Phase Space Sampling
for
Trajectory Simulations

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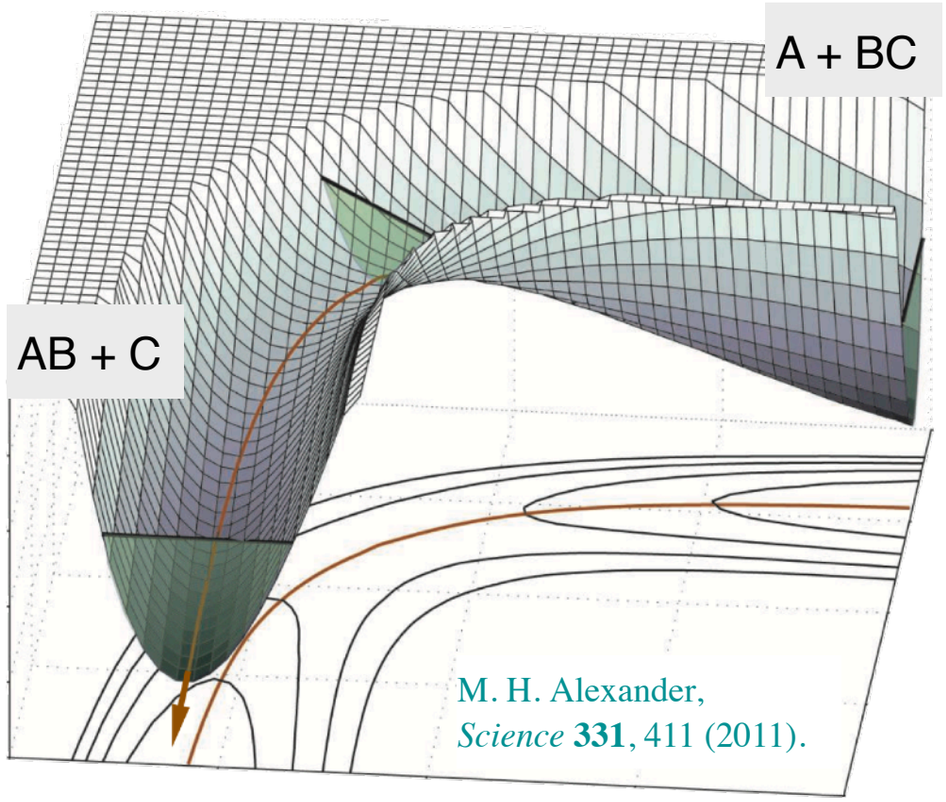
Quantum effects in reactive collisions

may change reaction rate by orders of magnitude!

- Tunnel effects:
  - through barrier,
  - corner cutting.
- Zero-point energy:
  - in reactants / products,
  - all along trajectories,
  - “energy leaking” below ground quantum level.



…not taken into account by classical trajectories.

Quantum effects in trajectory simulations

- Can we account for quantum effects—at least in part—by means of ***trajectories***?
- Here we will look specifically at the ***sampling*** of trajectory initial conditions.

First, need to get back to 1D **quantum** trajectories 

Quantum trajectory approach

the "no-wave" formulation

- Originates in (but quite different from) deBroglie-Bohm.
- The *trajectory ensemble itself* is the fundamental quantum state entity, rather than the wave function **Ψ**.

- **Bill Poirier**, Bohmian mechanics without pilot waves, *Chem. Phys.* **370**, 4 (2010).
- **J. Schiff and Bill Poirier**, Quantum mechanics without wavefunctions, *JCP* **136**, 031102 (2012).
- **G. Parlant, Y.-C. Ou, K. Park, and B. Poirier**, Classical-like trajectory simulations for accurate computation of quantum reactive scattering probabilities. *Comput. Theor. Chem.*, **990**, 3 (2012).

Stationary scattering state - 1D (#1)

Hamilton eqs of motion

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Hamilton eqs of motion

(x, p) "real space"

$$\dot{x} = \frac{s}{m}$$

$$\dot{p} = -\frac{\partial V}{\partial x}$$

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$$\dot{r} = \frac{p - s}{m} - \frac{8r^2 s^3}{m\hbar^2}$$

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Hamiltonian:

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

H(x, p, r, s) reduces to classical Hamiltonian when $\boldsymbol{r = 0}$ and $\boldsymbol{s = p}$

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☞ four initial conditions:

1 for time translation / 1 for total energy / 2 to specify particular quantum state $\Psi(x)$

Stationary scattering state - 1D

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Stationary scattering state - 1D (#2)

