Very Accurate Surface Hopping Calculations

Michael F. Herman
Department of Chemistry
Tulane University
New Orleans, LA 70118

CSCAMM, March 9, 2010

Born-Oppenheimer electronic states (adiabatic representation)

$H^{el}\varphi_n(r,R) = E_n(R)\varphi_n(r,R)$ $H^{el} = H - T^{(nuc)}$

$E_n(R)$ serves as potential for motion of nuclei.

Ignores action of $T^{(nuc)}$ on $\varphi_n(r,R)$. This gives rise to nonadiabatic transitions.

Adiabatic representation: coupling from kinetic energy

Diabatic representation: coupling from potential energy.

$< \varphi_m(r,R) |H^{el} |\varphi_n(r,R) >$ has off-diagonal elements.

Surface Hopping: Trajectories run on adiabatic energy surface $E_n(R)$ with abrupt hops between different energy surface to account for nonadiabatic coupling.

Tully, Truhlar, Rossky, Nakamura

Semiclassical Surface Hopping Expansion

$$\Psi(x) = \varphi_i(x)\psi_i^{(0)}(x) + \Sigma_j \varphi_j(x)\, \psi_j^{(1)}(x) + \Sigma_j\, \varphi_j(x)\, \psi_j^{(2)}(x) + \ldots$$

$$\psi_i^{(0)} = A \exp(iW/\hbar) \quad W = \int_{x_0}^{x} p dx' \quad A = [p(x_0)/p(x)]^{1/2}$$

$$\psi_j^{(1)} = \int_{x_0}^{x} dx_1 \tau_{ij}(x_1)\, A \exp(iW/\hbar)$$

$$\tau_{ij} = -[(p_i+p_j)/2(p_i p_j)^{1/2}]\eta_{ij} \qquad \eta_{ij} = \langle \varphi_j \mid d\varphi_i/dx \rangle$$

$$\psi_j^{(2)} = \Sigma_k{}' \int_{x_0}^{x} dx_2 \int_{x_0}^{x_2} dx_1 \tau_{ik}(x_1)\, \tau_{kj}(x_2)\; A \exp(iW/\hbar)$$

Corresponding SH expansions for propagator, IVR propagator, GUWF

$$\Psi(x) = \varphi_i(x)\psi_i^{(0)}(x) + \Sigma_j\varphi_j(x)\,\psi_j^{(1)}(x) + \Sigma_j\,\varphi_j(x)\,\psi_j^{(2)}(x) + \ldots$$

$$d^2[\varphi_i\psi_i^{(0)}]/dx^2 = \varphi_i\, d^2\psi_i^{(0)}/dx^2 + 2\, d\varphi_i/dx\, d\psi_i^{(0)}/dx + \psi_i^{(0)}\, d^2\varphi_i/dx^2$$

$$d\varphi_i/dx = \eta_{ij}\,\varphi_j \qquad d^2\varphi_i/dx^2 = -\,\eta_{ij}^2\,\varphi_i + \varphi_j\, d\eta_{ij}/dx$$

$$\frac{d}{dx}\,\varphi_j \int_{x_0}^{x} dx_1\tau_{ij}(x_1)\; A\,\exp(iW/\hbar) = \varphi_j\,\tau_{ij}(x)\; A\,\exp(iW/\hbar) + \text{other terms}$$

This has same factor of $\eta_{ij}\,\varphi_j$ as $d\varphi_i/dx$ term from $\varphi_i(x)\psi_i^{(0)}(x)$

Taking second $\frac{d}{dx}$ on this term gives $\eta_{ij}\,\varphi_j$, $\varphi_j\, d\eta_{ij}/dx$, and $\eta_{ij}^2\,\varphi_i$ terms

If amplitudes for non-classical events chosen correctly, can cancel terms in SE arising from action of d^2/dx^2 on $\varphi_i(x)\psi_i^{(0)}(x)$.

Need 3 Types of Non-Classical Events to Satisfy $(H - E)\,\Psi = 0$

First Order Term:

$$\Psi^{(1)}(x) = \varphi_f \int_{x_0}^{x} dx_1\, \tau_{if}(x_1) A_T e^{iW_T/\hbar} + \varphi_f \int_{x}^{\infty} dx_1\, \rho_{if}(x_1) A_R e^{iW_R/\hbar}$$

$$+ \varphi_i \int_{x}^{\infty} dx_1\, \rho_{ii} A_N e^{iW_N/\hbar}$$

T-type hop

R-type hop

non-hopping momentum reversal

$\Psi^{(n)}(x)$ contains all sequences of n non-classical events

Amplitudes for Non-Classical Events

T-type hop:

$$\tau_{if} = -\frac{(P_{\eta i} + P_{\eta f})}{2\sqrt{P_{\eta i} P_{\eta f}}}\,\eta_{if}$$

Hop with momentum reversal:

$$\rho_{if} = -\frac{(P_{\eta i} - P_{\eta f})}{2\sqrt{P_{\eta i} P_{\eta f}}}\,\eta_{if}$$

Momentum change without hop:

$$\rho_{ii} = \frac{\nabla A}{A}, \quad A = \text{prefactor}$$

In numerical calculations:

Ignore momentum changes without hop.

Use only T-type hops in allowed regions.

Steps of finite size are used in numerical calculations

Step amplitudes: $\psi_j(x_b) = m_{ji}(x_b,x_a)\psi_i(x_a)$ $\quad x_b = x_a + dx$ or $t_b = t_a + dt$

Treat T-type $i \rightarrow j$ hop as occurring at middle of step. (can do better)

$m_{ji} = [A_j(x_b)/A_i(x_a)] \exp(iW_{ij}/\hbar) \sin(\Delta\theta_{ij})$ $\quad \Delta\theta_{ij} = \int \tau_{ij} dx$ $\quad$ if $i \neq j$

$m_{ii} = [A_i(x_b)/A_i(x_a)] \exp(iW_{ii}/\hbar) \cos(\Delta\theta_{ij})$ $\quad$ (2 state case)

These step amplitudes contains 1, 3, 5, … or 0, 2, 4, … hop terms.

Allows larger steps near avoided crossing points.

In IVR method, have final point for the step fixed, allow initial point to vary.

$\boldsymbol{\psi}(x_b) = \mathbf{M}(x_b,x_a)\boldsymbol{\psi}(x_a)$

$\boldsymbol{\psi}(x_n) = \mathbf{M}(x_n,x_{n-1})\mathbf{M}(x_{n-1},x_{n-2}) \ldots \mathbf{M}(x_1,x_0)\boldsymbol{\psi}(x_0)$ $\quad$ MM approach (1-d)

If $d > 1$, use $P_j = |m_{ji}|/[\Sigma_k |m_{ki}|]$ as probability of ij hop in MC calc.

