Quantum Dynamics with Trajectories: One-Dimensional Scattering Problems

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Quantum reactional dynamics

Goal : Solve Schrödinger's equation for nuclei.

Born-Oppenheimer approximation

$$i\hbar\frac{\partial\Psi}{\partial t}(x_1,...,x_n,t) = \hat{T}\Psi(x_1,...,x_n,t) + \hat{V}(x_1,...,x_n)\Psi(x_1,...,x_n,t)$$

Variational principle :

- Wavefunction representation
- Few approximations (finite basis set)
- More accurate than perturbation methods

For systems with many degrees of freedom :
Curse of dimensionality

What other approaches for quantum dynamics ?

Outline

1. Time independent approach of quantum trajectories
2. Extension to curved space formulation
3. Time dependent approach of quantum trajectories

plan

1. Time independent approach of quantum trajectories
2. Extension to curved space formulation
3. Time dependent approach of quantum trajectories

From Bohmian dynamics ...

One-dimensional system with rectilinear coordinate

Take Madelung-Bohm's ansatz for the wavefunction,

$$\Psi(x) = R(x)e^{iS(x)/\hbar}, \quad R(x), S(x) \text{ **real functions**.}$$

Note that $S(x)$ is the classical action : $\quad S(x) = \int_{t_0}^{t(x)} L(x', \dot{x}')dt$

This allows the definition of a **velocity field** :

$$\boxed{\frac{dS(x)}{dx} = m\dot{x}}$$

Insert both in Schrödinger's equation,

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x)$$

From Bohmian dynamics ...

One gets two equations :

$$\begin{cases} \boxed{\dfrac{d}{dx}\left(R^2(x)\dot{x}\right) = 0} \Rightarrow \text{Continuity equation (incompressible flow)} \\ \boxed{E = \dfrac{1}{2}m\dot{x}^2 + V(x) + Q_\Psi(x)} \Rightarrow \text{Energy conservation} \end{cases}$$

Quantum potential $\boxed{Q_\Psi(x) = -\dfrac{\hbar^2}{2mR(x)}\dfrac{d^2R(x)}{dx^2}}$

It implies the e.o.m. : $\boxed{m\ddot{x} = -\dfrac{dV(x)}{dx} - \dfrac{dQ_\Psi(x)}{dx}}$

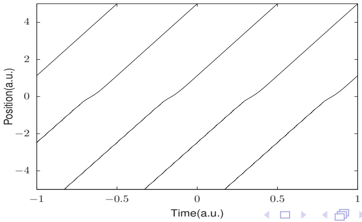
David Bohm Phys. Rev. 85, 166 (1952)

From Bohmian dynamics ...

- Coupled evolution of $R(x)$ and $\dot{x}$.
- Hydrodynamics of the density probability fluid.
- Time independent process $\longrightarrow$ Eulerian and Lagrangian frames are equivalent.

Eulerian frame		Lagrangian frame
$v = v(x,t)$	$\frac{d}{dt} = \underbrace{\frac{\partial}{\partial t}}_{\mathbf{0}} + \frac{1}{\dot{x}}\frac{\partial}{\partial x}$	$v = v(x_0, t)$
fixed grid		go with the flow

- Trajectories unchanged by a time translation.



No-wave Lagrangian formulation

Writing $R^2(x) = \frac{\alpha}{\dot{x}}$ and noting that $\frac{d}{dx} = \frac{1}{\dot{x}}\frac{d}{dt}$, one gets

$$Q(\dot{x}, \ddot{x}, \dddot{x}) = \frac{\hbar^2}{4m}\left(\frac{\dddot{x}}{\dot{x}^3} - \frac{5}{2}\frac{\ddot{x}^2}{\dot{x}^4}\right) = Q_{\not\psi}$$

B. Poirier, Chem. Phys. 370, 4 (2010)

Equation of motion :

$$m\ddot{x} = -\frac{dV}{dx} - \frac{\hbar^2}{4m}\left(10\frac{\ddot{x}^3}{\dot{x}^6} - 8\frac{\ddot{x}\dddot{x}}{\dot{x}^5} + \frac{\ddddot{x}}{\dot{x}^4}\right)$$

corresponds to the quantum Lagrangian :

$$L_Q(x, \dot{x}, \ddot{x}, \dddot{x}) = \underbrace{\frac{1}{2}m\dot{x}^2 - V(x)}_{L_{Cl}} - Q(\dot{x}, \ddot{x}, \dddot{x})$$

Variational principle

$$L(x,\dot{x},\ddot{x},\dddot{x}) = \frac{1}{2}m\dot{x}^2 - V(x) - \frac{\hbar^2}{4m}\left(\frac{\dddot{x}}{\dot{x}^3} - \frac{5}{2}\frac{\ddot{x}^2}{\dot{x}^4}\right)$$

$$\delta\mathcal{S} = \delta\left[\int_{t_0}^{t} L(x,\dot{x},\ddot{x})dt\right] = 0$$

$$\Longrightarrow \frac{\partial L}{\partial x} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) + \frac{d^2}{dt^2}\left(\frac{\partial L}{\partial \ddot{x}}\right) - \frac{d^3}{dt^3}\left(\frac{\partial L}{\partial \dddot{x}}\right) = 0$$

Gauge invariance :

$$L \longrightarrow L' = L + \frac{d}{dt}[f(x,\dot{x},\ddot{x},t)]$$

$$\text{Take} \quad f(x,\dot{x},\ddot{x},t) = \frac{\hbar^2}{4m}\left(\frac{\ddot{x}}{\dot{x}^3}\right)$$

$$\Longrightarrow Q(\dot{x},\ddot{x}) = \frac{\hbar^2}{8m}\left(\frac{\ddot{x}^2}{\dot{x}^4}\right)$$

Ostrogradski's Hamiltonian

$$L(x,\dot{x},\ddot{x}) = \frac{1}{2}m\dot{x}^2 - V(x) - \frac{\hbar^2}{8m}\left(\frac{\ddot{x}^2}{\dot{x}^4}\right)$$

$$\frac{\partial L}{\partial x} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) + \frac{d^2}{dt^2}\left(\frac{\partial L}{\partial \ddot{x}}\right) = 0$$

Can we build a Hamiltonian whose coupled equation are equivalent to the equation of motion ?