The classical limit!…

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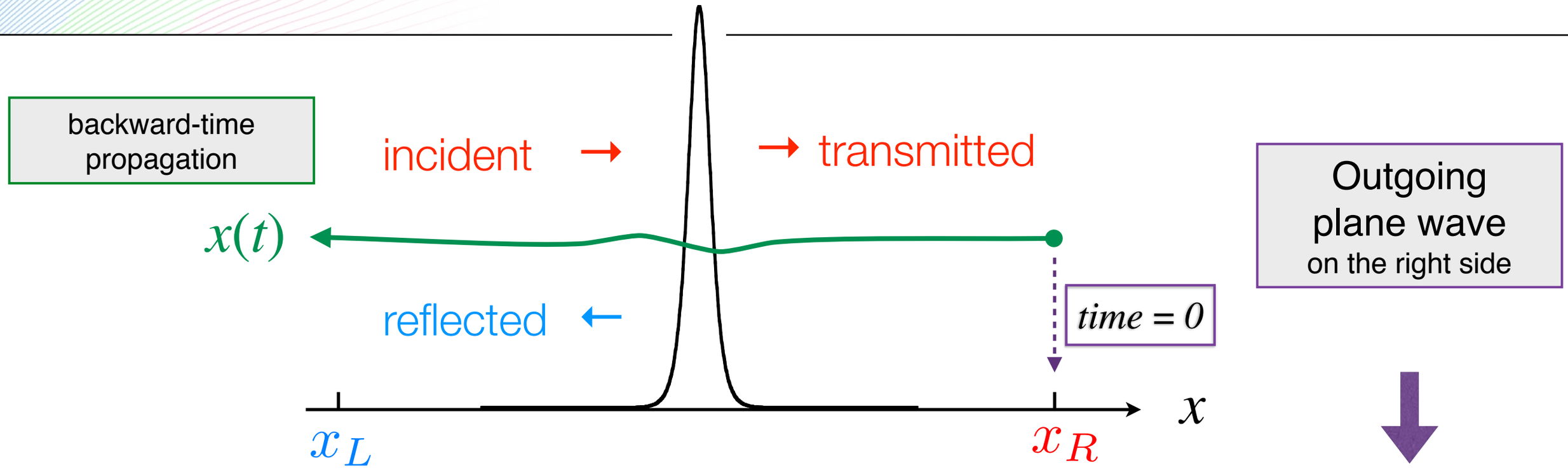
The classical limit!…

Tunneling through a 1D Eckart barrier (#1)



$$\Psi(x \to +\infty) = k_R^{-1/2} T \exp[ik_R x]$$

$$\Psi(x \to -\infty) = k_L^{-1/2} \left(\exp[ik_L x] + R \exp[-ik_L x]\right)$$

Initial conditions:

$$x_0 = x_R$$

$$\dot{x}_0 = \sqrt{2E/m}$$

$$\ddot{x}_0 = \dddot{x}_0 = 0$$

Transmission proba: $P_T = |T|^2$

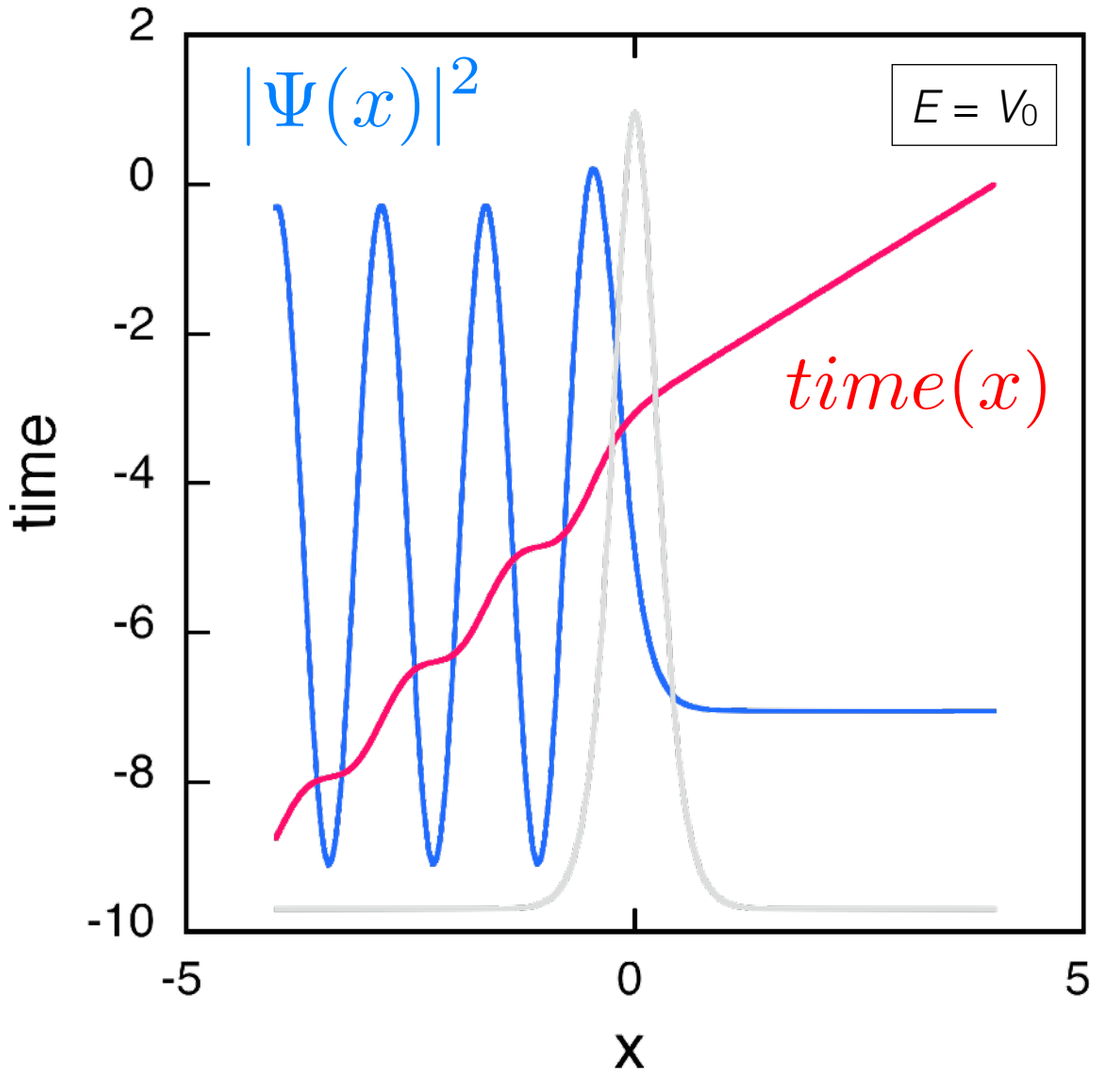
Reflection proba: $P_R = |R|^2$

Tunneling through a 1D Eckart barrier (#2)