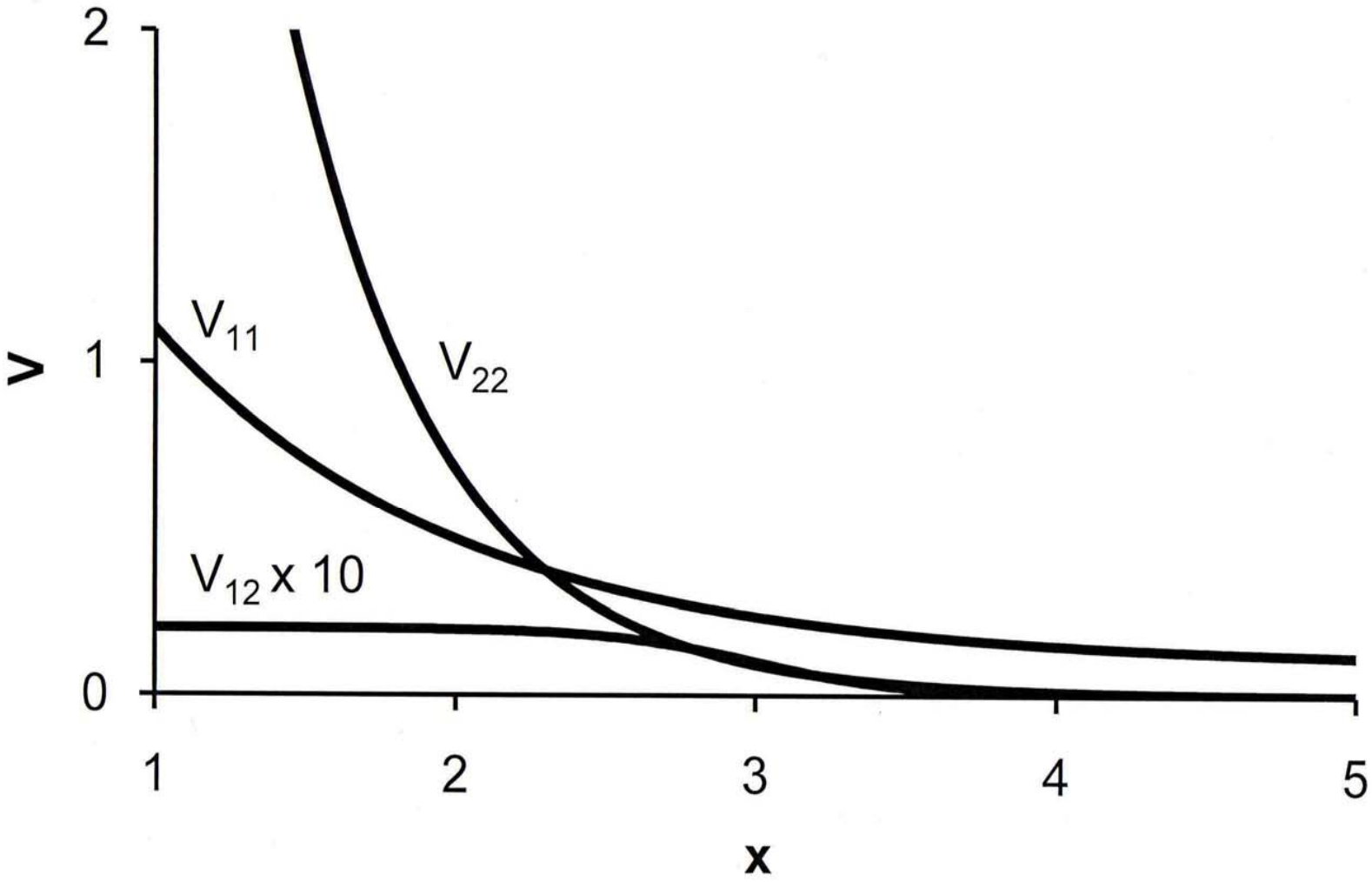
- Surface Hopping Expansion Formally Satisfies SE (TISE and TDSE). In General Not Convergent at All Points. (Proof applies in allowed region and for forbidden region in 1-d case.)

- Corresponding IVR Expansions for TDSE and TISE Satisfy SE to order $\hbar$.

- Recent Advances Show That It is Possible To Significantly Reduce The Statistical Errors in Monte Carlo Surface Hopping IVR Methods

Y. Wu and MFH, JCP 125, 154116 (2006); **127**, 044109 (2007)
MFH and Y. Wu, JCP 128, 114105 (2008)

Diabatic Potential Surface for Model Calculations



Comparison of quantum and semiclassical transition probabilities for $E > E_c$

$E_c \approx 0.37$

E	P_Q	$P_{S1}(x > x_{t1})$	$P_{S2}(x > x_{t2})$
0.38	0.618	0.440	0.576
0.40	0.951	0.819	0.918
0.45	0.142	0.179	0.143
0.50	0.835	0.761	0.838
0.60	0.543	0.508	0.544
0.75	0.356	0.348	0.356
0.90	0.118	0.120	0.118
1.20	1.87×10^{-2}	1.77×10^{-2}	1.86×10^{-2}
1.40	0.184	0.182	0.184

Both T-type and R-type hops in forbidden region.

Comparison of quantum and semiclassical transition probabilities of for $E < E_c$

E	P_Q	P_{S2}	$P_{S2}(FO)$
0.36	0.275	0.261	0.288
0.34	8.65×10^{-2}	8.54×10^{-2}	8.89×10^{-2}
0.32	1.93×10^{-2}	1.94×10^{-2}	1.97×10^{-2}
0.30	3.00×10^{-3}	3.03×10^{-3}	3.05×10^{-3}
0.28	3.16×10^{-4}	3.19×10^{-4}	3.20×10^{-4}
0.26	2.14×10^{-5}	2.16×10^{-5}	2.15×10^{-5}
0.24	8.54×10^{-7}	8.55×10^{-7}	8.56×10^{-7}
0.22	1.77×10^{-8}	1.76×10^{-8}	1.81×10^{-8}
0.20	1.49×10^{-10}	1.74×10^{-10}	1.42×10^{-10}
0.19	8.50×10^{-12}	7.07×10^{-12}	7.10×10^{-12}
0.18	3.06×10^{-13}	1.3×10^{-13}	3.4×10^{-13}
0.17	5.33×10^{-15}	2.4×10^{-15}	8.5×10^{-15}

Singular at x_{tp}. Significant cancellation between allowed and forbidden regions.

Why does it work so well?