Ostrograski's method

Ostrogradski's Method

$$L = L(x, \dot{x}, ..., \overset{(n)}{x})$$

$$\sum_{i=0}^{n} (-1)^i \frac{d^i}{dt^i} \left(\frac{\partial L}{\partial \overset{(i)}{x}} \right) = 0$$

$$\begin{cases} H(x, \dot{x}, ..., \overset{(n-1)}{x}, p_1, p_2, ...p_n) = p_1 \dot{x} + p_2 \ddot{x} + ... + p_n \overset{(n)}{x} - L \\ \overset{(i)}{x} = \frac{\partial H}{\partial p_i}, \qquad \dot{p_i} = -\frac{\partial H}{\partial \overset{(i-1)}{x}} \qquad \text{with } i = 1 \to n \end{cases}$$

$$\Longrightarrow \begin{cases} p_n = \frac{\partial L}{\partial \overset{(n)}{x}} \\ p_i = \frac{\partial L}{\partial \overset{(i)}{x}} - \frac{d}{dt} (p_{i+1}) \end{cases}$$

Ostrogradski's Hamiltonian

$$L = L(x, \dot{x}, \ddot{x})$$

$$\frac{\partial L}{\partial x} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) + \frac{d^2}{dt^2}\left(\frac{\partial L}{\partial \ddot{x}}\right) = 0$$

$$\begin{cases} H(x, \dot{x}, p, p') = p\dot{x} + p'\ddot{x} - L \\ \\ p' = \dfrac{\partial L}{\partial \ddot{x}} = -\dfrac{\hbar^2}{4m}\left(\dfrac{\ddot{x}}{\dot{x}^4}\right) \\ \\ p = \dfrac{\partial L}{\partial \dot{x}} - \dfrac{d}{dt}\left(\dfrac{\partial L}{\partial \ddot{x}}\right) = m\dot{x} + \dfrac{\hbar^2}{4m}\left(\dfrac{\dddot{x}}{\dot{x}^4} - 2\dfrac{\ddot{x}^2}{\dot{x}^5}\right) \end{cases}$$

Ostrogradski's Hamiltonian

$$\text{Introducing} \quad s = m\dot{x}\ , \quad r = -\frac{p'}{m}$$

$$\boxed{H(x,s,p,r) = \frac{s(2p-s)}{2m} + V(x) - \frac{2r^2s^4}{\hbar^2 m}}$$

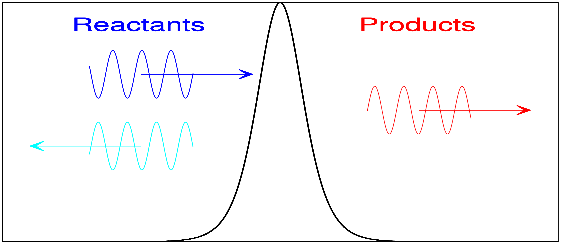
$$\text{4 coupled equations :} \begin{cases} \dot{r} = \dfrac{\partial H}{\partial s} = \dfrac{p-s}{m} - \dfrac{8r^2s^3}{\hbar^2 m} \\ \dot{p} = -\dfrac{\partial H}{\partial x} = -\dfrac{dV}{dx} \\ \dot{s} = -\dfrac{\partial H}{\partial r} = \dfrac{4rs^4}{\hbar^2 m} \\ \dot{x} = \dfrac{\partial H}{\partial p} = \dfrac{s}{m} \end{cases}$$

Hamiltonian formalism

$$H(x, s, p, r) = \frac{s(2p - s)}{2m} + V(x) - \frac{2r^2 s^4}{\hbar^2 m}$$

- 4 variables (x, p, r, s) instead of 2 (x, p).
- Classical limit : $r \to 0$ and $s \to p$
- p is the Noether Momentum for space translation
  $\longrightarrow$ If $V(x) = cte$, then $p = cte$
- First order coupled equations

1D Scattering processes



$$\Psi_I(x) \propto \frac{1}{\sqrt{k_L}} e^{ik_L x}\ , \quad \Psi_R(x) \propto \frac{1}{\sqrt{k_L}} e^{-ik_L x}\ , \quad k_L = \sqrt{2m(E - V_L)}$$

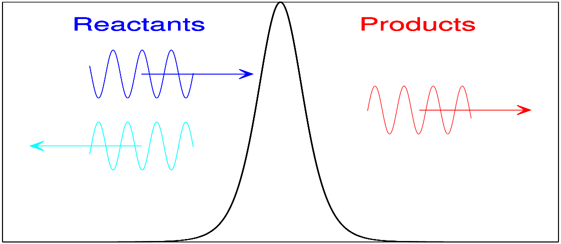
$$\Psi_T(x) \propto \frac{1}{\sqrt{k_R}} e^{ik_R x}\ , \quad k_R = \sqrt{2m(E - V_R)}$$

Product side corresponds to a classical-like behaviour.

$$r = 0 \qquad s = p = \hbar k_R$$

Method : Begin in the products asymptote and propagate *backwards* in time.

1D Scattering processes



Goal : Compute the Cumulated Reaction Probability $N(E)$.