solution quantum trajectory

Eckart potential:

$$V(x) = V_0 \, \mathrm{sech}^2(\alpha x)$$



$\alpha = 3.0\, a.u.$
$m = 2000\, a.u.$
$V_0 = 400\, cm^{-1}$

- ODE integration by means of a simple (adaptive step-size) Runge-Kutta propagator.
- typical CPU time = 0.03 s

extremely deep tunneling

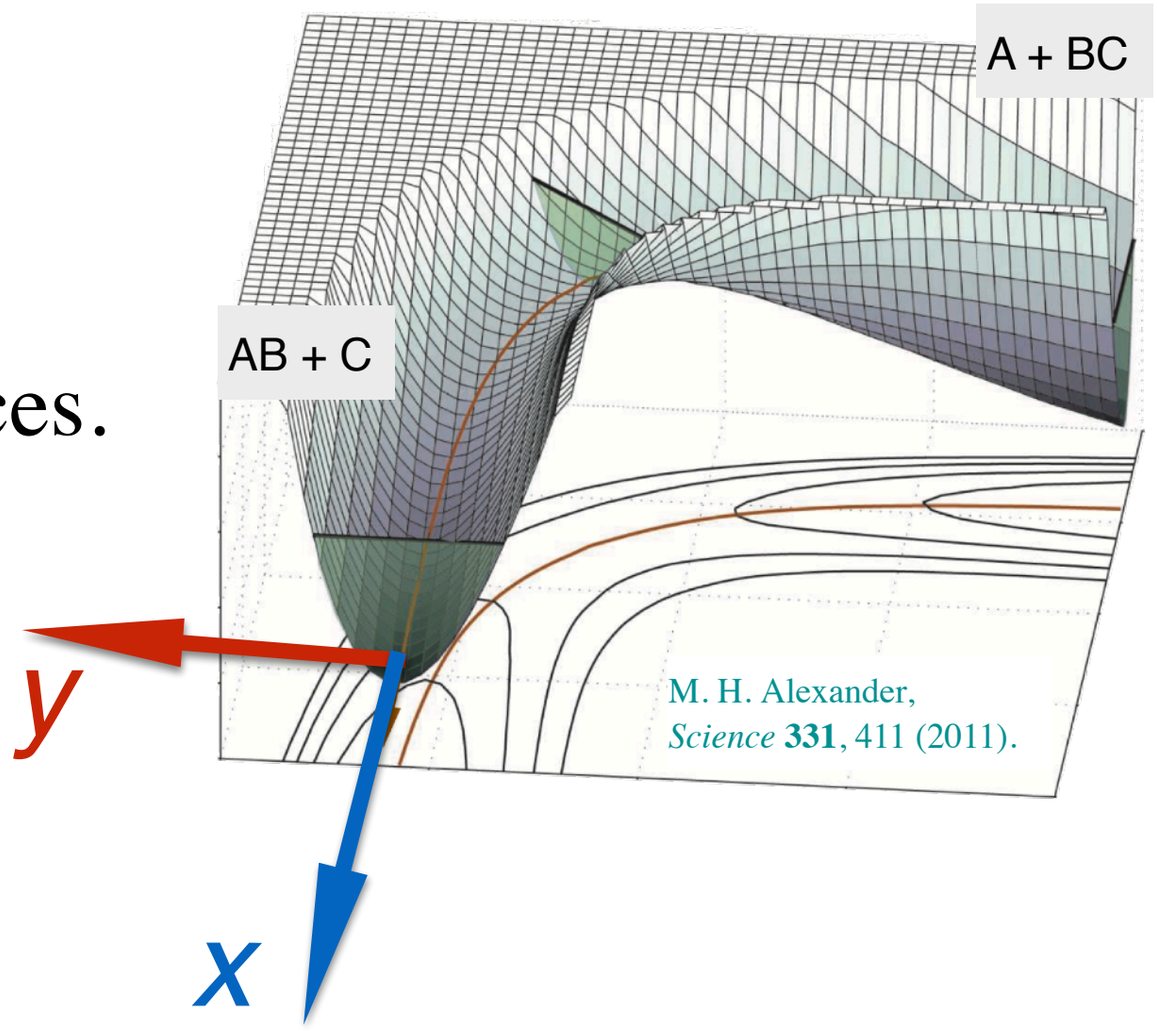
E/V_0		5.48 (– 43)
Exact	$P_{Transmission}$	1.564188807419903**9** (– 43)
Computed	$P_{Transmission}$	1.564188807419934**5** (– 43)
Relative Error		~ 2.0 (–14)

One single trajectory gives the exact solution

Extension to multi-D systems

assume tunneling is most important along reaction coordinate 'x'

- $x \rightarrow$ follows quantum motion along reaction path,
  - exact tunneling / interferences.
- $y \rightarrow$ classical vibration,
  - will need to choose the (undetermined vibrational phase *at random*.