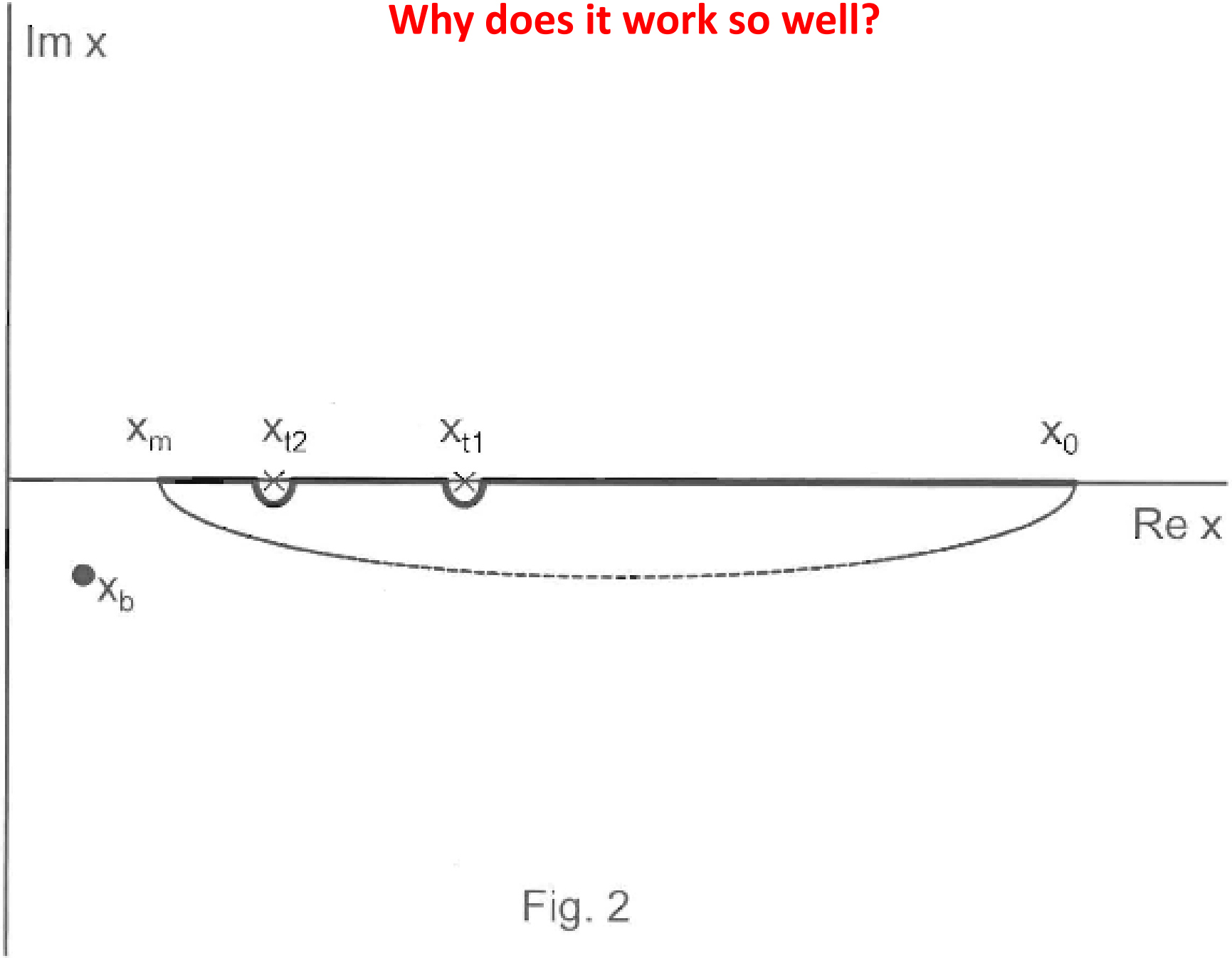


Fig. 2

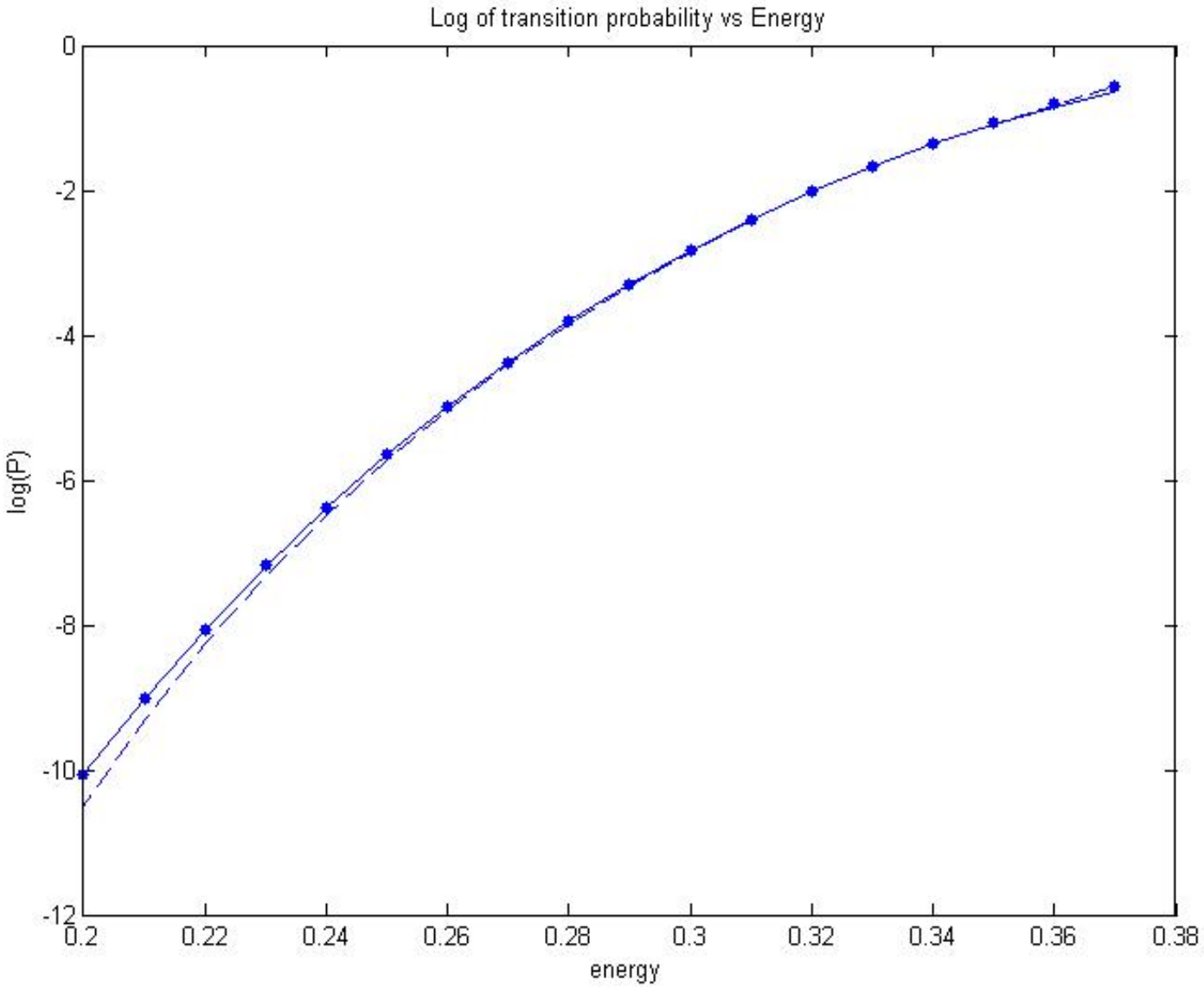
For transitions in forbidden zone

Wave function on upper surface (Ψ_u) decays rapidly when moving into the forbidden zone from turning point.

Nonadiabatic coupling (η) sharply peaked around crossing point (in forbidden region) and is decaying when moving from crossing point toward turning point.

Product of Ψ_u and η is peaked in forbidden zone near turning point.

Suggests approximation based on behavior near turning point may yield good results.



Probability of quantum state change in model collision system for forbidden transitions.

. . . . exact quantum results, —— semiclassical results, ----- results using "simple" approximation to semiclassical calculation.

For details see:

M. F. Herman, J. Phys. Chem. B **112**, 15966 (2008).

and

P.-T. Dang and M. F. Herman, J. Chem. Phys., **130**, 054107 (2009).

Singularity Free Surface Hopping

Break x axis into small regions or steps

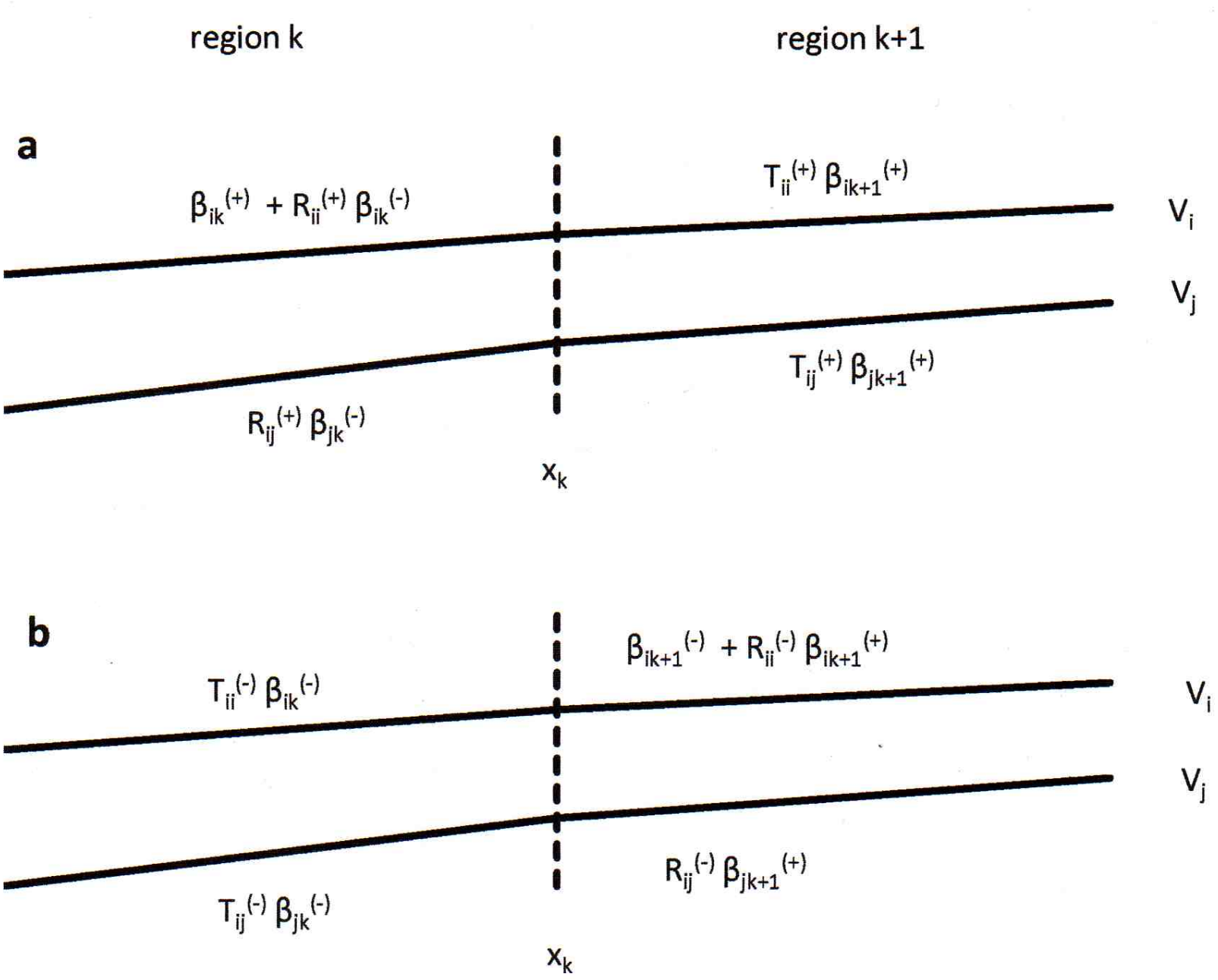
Treat adiabatic electronic states as constant across each step