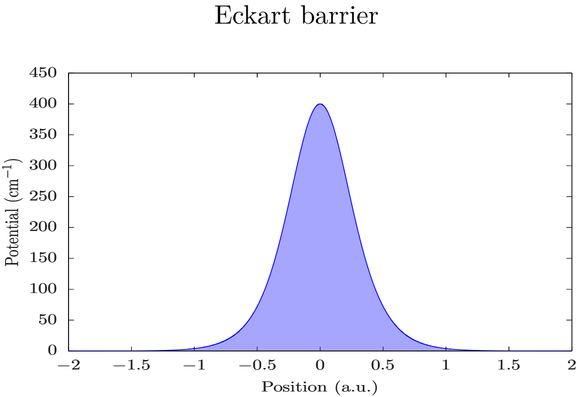
$$N(E) = \sum_r \sum_p \left| S_{\mathbf{n}_r \mathbf{n}_p}(E) \right|^2$$

In one dimension, $N(E) = T(E) = 4 \left| \Psi(x_L) - i\hbar \frac{\partial_x \Psi(x_L)}{\partial_x \Psi(x_R)} \right|^{-2}$

$T(E)$ is obtained through the asymptotic value of p.

$$T(E) = \frac{2\hbar k_L}{p_L + \hbar k_L}$$

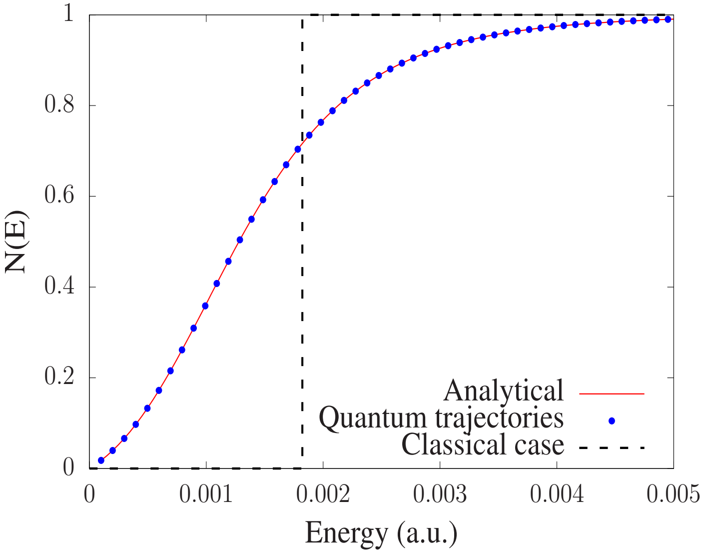
From simple barrier



$$V(x) = \frac{V_0}{cosh(\alpha x)^2}$$

$$V_0 = 400 \text{ cm}^{-1} \qquad \alpha = 3 \text{ a.u.} \qquad m = 2000 \text{ a.u.}$$

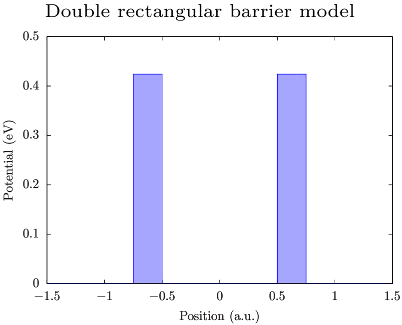
From simple barrier



From simple barrier

(E/V_0)	Exact $T(E)$	Relative error
1×10^{-12}	2.85078×10^{-13}	4.92×10^{-12}
1×10^{-9}	2.85078×10^{-10}	4.893×10^{-12}
1×10^{-6}	2.85079×10^{-7}	4.909×10^{-12}
1×10^{-3}	2.85757×10^{-4}	4.795×10^{-12}
1×10^{-1}	3.56449×10^{-2}	1.211×10^{-12}
0.5	0.31898	2.941×10^{-12}
1.0	0.71664	5.645×10^{-13}
1.5	0.90059	8.751×10^{-13}
2.0	0.96361	2.154×10^{-13}
10.0	0.99999	3.252×10^{-14}

To deep-tunneling regime

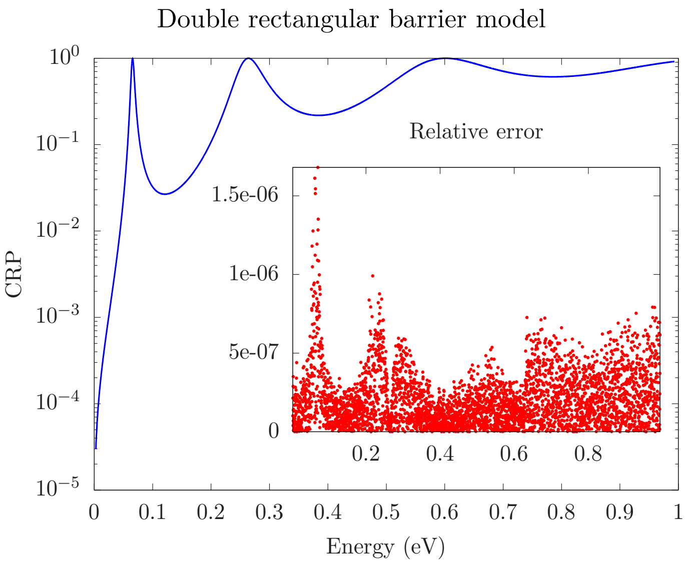


$$V(x) = \frac{V_0}{2\,th(\alpha d)}\left[V_R(x - x_1) + V_R(x - x_2)\right]$$

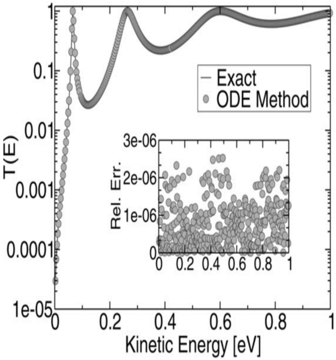
$$V_R(x) = \frac{1}{th[\alpha(d+x)] + th[\alpha(d-x)]}$$

m	α	d	x_1	x_2
1060	10^5	0.125	−0.625	0.625

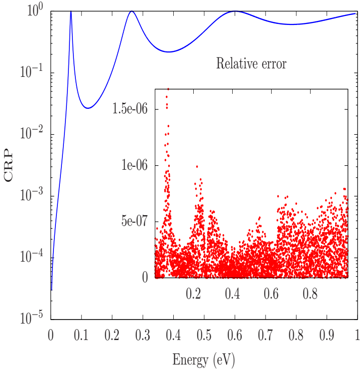
To deep-tunneling regime



To deep-tunneling regime

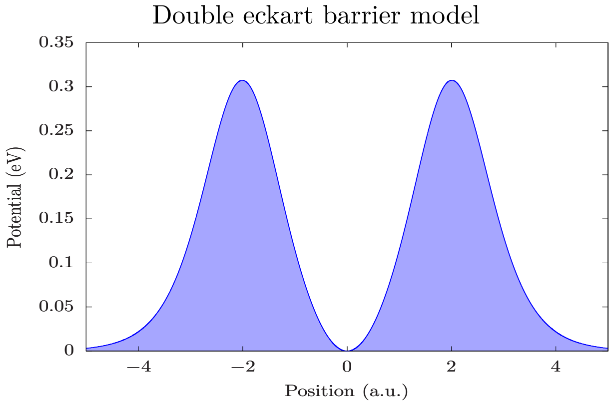


Mandrà S., Valleau S. and Ceotto M., Int. J. Quantum Chem. (2013)