Write down quantum and classical motion eqs

2D Hamilton eqs of motion

notice the tunnel / interference extra space!

$$\dot{x} = \frac{\partial H}{\partial p_x} \quad \dot{p_x} = -\frac{\partial H}{\partial x};$$

quantum

$$\dot{r} = \frac{\partial H}{\partial p_r} \quad \dot{p_r} = -\frac{\partial H}{\partial r};$$

tunnel / interference

$$\dot{y} = \frac{\partial H}{\partial p_y} \quad \dot{p_y} = -\frac{\partial H}{\partial y}$$

classical

x↔y coupling

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

Hamiltonian

prototype 2D chemical system

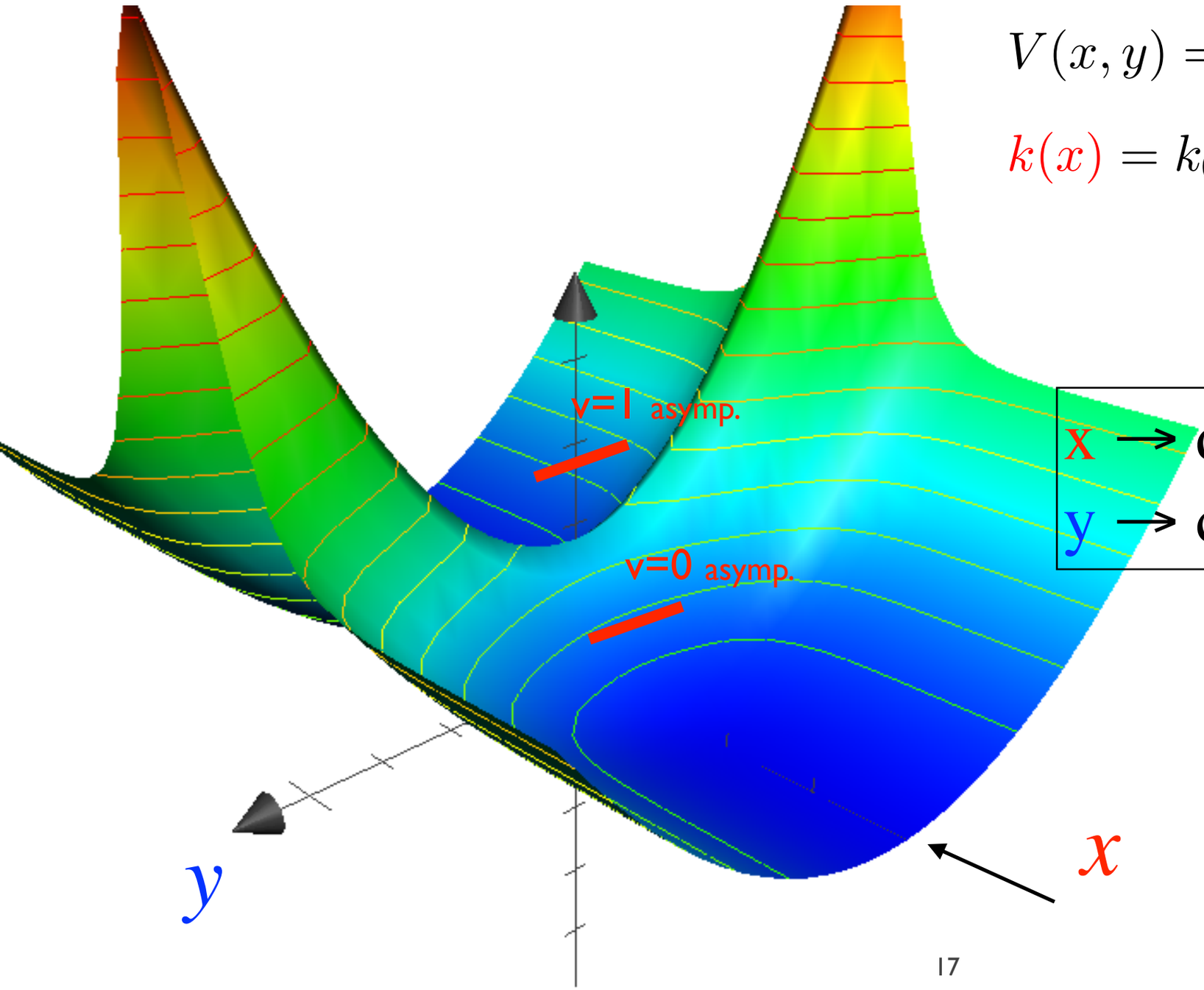
2D bottleneck potential

x-Eckart barrier + ***y***-harm. osc.