Treat adiabatic potential surface for each states as linear function of x across step

Use $\beta_j^{(\pm)} = Ai(z_j) \pm i\, Bi(z_j)$ as wave functions in each region

$z_j = [2m/(\hbar\, dV_j/dx)^2]^{1/3}[V_j(x)-E]$

$\beta_j^{(\pm)} \sim p^{-1/2} \exp(\pm i\int p dx/\hbar)$ as $\hbar \rightarrow 0$


region k
region k+1
a
$\beta_{ik}^{(+)} + R_{ii}^{(+)} \beta_{ik}^{(-)}$
$T_{ii}^{(+)} \beta_{ik+1}^{(+)}$
V_i
V_j
$T_{ij}^{(+)} \beta_{jk+1}^{(+)}$
$R_{ij}^{(+)} \beta_{jk}^{(-)}$
x_k
b
$\beta_{ik+1}^{(-)} + R_{ii}^{(-)} \beta_{ik+1}^{(+)}$
$T_{ii}^{(-)} \beta_{ik}^{(-)}$
V_i
V_j
$R_{ij}^{(-)} \beta_{jk+1}^{(+)}$
$T_{ij}^{(-)} \beta_{jk}^{(-)}$
x_k

Solve matching conditions that the wave function and its derivative are the same across the boundary

Get step amplitudes for hop and/or change in direction of propagation

Gives expansion with the same set of terms as the surface hopping expansion

Exact if all terms kept

Reduces to SC SH expansion in small step size and $\hbar \rightarrow 0$ limits

E	P_{12}(Q)	P_{12}(S)	P_{12}(SF)	P_{12}(S-SF,z_c=5)
0.20	8.44×10^{-11}	8.49×10^{-11}	8.4×10^{-11}	
0.24	4.09×10^{-7}	4.12×10^{-7}	4.09×10^{-7}	
0.28	1.53×10^{-4}	1.55×10^{-4}	1.53×10^{-4}	
0.32	9.57×10^{-3}	9.74×10^{-3}	9.57×10^{-3}	9.54×10^{-3}
0.36	0.141	0.154	0.141	0.141
0.38	0.324	0.366	0.324	0.324
0.42	0.538	0.554	0.538	0.537
0.46	2.48×10^{-2}	2.53×10^{-2}	2.48×10^{-2}	
0.50	0.325	0.327	0.235	
0.60	0.237	0.237	0.237	

MFH, J. Chem. Phys. **131,** 214108 (2009)

The Semiclassical Wave Function for d > 1 in the Forbidden Region

Single Surface Case

$V(r) = A\, e^{-\alpha r}$

$A = 10$

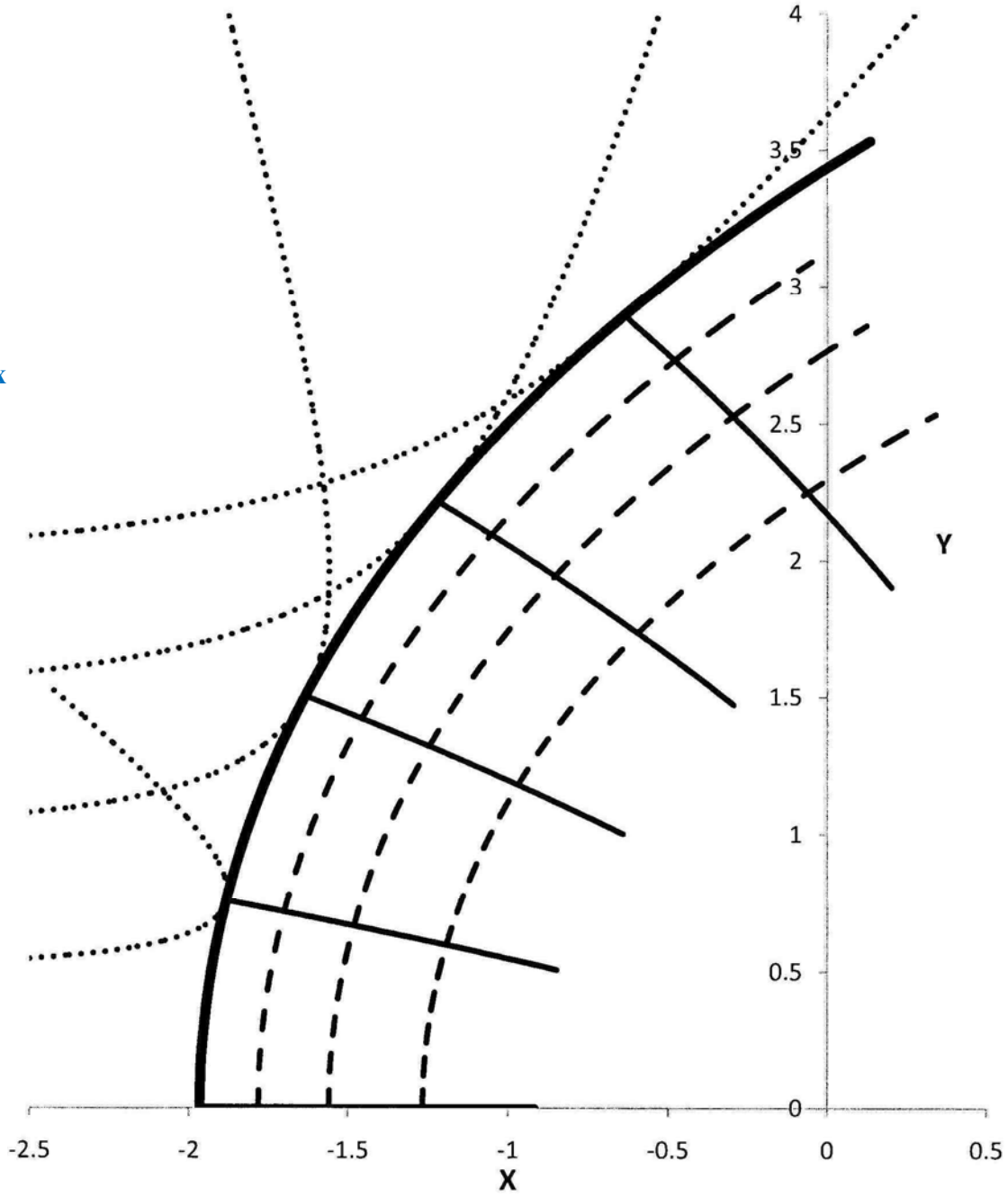
$\alpha = 1$

$m = 1836$

$\hbar = 1$

$E = 1.4$

$\Psi_{in}(x, y) = e^{ikx}$



$$\psi(\mathbf{r}) = A\, e^{iW/\hbar}$$

W can have real and imaginary parts in forbidden region:

$$W = W_a + i\, W_b$$

Substitute ψ in the time independent Schrodinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\,\psi = E\,\psi$$

Order h^0 equation:

