Quantum and Classical Evolution of Chemical Reaction Wave-Front by Fast Marching Method: A New Perspective of Reaction Dynamics

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Chemical reaction dynamics

"Understanding the motion of the constituent atoms in reacting molecules lies at the heart of chemistry and is the central focus of chemical reaction dynamics."

---- Fleming Crim

Question Asked?

- 1. Why chemical reaction occur?
 - Thermodynamics (Free energy, entropy,)

2. How to predict their behavior and to control them? _

- evolution of reactant Quantum state to product state
- quantum control by manipulating quantum interference
- State-to-state kinetics between reactant and product molecules in specific quantum states

3. What is the reaction path and the energy information?

- transition states, activation energy, rate constant (TST, VTST)
- Provides onset of bond breaking and making in a reaction
- energy distribution among translational, vibrational, rotational and electronic modes

Quantum mechanics
 Semi-classical mechanics

Statistical mechanics

Classical mechanics (MD simulation, reaction Path simulation) Quantum mechanics

Existing Methods

Molecular Dynamics simulation

IRC calculation (implemented in gaussian, gamess, molpro)

Gradient-following technique

Nudget elastic band methods

String method

Others (list is growing!)

Molecular Dynamics simulation

Solve Hamilton's equation of motion

$$\frac{dq_k}{dt} = \frac{\partial H(q, p, t)}{\partial p_k}$$

$$\frac{dp_k}{dt} = -\frac{\partial H(q, p, t)}{\partial q_k}$$

Drawbacks:

- Trajectory never reaches the product state over the course of time evolution.
- No way to know what should be the momentum.
- To resolve the high-frequency motions, Δt must be very small (10⁻¹² s). Typical time scale of reactive events 10 – 10 or higher. Reactive events are generally prohibitive in MD simulation.

Molecular dynamics is not a good candidate for reaction path simulation.

Intrinsic Reaction Coordinate (IRC)

 IRC is obtained by steepest descent from the first-order saddle point down to the reactant or product well floor.

$$\frac{dX(s)}{ds} = -\frac{g(X(s))}{\left\|g(X(s))\right\|}$$

- The transition state must be known to calculate the IRC. Often TS is hard to determine or inaccurately determined.
- IRC is a geometrically constrained curve on the PES. The curve is constrained by the fact that the curve cannot change from convex to concave.
- Because of this geometrical constraint, IRC always ends at the floor of the reactant/product well. IRC cannot be used to explore the states on the entire reactant/product basin.
- Because of this constraint, IRC is not useful for calculating dynamical properties.
 IRC is primarily used to find the transition barrier.

Intrinsic Reaction Coordinate

IRC calculation gets complicated for multistep reactions



$IRC = (IRP)_1 + (IRP)_2 + \dots (IRP)_6$

- Reactions where TS does not lead to the product (bifurcation reactions), IRC is undefined.
- Reactions where the PES contains higher-order saddle point (Monkey potential), IRC is undefined.

Common features to all these existing methods:

- Reactant and product states must be known beforehand.
- The transition states must be known accurately.
- The intermediates (multi-step reaction) must be known.
- Follow two-ways steepest descent on PES from each of the transition states.
- Does not mimic experimental situation where only the reactant state is known.

Quantum effect is completely ignored and cannot be incorporated.

What are we up to?

Develop a new method that

- Computes chemical reaction wave-front (CRWF) and incorporates quantum effects into classical mechanics : new insights
- computes the reaction paths (between two states) in a SINGLE run without prior information regarding the transition states.
- requires <u>the</u> reactant state as the only input configuration. -- Typical experimental situation
 computes a host of reaction paths (including the MEP, IRC).
- has the ability to study multi-step reactions.

<u> Chemical Reaction Wave-Fronts (CRWF)</u>

Bohmian mechanics was developed by David Bohm in 1952.