$$V(x,y) = V_0\ \mathrm{sech}^2(\alpha x) + \frac{1}{2}k(x)y^2$$

$$k(x) = k_0\left[1 + b/\cosh^2(\alpha x)\right]$$

coupling parameter



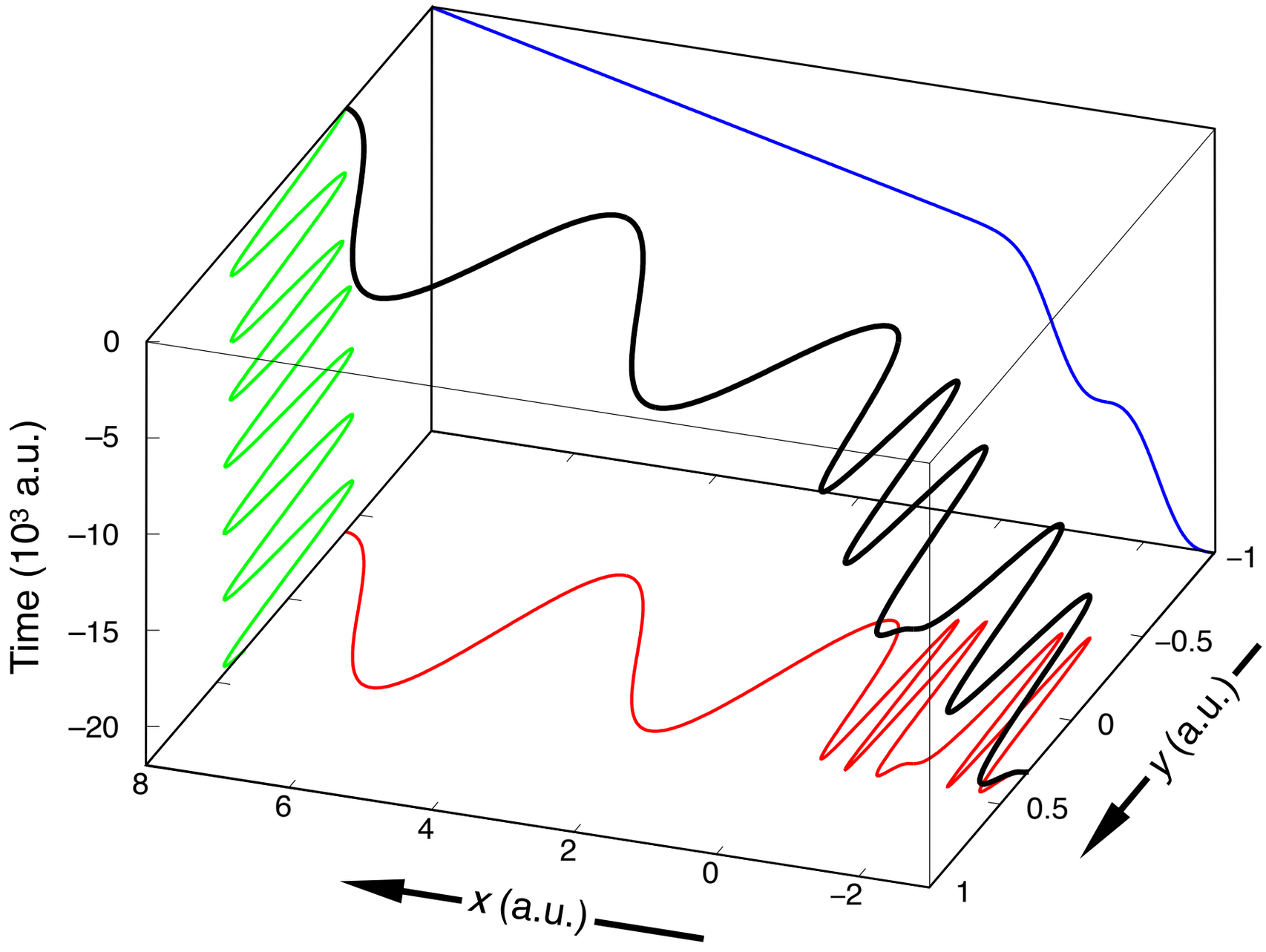
x → quantum motion

y → classical motion

☞ $\omega_y = V_0$

2D trajectory parametric plot

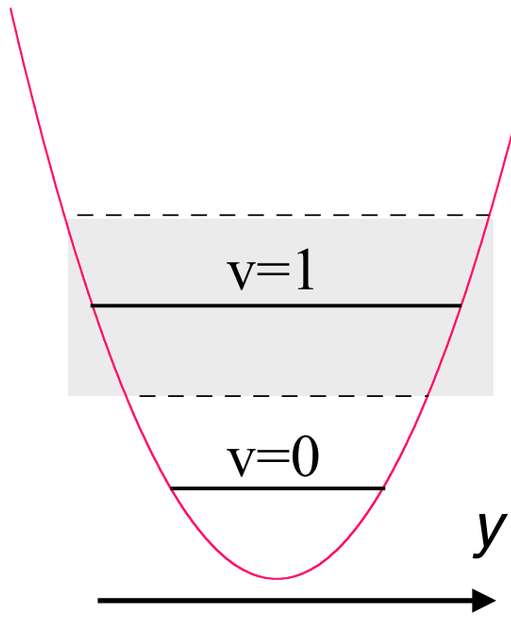
$x(t), y(t)$



Trajectory ensemble sampling (#1)

"Traditional" classical sampling

- Takes care of tunnel effects but does not account for *quantization* of reactant/product states.
- *State-resolved 'v' reaction probabilities* obtained by "binning" trajectories into energy regions centered on individual quantum states '*v*' of the classical *y*-oscillator.



- Solution? Restrict asymp. channel phase space to EBK quantization:
  - Problem: lack of micro-reversibility,
  - Problem: computationally inefficient.

To fix this we propose the Phase Space Approximation

Trajectory ensemble sampling (#2)

Phase Space Approximation (PSA)

Bill Poirier, Algebraically Self-Consistent Quasiclassical Approximation on Phase Space, *Found. Phys.* **30**, 1191 (2000).