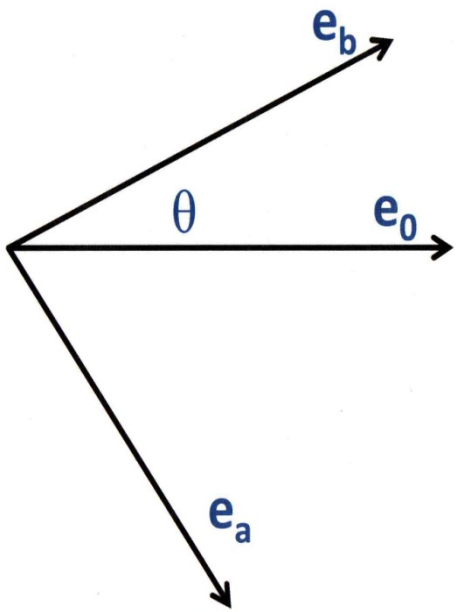
$$\frac{\nabla W^2}{2m} + V = E \qquad \frac{\nabla W_a^2 - \nabla W_b^2}{2m} = E - V$$

$$\mathbf{p}_a \cdot \mathbf{p}_b = 0$$

$$\nabla W = \mathbf{p} = \mathbf{p}_a + i\mathbf{p}_b \qquad \frac{p_a^2 - p_b^2}{2m} = E - V$$

Order $\hbar^1$ equation:

$$\nabla \cdot (\mathbf{p}_a + i\,\mathbf{p}_b)\,A + 2(\mathbf{p}_a + i\,\mathbf{p}_b) \cdot \nabla A = 0$$



$\mathbf{e_0}$ = unit vector along $\mathbf{p_0}$,

$\mathbf{e_a}$ = unit vector along $\mathbf{p_a}$, s_a is distance in $\mathbf{p_a}$ direction

$\mathbf{e_b}$ = unit vector along $\mathbf{p_b}$, s_b is distance in $\mathbf{p_b}$ direction

$$\frac{p_a^2 - p_b^2}{2m} = E - V \qquad p_a \cdot p_b = 0 \qquad \text{(order } \hbar^0 \text{ equations)}$$

$$p_b \frac{\partial p_b}{\partial s_b} = m\frac{\partial V}{\partial s_b} + p_a \frac{\partial p_a}{\partial s_b} \qquad \text{gives } \frac{\partial p_b}{\partial s_b} \quad (\text{need } \partial p_a/\partial s_b)$$

$V(r) = A\, e^{-\alpha r}$

$A = 10$

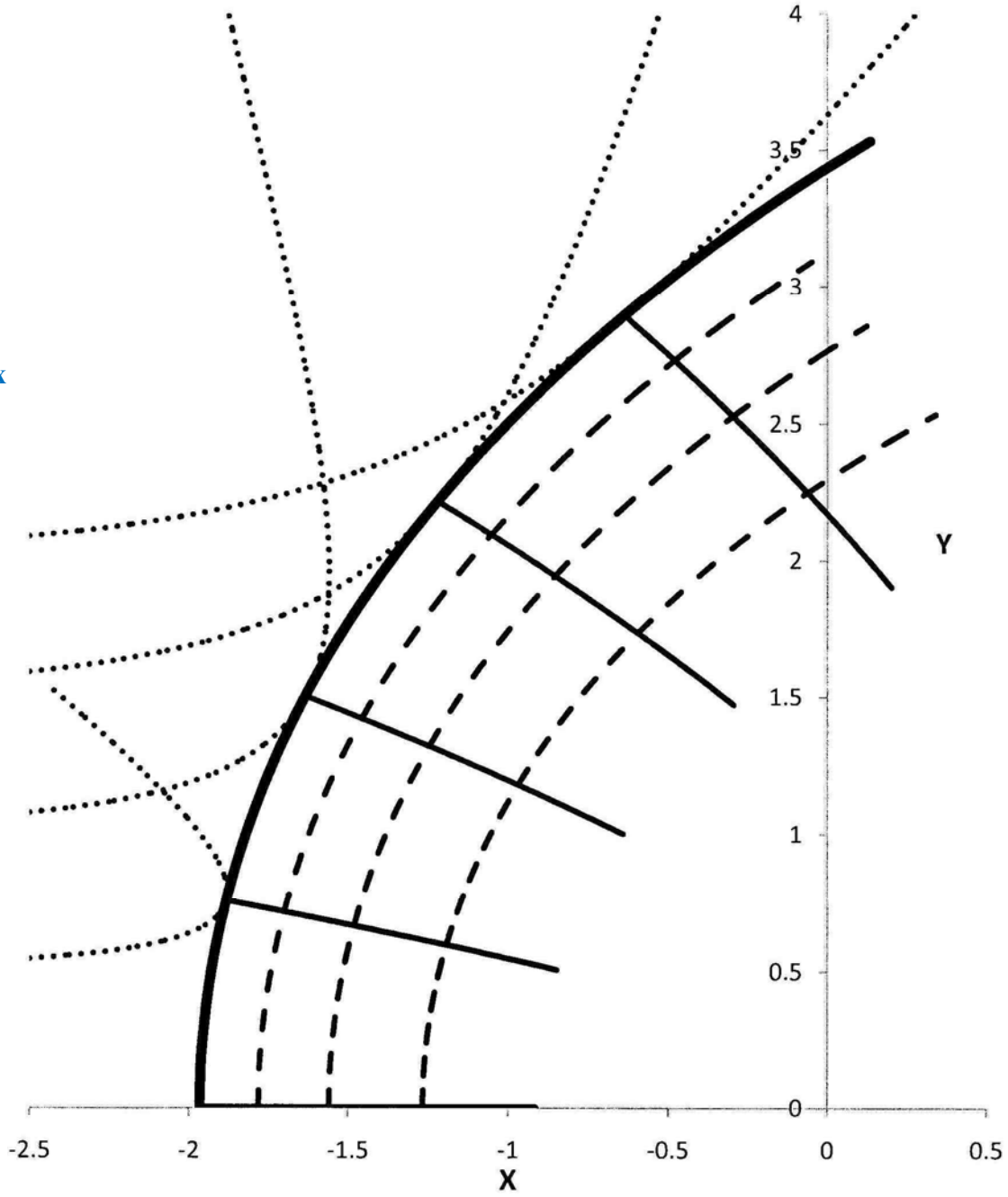
$\alpha = 1$

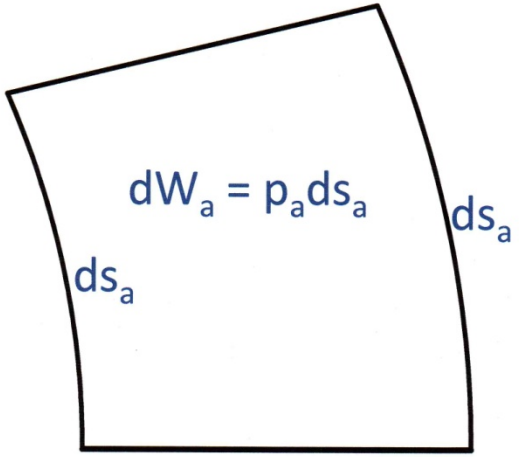
$m = 1836$

$\hbar = 1$

$E = 1.4$

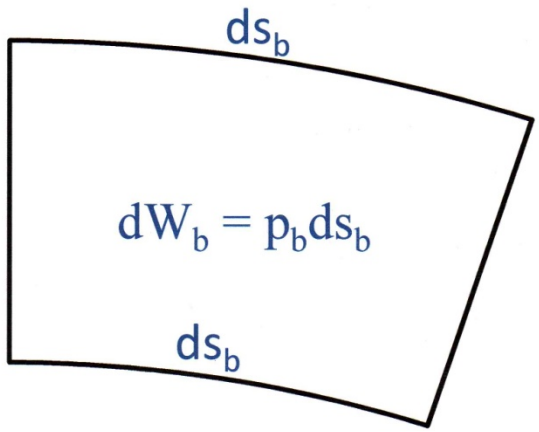
$\Psi_{in}(x, y) = e^{ikx}$





$$\frac{\partial p_a}{\partial s_b} = p_a \frac{\partial \theta}{\partial s_a}$$

$\frac{\partial \theta}{\partial s_a}$ determines $\frac{\partial p_a}{\partial s_b}$



$$\frac{\partial \theta}{\partial s_b} = -\frac{1}{p_b} \frac{\partial p_b}{\partial s_a}$$