Present work

To deep-tunneling regime



$$V(x) = V_0 \times \left(\frac{1}{cosh^2(x+a)} + \frac{1}{cosh^2(x-a)} - \frac{2}{cosh^2(a)cosh^2(x)} \right)$$

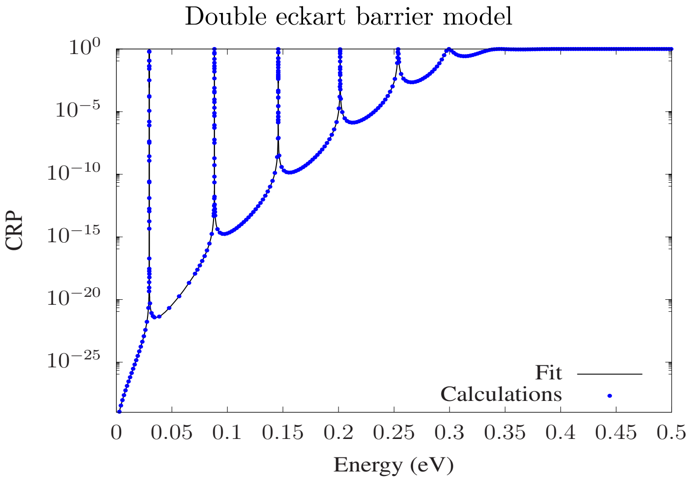
$$V_0 = 0.310 \text{ eV} \qquad a = 2 \text{ a.u.} \qquad m = 1834 \text{ a.u.}$$

Time independent

Curved space

Time dependent

To deep-tunneling regime



To deep-tunneling regime

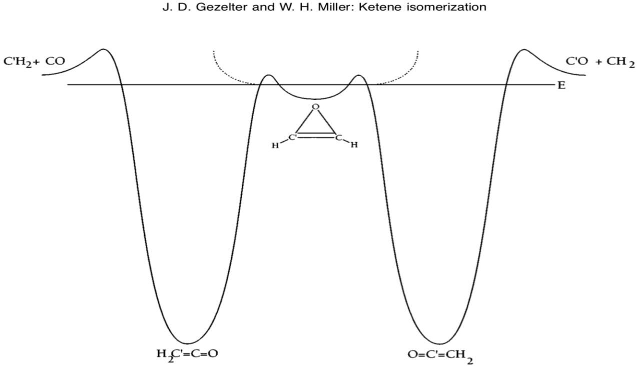
Breit-Wigner distribution

$$T_{BW}(E) = \frac{(\Gamma_r/2)^2}{(E - E_r)^2 + (\Gamma_r/2)^2}$$

Peak	Result	E_r (a.u.)	Γ_r (a.u.)
1	TIQT	1.09002×10^{-3}	2.97763×10^{-15}
	Mandrà et al.	1.08998×10^{-3}	2.93595×10^{-15}
2	TIQT	3.24570×10^{-3}	9.61459×10^{-12}
	Mandrà et al.	3.24695×10^{-3}	9.53968×10^{-12}
3	TIQT	5.35610×10^{-3}	3.30849×10^{-9}
	Mandrà et al.	5.35792×10^{-3}	3.27995×10^{-9}
4	TIQT	7.40497×10^{-3}	3.68954×10^{-7}
	Mandrà et al.	7.40790×10^{-3}	2.663962×10^{-7}

Application to isomerisation process

Ketene photo-isomerization



Gezelter & Miller, J. Chem. Phys., Vol. 103, No. 18 (1995)

Application to isomerisation process

Ketene photo-isomerization

$$V(x, \mathbf{q}) = V_{1d}(x) + \sum_{j=2}^{3} k_j \left(q_j + \frac{d_j x^4}{k_j} \right)^2$$

$$V_{1d}(x) = \alpha_2 x^2 + \alpha_4 x^4 + \alpha_6 x^6 + \beta x^2 e^{-\gamma x^2}$$

x is the reaction coordinate

α_2	α_4	α_6	β	γ
-2.3597 $\times 10^{-3}$	1.0408 $\times 10^{-3}$	-7.5496 $\times 10^{-5}$	7.7569 $\times 10^{-3}$	1.9769

Gezelter & Miller, J. Chem. Phys., Vol. 103, No. 18 (1995)

Application to isomerisation process

Discrete Variable Representation (DVR)

- Base of sinc functions

$$\phi_n(x) = \Delta^{-1/2} sinc\left[\pi(\frac{x}{\Delta} - n)\right]$$

- Potential operator : Diagonal representation
- Kinetic operator : Block representation
- CRP as a sum of eigenvalues

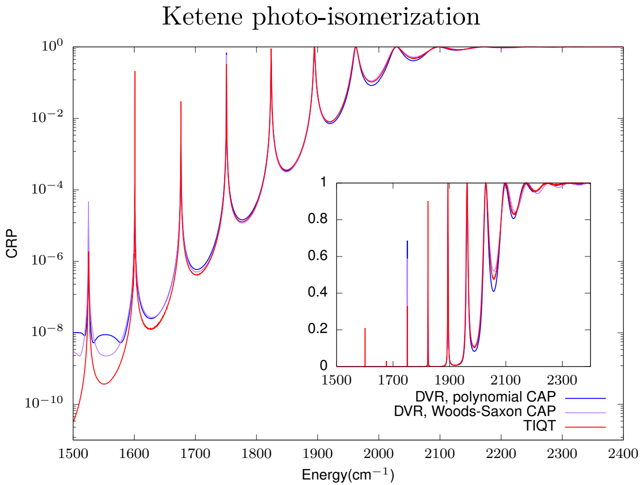
$$N(E) = Tr\left[\hat{P}(E)\right] = 4\,\hat{\epsilon}_r^{1/2}\,\hat{G}(E)^*\,\hat{\epsilon}_p\,\hat{G}(E)\,\hat{\epsilon}_r^{1/2}$$

$$\hat{G}(E) = (E + i\hat{\epsilon} - \hat{H})^{-1}$$

- Complex absorbing potential $\epsilon(x)$
  $\longrightarrow$ Needs to be optimized for a given E window