Express the complex time-dependent wave function in polar form

 $\Psi(q,t) = R(q,t)e^{iS(q,t)/\hbar}$, R(q,t) > 0: Amplitude of the wave function S(q,t): Action function or Phase of the wave function

Substitute this into time-dependent Schroedinger equation

$$i\hbar \frac{\partial \Psi(q,t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(q,t) + V_{cl}(q) \Psi(q,t)$$

It leads to two equations:

 ∂t

$$\frac{\partial \rho}{\partial t} = -\nabla \left(\rho \frac{\nabla S}{m} \right) = -\nabla \bullet j$$
$$\frac{\partial S}{\partial t} = \frac{(\nabla S)^2}{2m} + V_{cl} + V_{qu}$$

 $V_{qu} = -\frac{\hbar^2}{2m} \frac{\nabla^2 \rho^{1/2}}{\rho^{1/2}}$

Quantum Hydrodynamics OR **Bohmian mechanics**

Quantum Potential

Notes on Quantum Potential:

- The quantum potential is the only term that depends explicitly on \hbar
- Quantum potential is the only term that brings all quantum effects into the dynamics. Without it $(\frac{\hbar}{\hbar} \rightarrow 0, V_{qu} \rightarrow 0)$ its all classical mechanics.
- Quantum potential is explicitly identified as the source of nonlocality.

Classical Trajectory/ Classical Mechanics

Quantum trajectory/ Quantum Mechanics

$$-\frac{\partial S}{\partial t} = \frac{(\nabla S)^2}{2m} + V_{cl}$$

Classical trajectory: The state point move



 $-\frac{\partial S}{\partial t} = \frac{(\nabla S)^2}{2m} + V_{cl} + V_{qu}$

 Quantum HJ Equation, S is the quantum action surface

 Quantum Trajectory: State points are correlated through quantum potential



The starting point of our research is to investigate the classical HJ equation and bring back some quantum effect by introducing the quantum potential later.

Classical Hamilton-Jacobi Equation

Hamilton-Jacobi equation has never been exploited in studying reaction dynamics.

In the classical domain, phase is a constant of motion. This leads to the eikonal equation

$$\left|\nabla S\right| = \sqrt{2m(E - V_{cl})}$$

We have modified this equation as

$$\left|\nabla S\right| = \sqrt[n]{2(E - Vcl)}$$

Chemical Reaction Wave-Fronts (CRWF) Potential energy surface (PES)

- 1) We solve this by applying Fast marching algorithm
- 2) PES is converted to CRWF
- 3) CRWF contains all the information of the reaction event.
- 4) Analyze CRWF

 $\left|\nabla S\right| = \sqrt[n]{2(E - Vcl)}$

Potential energy surface (PES)

Chemical Reaction Wave-Fronts (CRWF)

□ We solve this by applying Fast marching algorithm

PES is converted to CRWF

CRWF contains all the information of the reaction event.

Analyze CRWF and extract information on the reaction event.

Introduce quantum potential, V_{qu}, as an added term to the above equation and analyze the quantum effect. <u>Research Status:</u>
 Partly done,
 ongoing research

Research status: Hatching stage

PES → CRWF (SN² Reaction







Potential energy surface of a SN² reaction

Chemical Reaction Wave Front of a SN² reaction (n=-12)

Significance of n

n	Equation	The S- surface	Path	Optimal path
1 E > V(Q)	H-J equation	Action Surface	Action path	Minimum action path
1 E < V(Q)	Imaginary H-J equation	Imaginary action surface	Tunneling path	Tunneling path
0	Geodesic equation	Distance surface	Distance path	Minimum distance path
-1	Fermat's equation (optics)	Time surface	Time path	Minimum time path
-2				
-3				
- large number (typically -10 or smaller)	Reaction action equation	Reaction action surface	reaction action path	Minimum energy path (MEP)

Solving the eikonal equation – Fast Marching Algorithm

This constitutes three parts:

A. Construct an initial front:

 $\Gamma_{int}(a) = \{Q_{int} \text{ in } \mathbb{R}^{N}; S = a\}$

Γ (a) = {Q in R^N; S = a} is the reaction wave-front, (a set of points, {Q}, for which S=a.)

B. Propagate the front:

This is the most crucial part. We have adapted the fast-marching algorithm widely used in fluid dynamics. In the end we obtain the CRWF.