$\frac{\partial p_b}{\partial s_a}$ determines $\frac{\partial \theta}{\partial s_b}$

$$p_b \frac{\partial p_b}{\partial s_b} = m\frac{\partial V}{\partial s_b} + p_a \frac{\partial p_a}{\partial s_b} \qquad \text{(order } \hbar^0 \text{ equation)}$$

$$\frac{\partial p_b}{\partial s_b} = \frac{m}{p_b}\frac{\partial V}{\partial s_b} + \frac{p_a^2}{p_b}\frac{\partial \theta}{\partial s_a} \qquad \text{uses } \frac{\partial p_a}{\partial s_b} = p_a \frac{\partial \theta}{\partial s_a}$$

$$\nabla \cdot (p_a + i\, p_b)\, A + 2(p_a + i\, p_b) \cdot \nabla A = 0 \qquad \text{(order } \hbar^1 \text{ equation)}$$

$$2\, p_a \frac{\partial A}{\partial s_a} + 2i\, p_b \frac{\partial A}{\partial s_b} + A\, \nabla \cdot (p_a + i\, p_b) = 0$$

$$\frac{\partial A}{\partial s_b} = (i/p_b)\, [\, p_a \frac{\partial A}{\partial s_a} + \tfrac{1}{2} A\, \nabla \cdot (p_a + i\, p_b)]$$

$$\nabla \cdot p_a = \frac{\partial p_a}{\partial s_a} + p_a \frac{\partial \theta}{\partial s_b} = \frac{\partial p_a}{\partial s_a} - \frac{p_a}{p_b}\frac{\partial p_b}{\partial s_a} \qquad \text{uses } \frac{\partial \theta}{\partial s_b} = -\frac{1}{p_b}\frac{\partial p_b}{\partial s_a}$$

$$\nabla \cdot p_b = \frac{\partial p_b}{\partial s_b} + p_b \frac{\partial \theta}{\partial s_a}$$