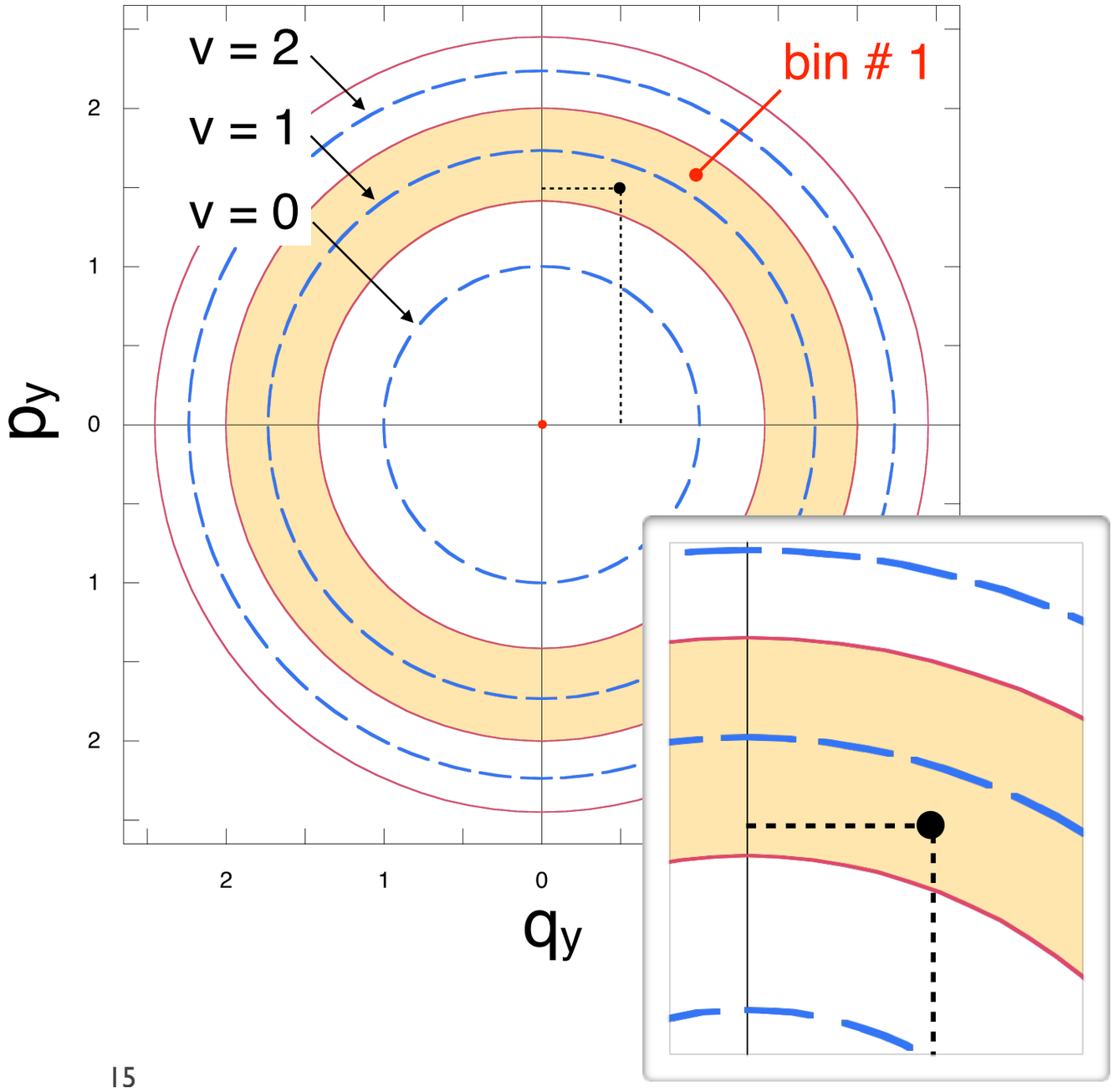
- Derives from exact Wigner-Weyl formalism (Bill Poirier).
- Vibrational quantum state → classical phase space region of area $2\pi\,\hbar$.
- Main difference with traditional sampling:
  for a given quantum state v all trajectories have *the same **kinetic** energy*
  $\Longrightarrow$ energy conservation is not enforced.

Provides exact reactive scattering for separable systems 

trajectory ensemble sampling (#3)

…more on PSA sampling

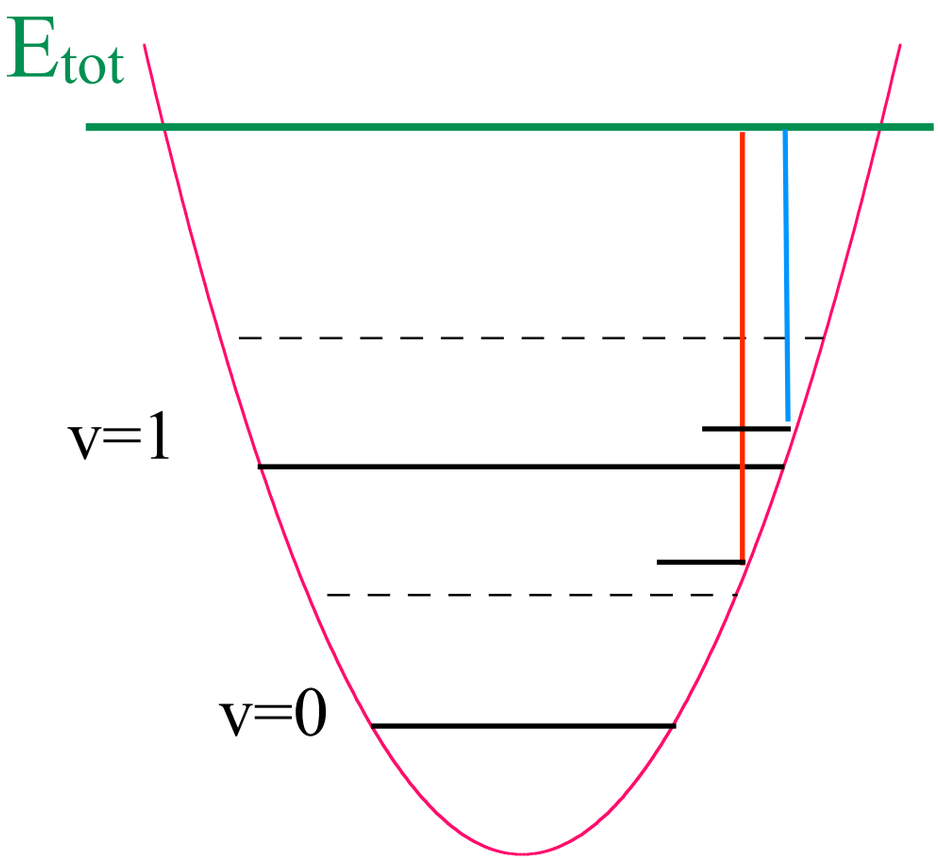
- Individual 1D quantum states for the y-oscillator are represented by phase-space regions of area $2\pi\hbar$
- All trajectories have different energies: $E_{\mathrm{traj}} \neq E_{\mathrm{total}}$