Gezelter & Miller, J. Chem. Phys., Vol. 103, No. 18 (1995)

Application to isomerisation process



plan

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Exact kinetic energy operator

Body-fixed frame :

$$\hat{T} = \hat{T}(\mathbf{x}, \partial_{\mathbf{x}}) = -\frac{\hbar^2}{2} \sum_{ij} \left[G^{ij} \partial^2_{ij} + \left(G^{ij} \partial_j [\ell n(J)] + \partial_j (G^{ij}) \right) \partial_i \right]$$

D. Lauvergnat, A. Nauts, J. Chem. Phys., 116(19) 2002

with $G(\mathbf{x}) = G_{n \times n}(\mathbf{x})$ the metric tensor for internal coordinates

$$\partial_i = \frac{\partial}{\partial x^i} \; ; \; \partial^2_{ij} = \frac{\partial^2}{\partial x^i \partial^j}$$

$$J(\mathbf{x}) = \sqrt{det(G^{-1}(\mathbf{x}))}$$

In general, $\hat{T} = \left(\frac{\varrho}{J}\right)^{-1/2} \hat{T}(\mathbf{x}, \partial_{\mathbf{x}}) \left(\frac{\varrho}{J}\right)^{1/2}$

ϱ is the volume element

One-Dimensional case

We restrict to a 1D curvilinear reaction coordinate $x(\mathbf{q})$.

$$G^{-1}(x) = \frac{d\mathbf{q}}{dx}^T \frac{d\mathbf{q}}{dx}$$

$\mathbf{q} = \{q_1, ..., q_n\}$ is the primitive (rectilinear) set of coordinates

In the polar form of the wavefunction, $\Psi(x) = R(x)e^{iS(x)/\hbar}$,

$$S(x) = \int^{t(x)} L(\mathbf{q}, \dot{\mathbf{q}})dt$$

$$L(\mathbf{q}, \dot{\mathbf{q}}) = \frac{1}{2} m_0 \dot{\mathbf{q}}^2 - V(\mathbf{q})$$

Velocity field

$$\frac{dS(x)}{dx} = \sum_{i=1}^{n} \frac{\partial S(x)}{\partial q_i}\ \frac{\partial q_i}{\partial x} = \sum_{i=1}^{n} p_{q_i}\ \frac{\partial q_i}{\partial x}$$

$$= \sum_{i=1}^{n} m_0\, \dot{q}_i\ \frac{\partial q_i}{\partial x} = \sum_{i=1}^{n} m_0\ \frac{\partial q_i}{\partial x}\ \dot{x}\ \frac{\partial q_i}{\partial x}$$

$$= m_0\, \dot{x} \sum_{i=1}^{n} \frac{\partial q_i}{\partial x}\ \frac{\partial q_i}{\partial x} = m_0\, \dot{x}\ \left\{ \frac{\partial \mathbf{q}}{\partial x} \right\}^T \frac{\partial \mathbf{q}}{\partial x}$$

$$= p_x = \frac{m_0}{G(x)} \dot{x} = m(x)\, \dot{x}$$

New equations

Inserting the polar form in Schrödinger's equation with a curvilinear kinetic operator yields :

$$\frac{d}{dx}\left[\varrho(x)\, G R^2 \frac{dS}{dx}\right] = 0 \Longrightarrow \frac{d}{dx}\left[\varrho(x)\, R^2 \dot{x}\right] = 0$$

$$\boxed{\frac{d}{dx}\left(\varrho(x) R^2(x) \dot{x}\right) = 0}$$ ⇒ Continuity equation

$$\boxed{\begin{aligned} E = \frac{1}{2} m(x)\dot{x}^2 &- \frac{\hbar^2}{4m_0}\frac{d}{dt}\left(\frac{\varrho(x)G(x)}{\dot{x}}\frac{d}{dt}\left(\frac{1}{\varrho(x)\dot{x}}\right)\right) \\ &+ \frac{\hbar^2 G(x)}{8m_0}\left[\frac{1}{\varrho^2}\left(\frac{d\varrho}{dx}\right)^2 + \frac{\ddot{x}^2}{\dot{x}^4} + \frac{2}{\varrho}\frac{\ddot{x}}{\dot{x}^2}\frac{d\varrho}{dx}\right] + V(x) + v(x) \end{aligned}}$$

⇒ Energy conservation

Hamiltonian form

We derive the associated Lagrangian :

$$L(x,\dot{x},\ddot{x}) = \frac{1}{2}m_0\frac{\dot{x}^2}{G(x)} - \frac{\hbar^2 G(x)}{8m_0}\left[\frac{\ddot{x}^2}{\dot{x}^4} + \left(\frac{d\,\ell n(\varrho)}{dx}\right)^2 + 2\frac{\ddot{x}}{\dot{x}^2}\frac{d\,\ell n(\varrho)}{dx}\right] - V(x) - v(x)$$

$$v(x) = \frac{\hbar^2}{4m_0}\frac{d}{dx}\left[G(x)\frac{d\,\ell n(J/\varrho)}{dx}\right] - \frac{\hbar^2 G(x)}{8}\left[\left(\frac{d\,\ell n(\varrho)}{dx}\right)^2 - \left(\frac{d\,\ell n(J)}{dx}\right)^2\right]$$

Using Ostrogradski's method, we build the modified Hamiltonian :