$V(r) = A\, e^{-\alpha r}$

$A = 10$

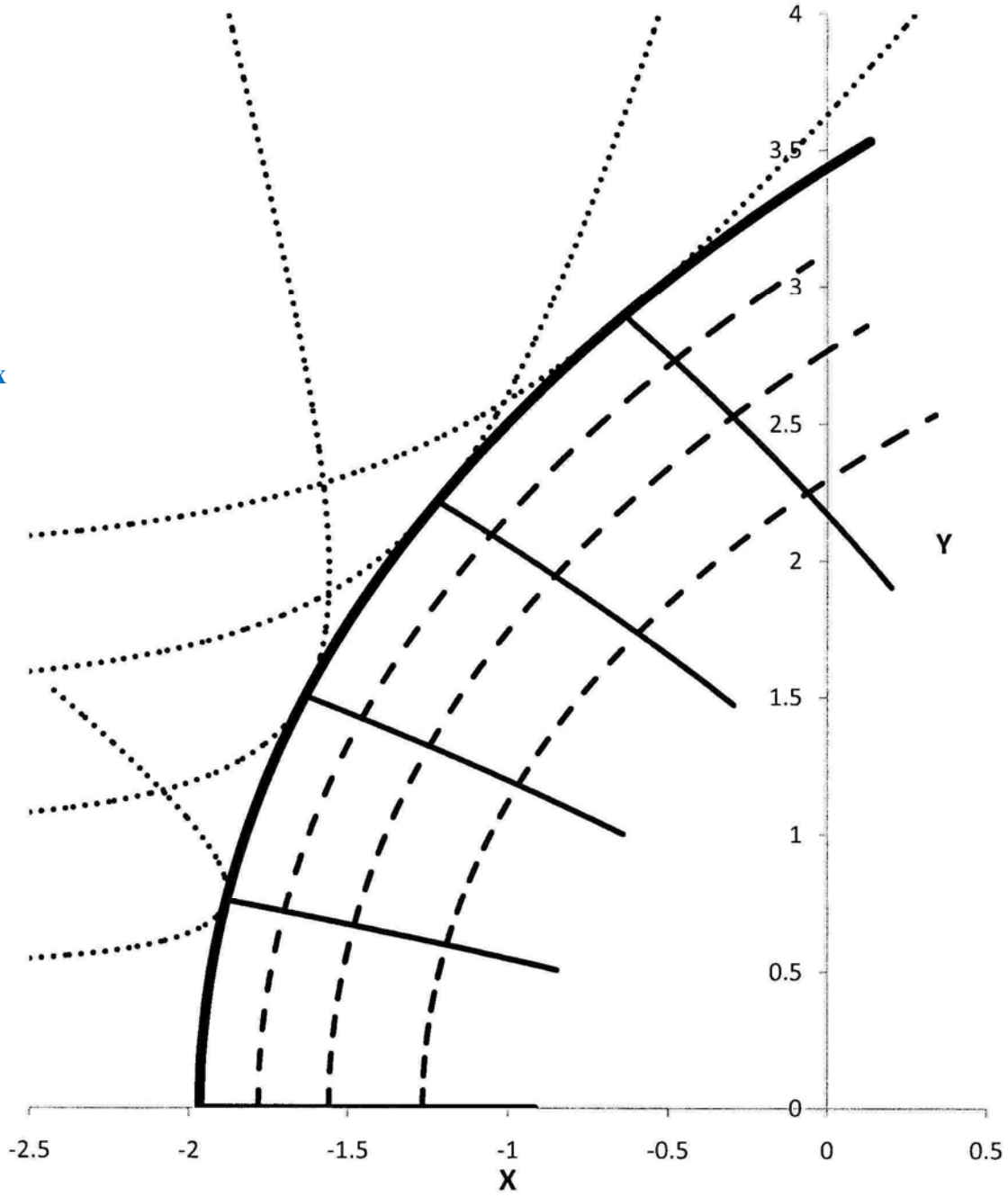
$\alpha = 1$

$m = 1836$

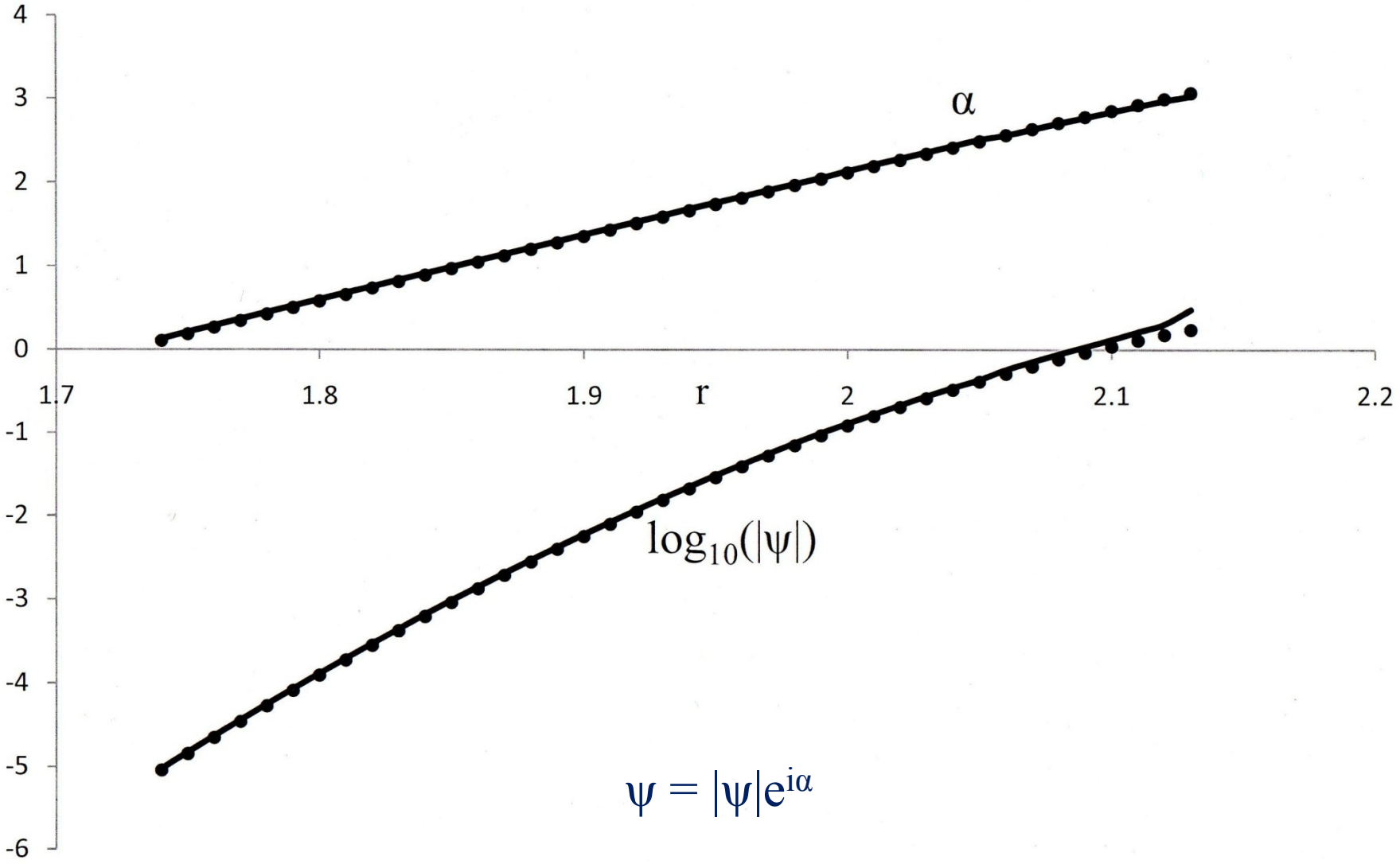
$\hbar = 1$

$E = 1.4$

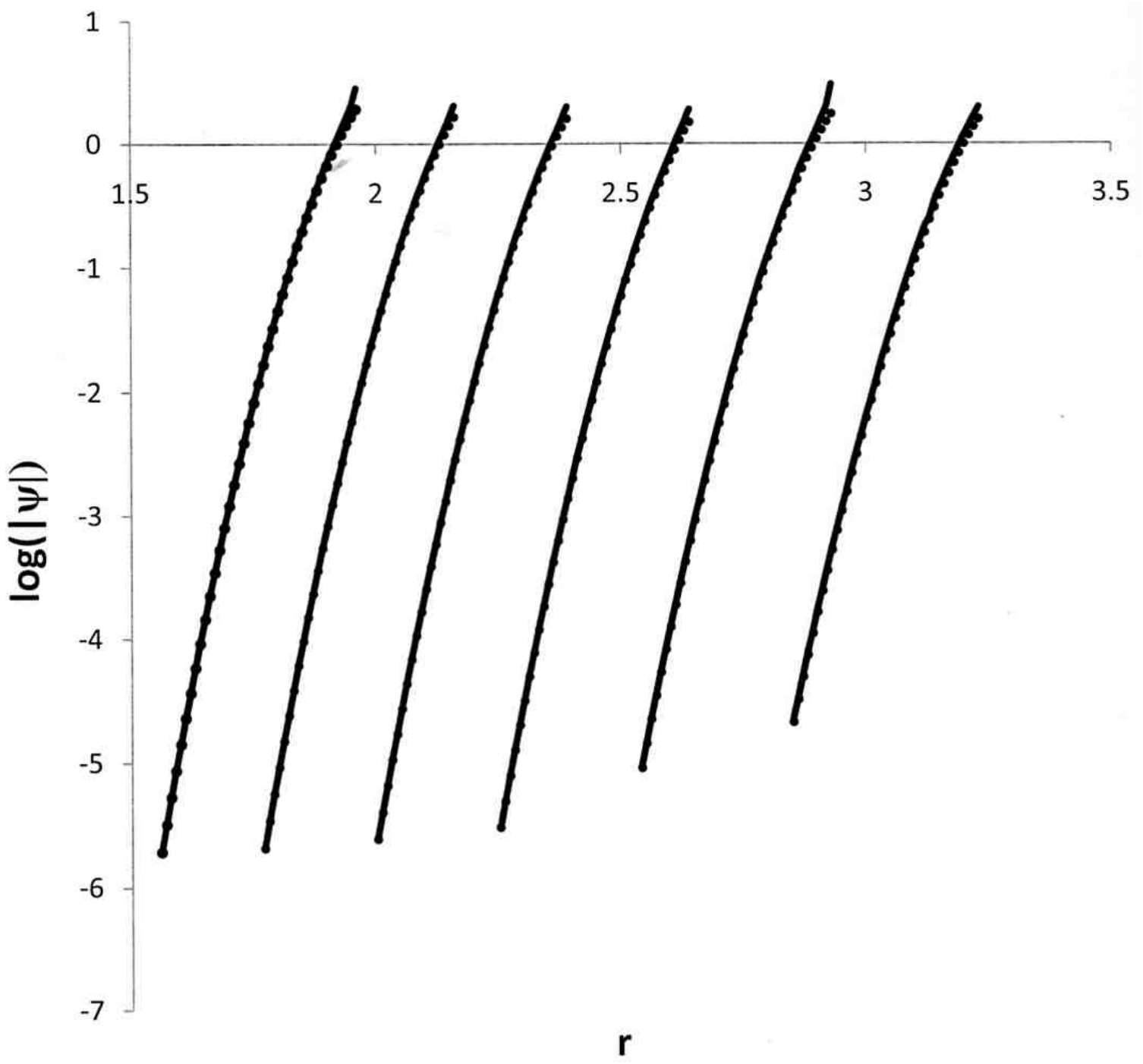
$\Psi_{in}(x, y) = e^{ikx}$



$\Theta = 4\pi/5$



$\psi = |\psi| e^{i\alpha}$


1
0
-1
-2
-3
-4
-5
-6
-7
1.5
2
2.5
3
3.5
log(|ψ|)
r

Why does proof that SH expansion satisfies SE not apply in forbidden region

Proof implicitly assumes $\mathbf{p}$ is a vector. It can be real or imaginary.

In forbidden region $\mathbf{p} = \mathbf{p}_R + i\mathbf{p}_I$ has both real and imaginary parts and these are perpendicular.

SH expansion must be generalized:

Instead of a single hop in the $\boldsymbol{\eta}$ direction, use $\boldsymbol{\eta} = \boldsymbol{\eta}_a + \boldsymbol{\eta}_b + \ldots$ where $\boldsymbol{\eta}_a \cdot \boldsymbol{\eta}_b = 0$.

Choose $\boldsymbol{\eta}_b$ parallel to $\mathbf{p}_I$.

Work in progress! (Both formal analysis and numerical calculations.)

Using Surface Hopping for Calculations of Accurate Wave Functions for d > 1 Test Problems

$\Psi(r, \theta) = \Sigma_k \psi_k(r) P_k(\theta)$

$P_k(\theta)$ angular momentum eigenfunction

$\psi_k = \chi_k / r^{(d-1)/2}$

Consider d = 2 for simplicity

$$\mathbf{H} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{(d-1)}{r}\frac{\partial}{\partial r}\right] + \mathbf{J}^2/2\mu r^2 + V(r, \mathbf{u})$$

$$\Psi(r, \theta) = \Sigma_k \psi_k(r) P_k(\theta)$$

$$\psi_k = \chi_k / r^{1/2}$$

$$V_{j\text{-}m} = \int d\theta \; P_j(\theta)^* V(r,\theta) P_m(\theta)$$

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2\chi_j}{dr^2} + \frac{j^2\hbar^2}{2\mu r^2}\chi_j(r)\right) + \Sigma_m V_{j\text{-}m}(r)\,\chi_m(r) = E\,\chi_j(r)$$

(Langer modification included)

$$V_{ij}(r) = \delta_{ij}\frac{j^2\hbar^2}{2mr^2} + V_{i\text{-}j}(r) \qquad \text{diabatic potential}$$

$$\mathbf{V}^{(a)}(r) = \mathbf{U}(r)^T\,\mathbf{V}(r)\,\mathbf{U}(r) \qquad \text{adiabatic potential}$$

$$Q_k(\theta, r) = \Sigma_m\, u_{mk}(r)\, P_m(\theta) \qquad \text{adiabatic angular states}$$

$P_m(\theta)$ angular momentum states

$$\eta_{ij} = \langle Q_j \mid dQ_i/dr \rangle \qquad \text{nonadiabatic coupling}$$

$$\psi(r,\theta) = \sum_{k=0}^{\infty} Q_k \chi_k^{(a)}(r)/r^{1/2}$$

$\chi_k^{(a)}(r)$ obtained from 1-d surface hopping expansion for radial Hamiltonian in adiabatic representation (use MM approach).