C. Post-analysis of the CRWF:

- Determine reaction Path (Trajectory)
- Reaction Force Surface (RFS)
- Reaction Path Force (RPF)
- Reaction force constant surface (RFCS)
- Reaction Path force constant (RPFC)
- Determine transition states, reaction rate constant, activation force, activation energy, etc.

We have some results on these.



Reaction Path from CRWF:

$dQ(s)/ds = -\nabla S/|\nabla S|; \quad Q(0) = Q_{int}$



Numerical Method

The numerical method ensures that the wave-front propagates at the fastest speed at every grid point points. This is done by

(i) implementing an "UPWIND" derivative scheme – Rouy et. al SIAM J. Num. 1992)

$$\max\left(\frac{S_{i,j} - S_{i-1,j}}{\Delta q_1}, \frac{S_{i,j} - S_{i+1,j}}{\Delta q_1}, 0\right)^2 + \max\left(\frac{S_{i,j} - S_{i,j-1}}{\Delta q_2}, \frac{S_{i,j} - S_{i,j+1}}{\Delta q_2}, 0\right)^2$$
$$= \left(\sqrt{2\left(E - V(q_i, q_j)\right)}\right)^n$$

Solve for S at the point (i, j) from the knowledge of S at the points (i-1, j), (i+1,j), (i,j-1) and (i,j+1). The condition is that these points must be 'upwind' to the point (i, j).

(ii) This gives rise to a quadratic equation for S_{i,j}. The larger of the two solutions is the resultant reaction action value, ensuring highest local speed.
 -- Dey B., J. Chem. Phys., 2011

Fast Marching Algorithm

- Define an initial wave front around the reactant zone.
- Construct 1st narrow band, around this wave-front, where S values are known
- Tag the grid points as follows:

 $tagged \quad point = \begin{cases} alive, for initial state\\ close, for 1st narrow band\\ far, for others \end{cases}$

- Select a trial point from 1st narrow band with smallest S value, tag it alive.
- Construct 2nd narrow band by including the nearest neighboring points of the trial point. Values of S at these neighboring points are updated based on the above quadratic equation.
- Continue this until the narrow bands are empty, that is, until all points become alive.

Pictorial description of the algorithm



A. 4-well Potential (Conformational dynamics of Alanine dipeptide)



Chemical reaction wave-fronts



Reaction Path plotted on the PES



B. Isomerization of Malonaldehyde:





Path plotted on the CRWF



A look at the ALIVE POINTS in Malonaldehyde – Important Sampling



Red dots are the alive points accumulating along the most important regions.

C. Rotation of BH₂

Chemical Reaction Wave Fronts Two symmetric paths on the PES



 q_2

<u>D. F+H2 \rightarrow FH + H reaction:</u>

Chemical Reaction Wave-Fronts

Path on the PES



Bifurcation Reaction:

Isomerization of methoxy radical to hydroxymethylene radical

 $H_3C\dot{O} \rightarrow H_2\dot{C}OH$



Mechanistic route shows bifurcation at VRI. IRC (middle curve) deviates from the actual path.

Reaction action surface



Dey et. al, J. Mol. Phys, 2014

Path Ensemble made easy



Reaction Force Surface: A New Concept

A. Classical Potential energy surface

Chemical Reaction Wave Front





- Rugged, with several stationary states (minima, maxima, etc.)
- Information are not easy to extract because
 Of its ruggedness
- Old concepts

- Smooth, with only one minima
- Information are easy to extract
- Provides new insights on reaction dynamics

Reaction Force Surface: A New Concept

B. Classical Force Field

 $\vec{F}(Q) = -\nabla V$

Reaction force field:

 $\vec{F}_r(Q) = -\nabla S$

 The field vectors do not align along the reaction path



• The field vectors do align along the reaction path



C. Reaction force surface:

Reaction Force surface is defined as

$$\Im(q) = \vec{F}_{cl}(q) \bullet \vec{\eta}(q) \qquad \qquad \vec{\eta}(q) = \frac{\nabla S}{|\nabla S|}$$



D. Reaction Path Force (RPF)

- Q. Should it be an Energy-based mechanism or a Force-based mechanism?
- Tradition description of a reacting event is entirely based on energy. Thus, we talk about the potential energy surface, activation energy, etc.