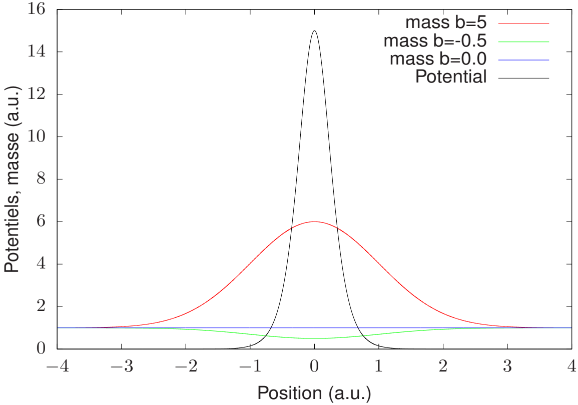
$$H(x,s,p,r) = \frac{s(2p - s/G(x))}{2m_0} - \frac{2r^2 s^4}{\hbar^2 m_0 G(x)} + \frac{rs^2}{m_0}\frac{d\,\ell n(\varrho)}{dx} + V(x) + v(x)$$

Hamiltonian equations

$$H(x,s,p,r) = \frac{s(2p - s/G(x))}{2m_0} - \frac{2r^2 s^4}{\hbar^2 m_0 G(x)} + \frac{rs^2}{m_0}\frac{d\,\ell n(\varrho)}{dx} + V(x) + v(x)$$

$$\begin{cases} \dot{p} = -\dfrac{\partial H}{\partial x} = -\dfrac{dV}{dx} - \dfrac{1}{G^2(x)}\dfrac{dG}{dx}\left[\dfrac{s^2}{2} + \dfrac{2r^2 s^4}{\hbar^2}\right] - rs^2\dfrac{d^2\,\ell n(\varrho)}{dx^2} - \dfrac{dv}{dx} \\ \dot{r} = \dfrac{\partial H}{\partial s} = \dfrac{p}{m_0} - \dfrac{s}{m_0 G(x)} - \dfrac{8r^2 s^3}{\hbar^2 m_0 G(x)} + \dfrac{2rs}{m_0}\dfrac{d\,\ell n(\varrho)}{dx} \\ \dot{s} = -\dfrac{\partial H}{\partial r} = \dfrac{4rs^4}{\hbar^2 m_0 G(x)} - \dfrac{s^2}{m_0}\dfrac{d\,\ell n(\varrho)}{dx} \\ \dot{x} = \dfrac{\partial H}{\partial p} = \dfrac{s}{m_0} \end{cases}$$

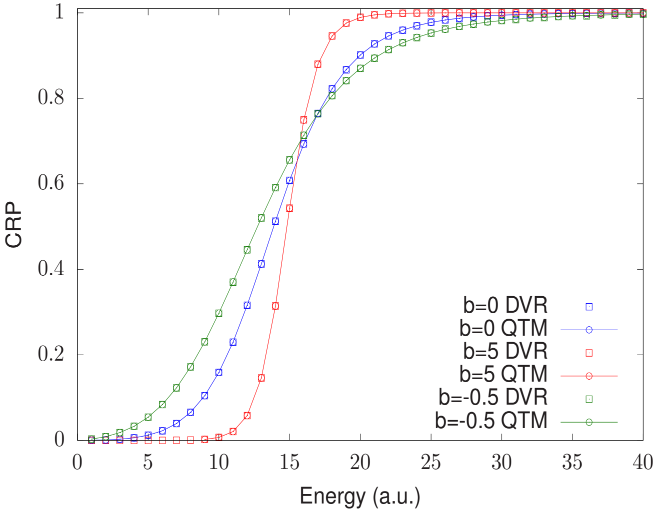
1D-Scattering Problem



$$\text{Eckart Barrier}: \; V(x) = 15 \; sech^2(3x)$$

$$m(x) = m_0 \; \left(1 + b \times e^{-x^2/2} \right)$$

1D-Scattering Problem



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Time-dependent equations

$$x = x(x_0, t)\ , \qquad x(x_0, t=0) = x_0$$

$$\frac{d}{dt} = \frac{\partial}{\partial t}\Big|_x + \dot{x}\frac{\partial}{\partial x}\Big|_t = \frac{\partial}{\partial t}\Big|_{x_0}$$

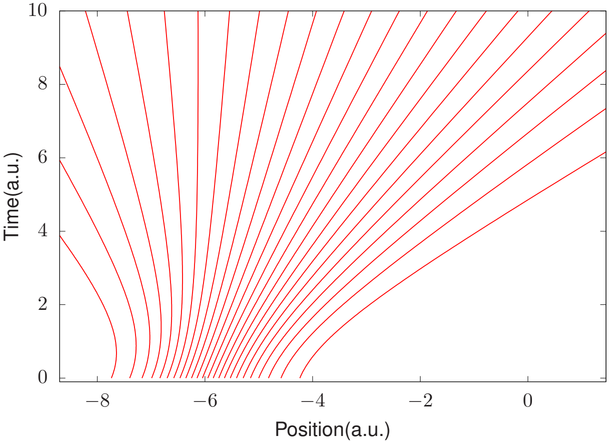
$$\Psi(x,t) = R(x,t)e^{iS(x,t)/\hbar}$$

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t}\Big|_x = \hat{H}\Psi(x,t)$$

$$\begin{cases} R^2(x,t) = \dfrac{R_0^2(x_0)}{x'}\ , \quad x' = \dfrac{\partial x}{\partial x_0} \\ \\ \dfrac{\partial S}{\partial t}\Big|_x = -\dfrac{1}{2}m\dot{x}^2 - V(x) - Q_\Psi(x,t) \end{cases}$$

$$\Rightarrow m\ddot{x} = \frac{\partial V(x)}{\partial x} - \frac{\partial Q_\Psi(x,t)}{\partial x}$$

Lagrangian frame



Free gaussian wavepacket

$$\rho_0(x_0) = \frac{1}{\sqrt{2\pi}\omega_0} e^{-\frac{(x_0-\delta_0)^2}{2\omega_0^2}}$$

