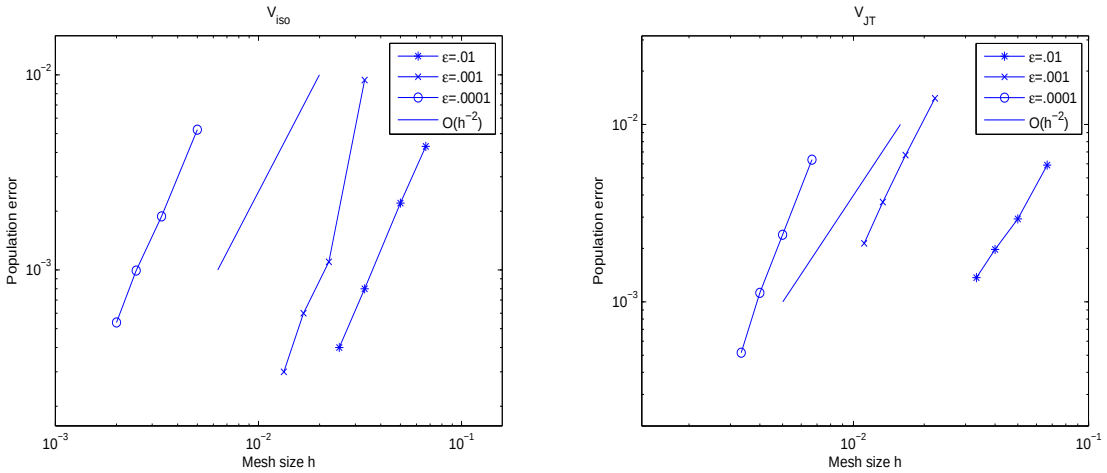

Figure 4.4: E_{pop}'sfor different ε's. The left is for the linear isotropic potential V_{iso}, and the right is for the linear $E \otimes e$ Jahn-Teller potential V_{JT}.

cannot resolve the possible interferences between parts of the wave function originating from different levels. Such interferences might occur if classical trajectories on the upper and the lower energy levels arrive to the same point in the crossing set at the same time. This will be studied in our future work.

Recently, Jin and Novak develop a coherent semiclassical transport model for pure-state quantum scattering problem using a complex Liouville equation, which retains the phase information needed for interference and has promising application, see [13].

6 Appendix: The Schrödinger Solver

The reference solver for Schrödinger equation (33) is the operator splitting spectral method (refer to [22]). Consider the numerical solution on the bounded computational domain $D = [a_1, a_2] \times [b_1, b_2] \times [t_i, t_f]$. We divide the domain D by a set of lines parallel to the x-, y- and t-axis to form a grid, and write $h_x = \frac{a_2 - a_1}{I}$, $h_y = \frac{b_2 - b_1}{J}$ and $\tau = \frac{t_f - t_i}{N}$ for the line spacings, where I, J and N are three positive integers. For simplicity, we assume $h = h_x = h_y$. The crossing points Ω are called the grid points,

$$\Omega = \{(x_i, y_j, t_n) | x_i = a_1 + ih, y_j = b_1 + jh, t_n = n\tau, i = 0, ..., I, j = 0, ..., J, n = 0, ..., N\}.$$

Suppose $\Psi_{ij}^n = \{(\psi_{ij}^{n1}, \psi_{ij}^{n2})^T | 0 \le i \le I,\ 0 \le j \le J,\ 0 \le n \le N\}$ is the numerical solution on Ω, where Ψ_{ij}^n represents the approximation solution of wave function $\psi^\varepsilon(t, x, y)$ on the grid point (x_i, y_j, t_n).