Numerical Problem with single electronic state:

$V(r,\theta) = A\, e^{-\alpha r}\,(1 + a\, xy/r^2) = A\, e^{-\alpha r}\,[1 + a \sin(2\theta)/2]$

$A = 10, \quad \alpha = 3, \quad a = 0.7, \quad m = 1836.2, \quad \hbar = 1$

Use symmetry adapted eigenfunctions of $\mathbf{J}_z$ as diabatic angular states

Calculate state-to-state transition probabilities

Calculation of transition probabilities 2-state tests (exact quantum results can be obtained numerically)

States	E=0.1	E=0.4	E=0.7	E=1.0
1,5	6.67×10^{-3}(S)	2.80×10^{-2}	0.603	0.491
	6.79×10^{-3}(Q)	2.83×10^{-2}	0.603	0.492
3,6	0.469(S)	0.808	2.61×10^{-2}	0.587
	0.469(Q)	0.808	2.60×10^{-2}	0.587
5,8	0.612(S)	0.953	0.106	0.545
	0.611(Q)	0.953	0.106	0.545
10,15	0.650(S)	0.923	0.150	0.464
	0.650(Q)	0.923	0150	0.465
20,25	0.749(S)	0.802	0.315	0.239
	0.749(Q)	0.802	0.314	0.240
50,55	0.667(S)	4.31×10^{-2}	0.915	0.392
	0.667(Q)	4.33×10^{-2}	0.915	0.391
100,105	9.54×10^{-3}(S)	0.568	0.175	3.09×10^{-2}
	9.54×10^{-3}(Q)	0.568	0.175	3.09×10^{-2}
150,155	8.31×10^{-6}(S)	8.24×10^{-2}	0.358	0.461
	8.35×10^{-6}(Q)	8.24×10^{-2}	0.358	0.461
200,205	4.76×10^{-9}(S)	3.30×10^{-3}	5.19×10^{-2}	0.166
	4.80×10^{-9}(Q)	3.30×10^{-3}	5.19×10^{-2}	0.166

Many State Calculations

Total Cross Section

E	number of states	σ(comp)	σ(approx)
0.1	251	11.1347	11.1362
0.1	301	11.1347	11.1361
0.4	301	10.1698	10.1705
0.4	351	10.1698	10.1704
0.7	351	9.7766	9.7769
0.7	401	9.7763	9.7765
1.0	401	9.5250	9.5251
1.0	451	9.5256	9.5258

$\Psi_{in}(x,y) = \exp(i\mathbf{p}\cdot\mathbf{r}/\hbar)$

Approximate calculation:

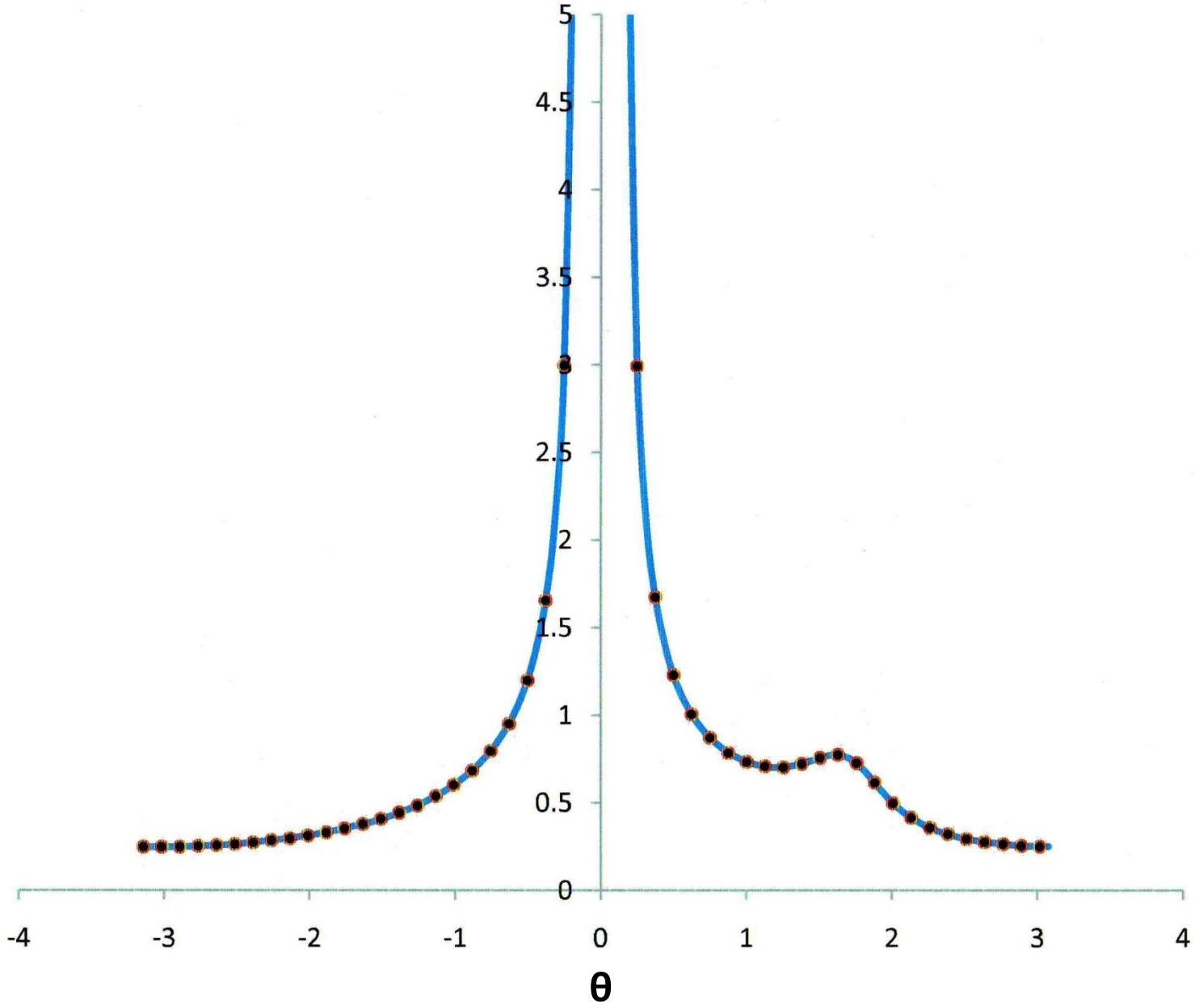
For τ_{ij}: $\frac{1}{2}(p_i + p_j)/\sqrt{|p_i p_j|} = 1$ in allowed region

$\frac{1}{2}(p_i + p_j)/\sqrt{|p_i p_j|} = (1+i)/2$ in forbidden region

For ρ_{ij}: $\frac{1}{2}(p_i - p_j)/\sqrt{|p_i p_j|} = 0$ in allowed region

$\frac{1}{2}(p_i - p_j)/\sqrt{|p_i p_j|} = (1-i)/2$ in the forbidden region

Differential cross section, E = 0.7, 401 states



CONCLUSIONS

- Detailed formal analysis shows what terms must be included in order to have highly accurate SH method.
- Surface Hopping Expansion provides very good transition probabilities even for strongly forbidden transitions.
- Cancellation between contributions from allowed and forbidden regions must be accurately accounted for.
- Good approximation obtained using only information evaluated at turning point. (Only 1-d case so far.)
- Singularity-Free version improves results near crossing energy of diabatic surfaces

Acknowledgements:

Yinghua Wu, Phuong Thanh Dang

Feng Ding (Terry)

NSF