Quantum potential

$$\left.\frac{\partial}{\partial x}\right|_t = \frac{1}{x'}\left.\frac{\partial}{\partial x_0}\right|_t$$

$$\begin{aligned} Q(x', x'', x''', x_0) = &- \frac{\hbar^2}{2mx'}\frac{R_0''(x_0)}{R_0(x_0)} + \frac{\hbar^2}{m}\frac{R_0'(x_0)}{R_0(x_0)}\frac{x''}{x'^3} \\ &- \frac{5\hbar^2}{8m}\frac{x''^2}{x'^4} + \frac{\hbar^2}{4m}\frac{x'''}{x'^3} \end{aligned}$$

Lagrangian formulation

$$\mathscr{L}(x,\dot{x},x',x'',x''',x_0) = \rho_0(x_0)\left(\frac{1}{2}m\dot{x}^2 - V(x) - Q(x',x'',x''',x_0)\right)$$

$$\mathcal{S}(T) = \int_0^T \int_{-\infty}^{+\infty} \mathscr{L}(x,\dot{x},x',x'',x''',x_0)\,dx_0\,dt$$

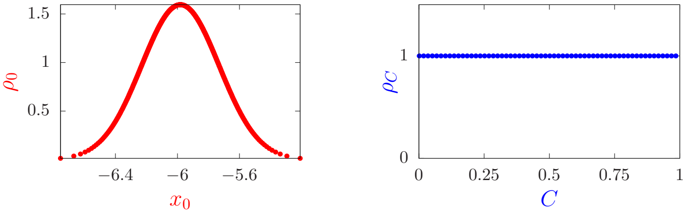
$$\frac{\partial\mathscr{L}}{\partial x} - \frac{d}{dt}\left(\frac{\partial\mathscr{L}}{\partial\dot{x}}\right) - \left(\frac{\partial\mathscr{L}}{\partial x'}\right)' + \left(\frac{\partial\mathscr{L}}{\partial x''}\right)'' - \left(\frac{\partial\mathscr{L}}{\partial x'''}\right)''' = 0$$

Uniform density label

$$x(x_0, t) \to x(C(x_0), t)$$

$$\rho_C(C)\, dC = \rho(x, t)\, dx$$

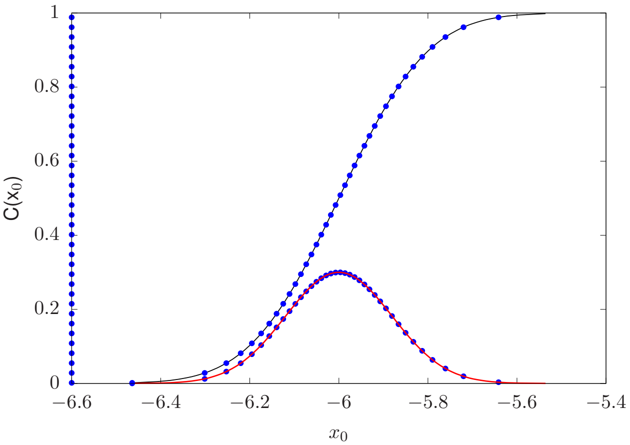
$$C(x_0) = \int_{-\infty}^{x_0} \rho_0(x_0')\, dx_0' \;\Rightarrow\; \rho_C = 1$$



Every trajectory bears the same density

Uniform density label

Initial distribution follows the initial density profile



Uniform density label

$$\frac{\partial}{\partial x_0} \to \frac{\partial}{\partial C}$$

$$\Rightarrow Q(x, x', x'') = \frac{\hbar^2}{4m}\left(\frac{x'''}{x'^3} - \frac{5}{2}\frac{x''^2}{x'^4}\right)$$

$$m\ddot{x} = -\frac{\partial V(x)}{\partial x} \underbrace{- \frac{\hbar^2}{4m}\left(\frac{x''''}{x'^4} - 8\frac{x'''x''}{x'^5} + 10\frac{x''^3}{x'^6}\right)}_{f_Q}$$

f_Q is the Quantum force

Uniform density label

Quantum force between neighboring trajectories

- Density core : finite differences

$$f_Q(x_{n-2}, x_{n-1}, x_n, x_{n+1}, x_{n+2}) = \frac{\hbar^2}{4m} \times$$
$$\left[\frac{1}{(x_{n+1}-x_n)^2} \left(\frac{1}{x_{n+2}-x_{n+1}} - \frac{2}{x_{n+1}-x_n} + \frac{1}{x_n - x_{n-1}} \right) \right.$$
$$\left. - \frac{1}{(x_n - x_{n-1})^2} \left(\frac{1}{x_{n+1}-x_n} - \frac{2}{x_n - x_{n-1}} + \frac{1}{x_{n-1}-x_{n-2}} \right) \right]$$

M. J. W. Hall, D.-A. Deckert, & H. M. Wiseman, Phys. Rev. X 4, 041013 (2014)

Density core > 95 % of total trajectories.

Uniform density label

- Tails : gaussian fit

$$\rho(x,t) = \frac{1}{\sqrt{2\pi}\omega(t)} e^{-\frac{(x-\delta(t))^2}{2\omega(t)^2}}$$

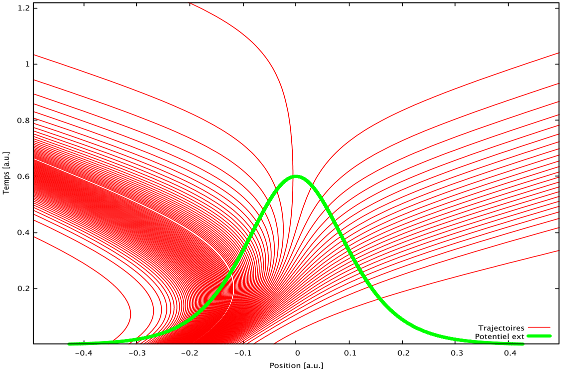
$$C(x,t) = \frac{1}{2}\left[1 + erf\left(\frac{x-\delta(t)}{\sqrt{2}\omega(t)}\right)\right]$$

$$x(C,t) = \sqrt{2}\,\omega(t)\; erf^{-1}(2C-1) + \delta(t)$$

1. Fit the parameters between each pair of neighbors.
2. Place virtual trajectories inbetween the neighbors.
3. Compute f_Q using finite differences formula.