From time $t = t_n$ to time $t = t_{n+1}$, where $t_{n+1} = t_n + \tau$, $t_0 = 0$, the numerical solution can be approximated by,

$$\Psi_{ij}^{n+1} \approx \exp\left(\frac{i\epsilon\tau}{2}\Delta_{\mathbf{x}}\right) \exp\left(-\frac{i\tau}{\varepsilon}V(\mathbf{x})\right) \exp\left(\frac{i\varepsilon\tau}{2}\Delta_{\mathbf{x}}\right) \Psi_{ij}^n, \quad \mathbf{x} = (x, y).$$

The Laplace operator $\frac{i\epsilon\tau}{2}\Delta_{\mathbf{x}}$ can be efficiently approximated by the two-dimensional

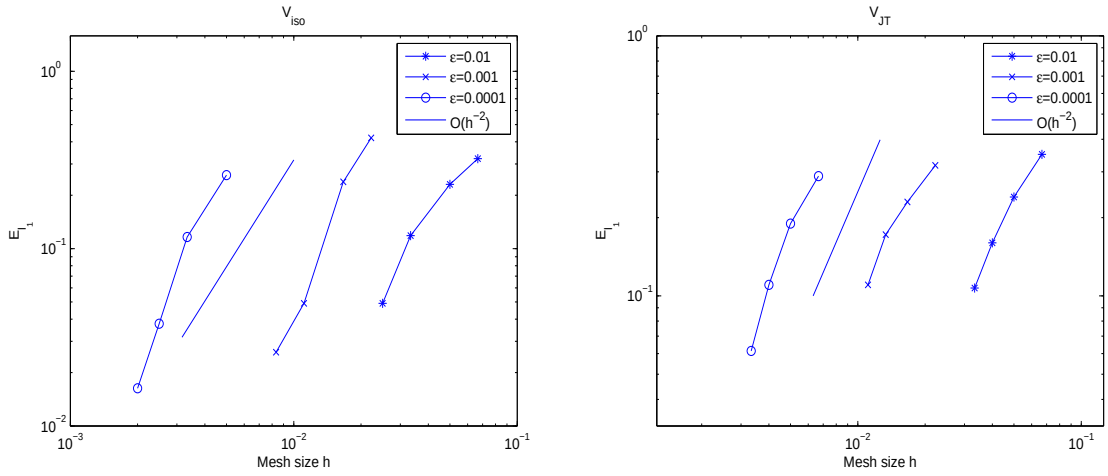

Figure 4.5: E_{l^1}'sfor different ϵ's. The left is for the linear isotropic potential V_{iso} and the right is for the linear $E \otimes e$ Jahn-Teller potential V_{JT}.

fast Fourier transform algorithm. For the linear isotropic potential,

$$V_{iso}(\mathbf{x}) = \begin{pmatrix} x & y \\ y & -x \end{pmatrix}, \quad \mathbf{x} = (x, y) \in \mathbb{R}^2,$$

the operator $\exp(-\frac{i\tau}{\epsilon}V(\mathbf{x}))$ can be approximated exactly by,

$$\exp(-\frac{\tau}{\varepsilon}V_{iso}(\mathbf{x})) = \cos(\frac{\tau}{\varepsilon}|\mathbf{x}|)I - \frac{i}{|\mathbf{x}|}\sin(\frac{\tau}{\varepsilon}|\mathbf{x}|)V_{iso}(\mathbf{x}).$$

The linear $E \otimes e$ Jahn-Teller potential V_{JT} can be handled in the same way. In [1, 23], the authors prove the meshing strategy $h = O(\varepsilon)$, $\tau = o(\varepsilon)$ giving the l^2-approximation of the wave function. Therefore the operator splitting spectral method is more advantagous in mesh size compared with finite difference method. However when the semiclassical parameter ε is very small, the operator splitting spectral method is still very expensive.

7 Acknowledgment

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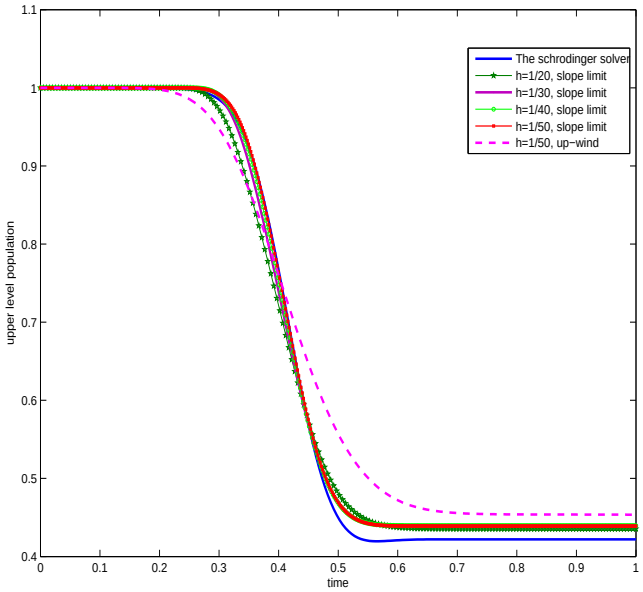