ENERGY DOES NOT explain why things happen.

- FORCE is more fundamental than ENERGY when it comes to describing the dynamics of a system, such as reaction.
- Everything that happens in the Universe is ultimately caused by FORCE, not ENERGY.
- Yet, force has never gotten any importance in the theoretical chemistry community because:
- 1. Most chemical property ultimately depends on the energetic information.
- 2. Force is difficult to calculate, in particular, the reaction path force (RPF).

Energy-based mechanism:

Reaction path energy:

 $V(Q) = V(\gamma (Q)), \gamma (Q)$ is the reaction path

Force-based mechanism

Reaction path force:

$$F(\gamma) = -\frac{\partial V}{\partial \gamma} = -\left(\frac{\partial V}{\partial q_1}, \frac{\partial V}{\partial q_2}, \cdots, \frac{\partial V}{\partial q_N}\right) \begin{pmatrix} \frac{\partial q_1}{\partial \gamma} \\ \frac{\partial q_2}{\partial \gamma} \\ \vdots \\ \frac{\partial q_N}{\partial \gamma} \end{pmatrix}$$

$$= \vec{F} \bullet \frac{\vec{\nabla}S}{\left|\vec{\nabla}S\right|}$$

Reaction force constant:

$$\boldsymbol{\kappa} = \frac{\partial}{\partial \gamma} \left(\frac{\partial V}{\partial \gamma} \right) = -\vec{\nabla} \left(\vec{F} \bullet \vec{\nabla} S \right) \bullet \vec{\nabla} S$$

 $\vec{\nabla} \left(\vec{A} \bullet \vec{B} \right) = \vec{\nabla}_A \left(\vec{A} \bullet \vec{B} \right) + \vec{\nabla}_B \left(\vec{A} \bullet \vec{B} \right)$

Model potential energy surface of Alanine dipeptide showing four conformers.







Three Elementary steps for $A \rightarrow B$: $A \rightarrow T \rightarrow C$ Setp-1 $C \rightarrow T \rightarrow D$ Setp-2 $D \rightarrow T \rightarrow B$ Step-3

Mechanism of Elementary Reaction: $A \rightarrow C$

Q. Is an elementary reaction REALLY an elementary reaction?

Energy-based mechanism (Energy along the path)



 $A \rightarrow TS \rightarrow C$

Force-based mechanism (Force along the path (RFP)



A → SBTS → TS → SATS → C SBTS = State Before Transition State SATS = State After Transition State

Indeed, an elementary reaction is NOT an elementary reaction from the force point of view.

Mechanism of the three-step reaction: $A \rightarrow B$

Q. Is a three-step reaction really a three-step reaction?

Energy-based mechanism

Force-based mechanism





A three-step reaction actually has 6 unique steps.

A complex reaction is characterized by a large number of states (points in the PES).

Mechanism of a bifurcation reaction

Mechanism based on Energy

Mechanism based on force



$R \rightarrow BTS \rightarrow TS \rightarrow VRI \rightarrow BP \rightarrow P_1, P_2$

 $R \rightarrow TS \rightarrow BP \rightarrow P_1 P_2$

Dey et. al., Chem. Phys. Lett., 2013

Looking Beyond: Re-defining reaction Dynamics

- It is clear that our traditional understanding of reaction mechanism needs a renewed investigation based on our formulation.
- CRWF is provides new insights in our understanding of reaction dynamics
 - o An elementary reaction is NOT an elementary reaction.
 o the existence of new states
 - **SBTS** = State before the transition state (The magnitude of the force is the maximum here. This is the retarding force initially operates on the reactants and it reaches the maximum at SBTS. The reactant species are jolted around because of this force. The new jolted state is the SBTS. retarding force's magnitude starts diminishing when the driving force starts operating. when these two forces are equal transition state (TS) is formed.

o ATS = after transition state (the magnitude of the force is the maximum)

- Reaction force surface is an entirely new concept and need detail
- investigation with reference to several chemical reactions.
- Effect of quantum potential on the reaction force surface.

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QUESTION?