PSA vs traditional sampling

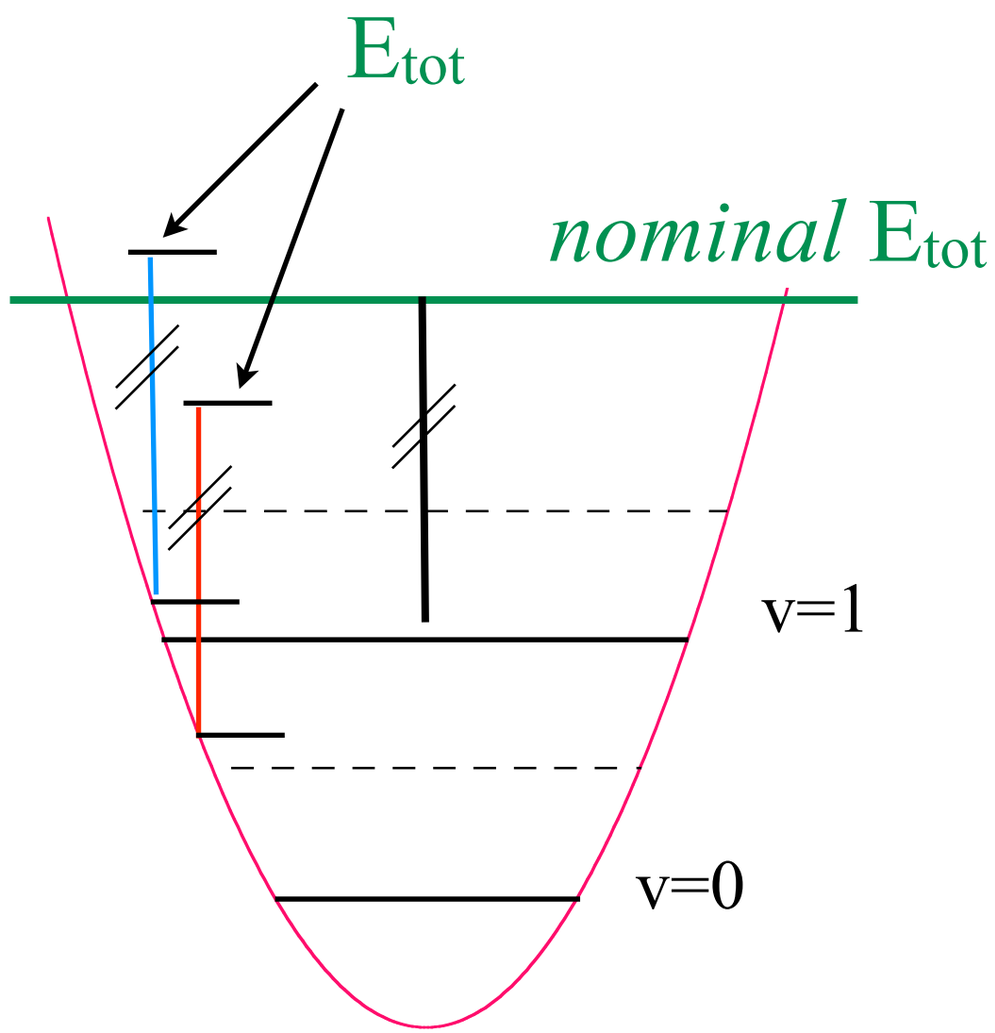
Standard sampling

E_{tot} ***is*** *conserved*



PSA sampling

E_{tot} ***is not*** *conserved*



cumulative reaction probabilities - CRPs

x and y motions decoupled (b=0)

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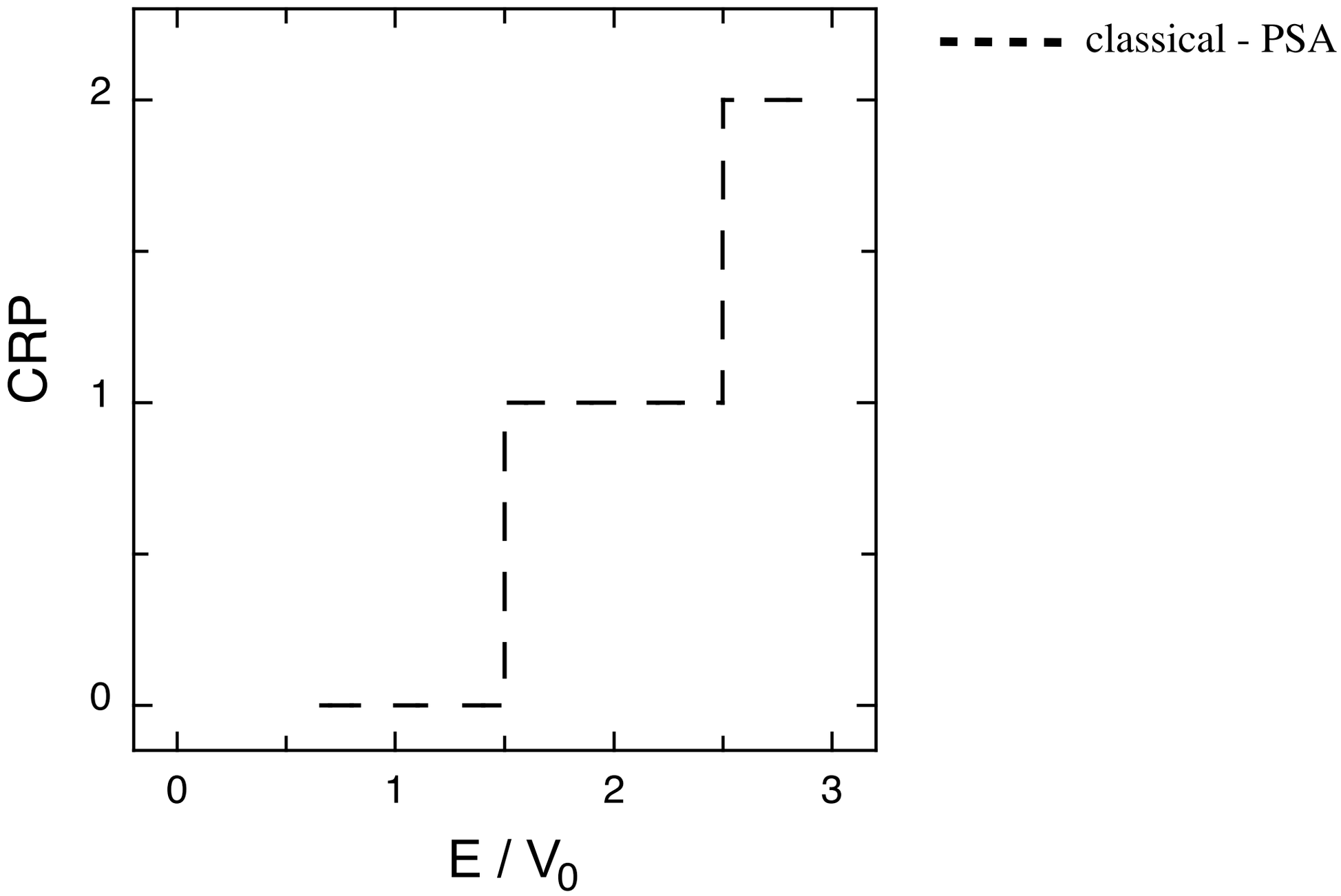