Figure 4.6: The comparison of different schemes and mesh sizes. The population of the upper energy level versus time are plotted. ε= 0.01.

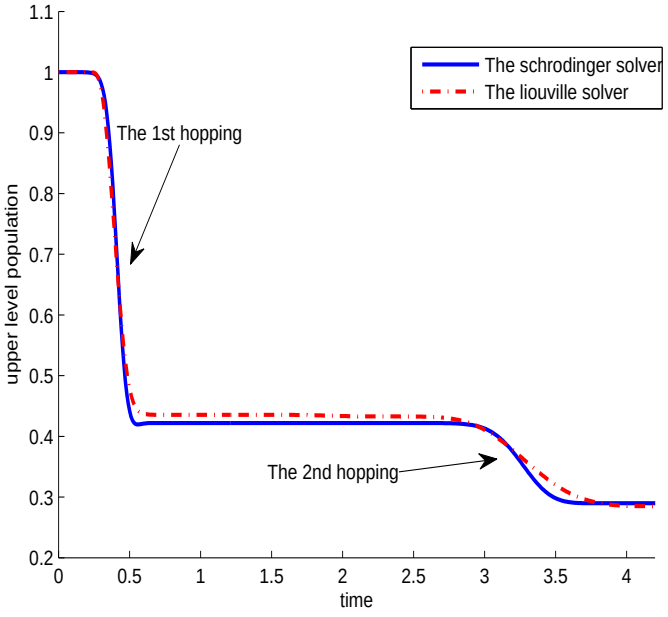

Figure 4.7: The long time behavior of the surface hopping process with the potential V_{iso}. The plot shows the population of the upper energy level versus time. The solid line corresponds to the Schrödinger solver and the dashed line corresponds to the Liouville solver. $h = \frac{1}{20}$, $\Delta t = \frac{1}{100}$ and $\varepsilon = 0.01$.

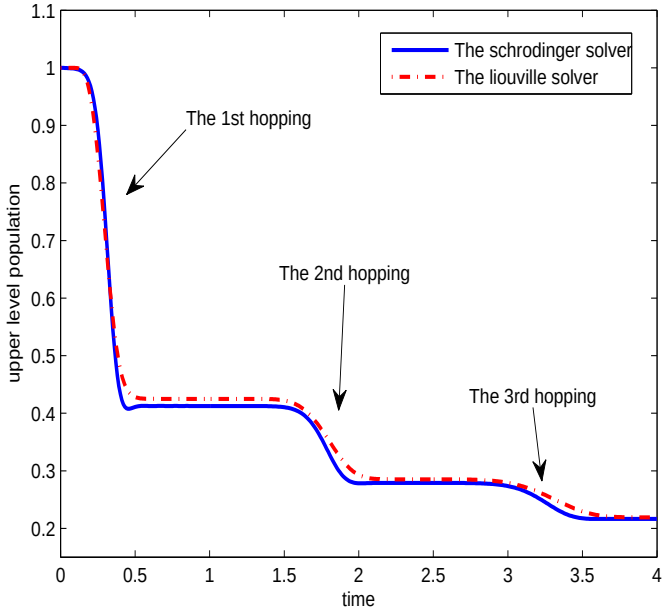

Figure 4.8: The long time behavior of the surface hopping process with the potential V_{JT}. The plot shows the population of the upper energy level versus time. The solid line corresponds to the Schrödinger solver, and the dashed line corresponds to the Liouville solver. $h = \frac{1}{20}$, $\Delta t = \frac{1}{100}$ and $\epsilon = 0.01$.

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