Scattering process

Application : scattering through Eckart Barrier



Eckart parameters : $V_0 = 8000 \text{ cm}^{-1}$, $\alpha = 0.4$ a.u.

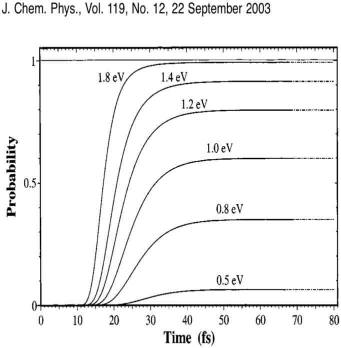
Gaussian wp parameters : $\omega_0 = 0.25$ a.u. , $\delta_0 = -5$ a.u.

400 trajectories, 5 fitted at each border, $m = 2000$ a.u.

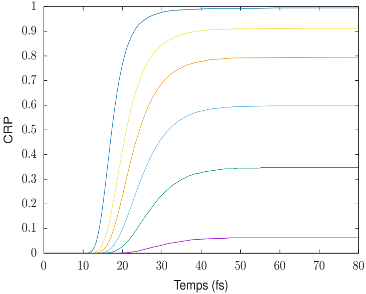
Scattering process

Application : scattering through Eckart Barrier

$P(E) \longrightarrow$ proportion of transmitted trajectories.



This work :



Kendrick (2003) :
Artificial viscosity force

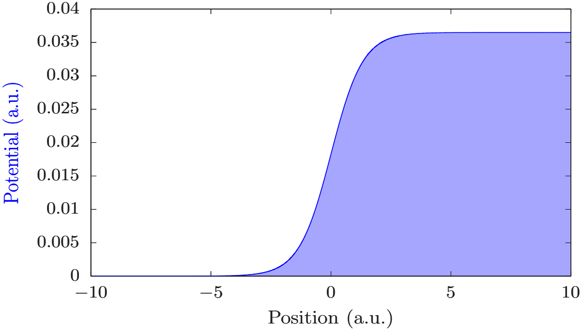
Scattering process

Application : scattering through Eckart Barrier

E	P(E)		
	This work	Kendrick (Quantum Trajectories)	Kendrick (Crank-Nicolson)
0.4	0.0250	0.02378	0.02374
0.5	0.0625	0.06325	0.06323
0.8	0.3475	0.34782	0.34749
1.0	0.5975	0.59773	0.59736
1.2	0.7950	0.79498	0.79473
1.4	0.9125	0.91194	0.91179
1.8	0.9950	0.98938	0.98943

Scattering process

Application : scattering through potential ramp



$$V(x) = \frac{\lambda}{1 + e^{-b\,x}}$$

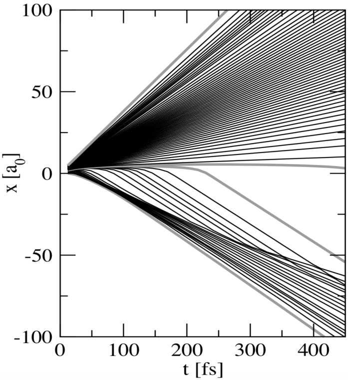
$\lambda = 3.65 \times 10^{-2}$ a.u. , $b = 1.5$ a.u. $m = 2000$ a.u.

Gaussian wp parameters : $\omega_0 = 0.25$ a.u. , $\delta_0 = -1$ a.u.

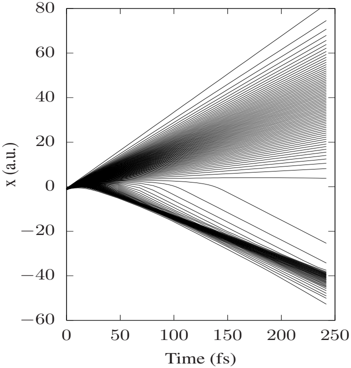
300 trajectories, 5 fitted at each border

Scattering process

Application : scattering through potential ramp



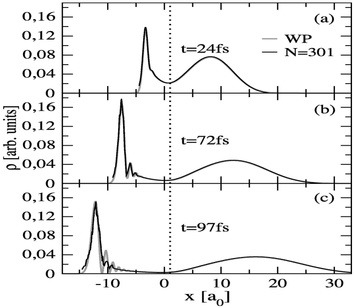
Cruz-Rodriguez et al., Chemical Physics (2018)



This work

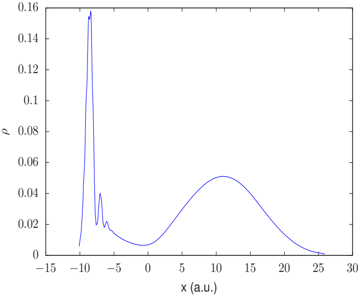
Scattering process

Application : scattering through potential ramp



Cruz-Rodriguez et al., Chemical Physics (2018)

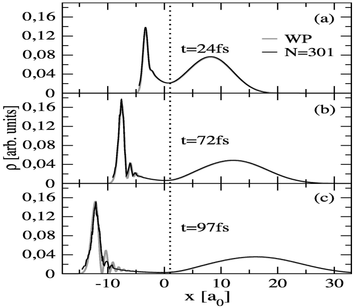
This work :



$t = 72 \quad \text{fs}$

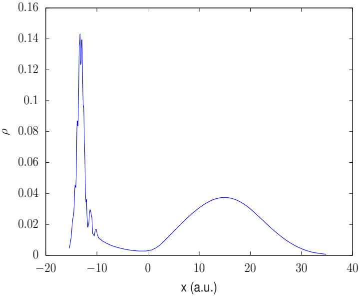
Scattering process

Application : scattering through Potential ramp



Cruz-Rodriguez et al., Chemical Physics (2018)

This work :



$t = 97 \quad \text{fs}$

Perspectives

Strengths

- Accurate
- Numerically stable

What's next ?

- Time independent : Approximate multidimensional dynamics

$$H(x, p_x, r, s, y, p_y) = \frac{s(2p - s)}{2m} - \frac{2r^2 s^4}{\hbar^2 m} + \frac{p_y^2}{2m} + V(x, y)$$

- Extension to nD from Time-Dependent approach.
- Extension to non-adiabatic problems ?

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