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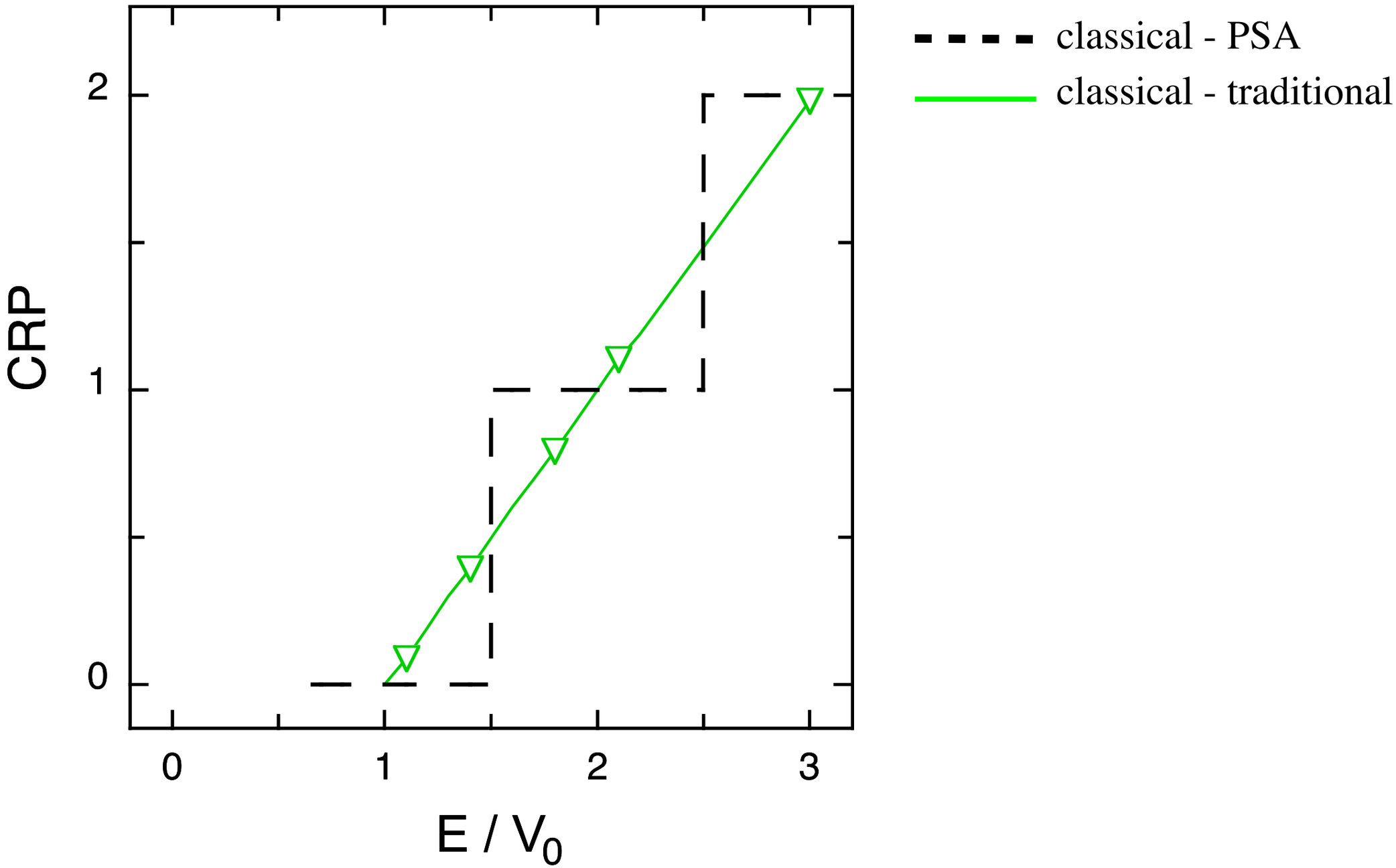

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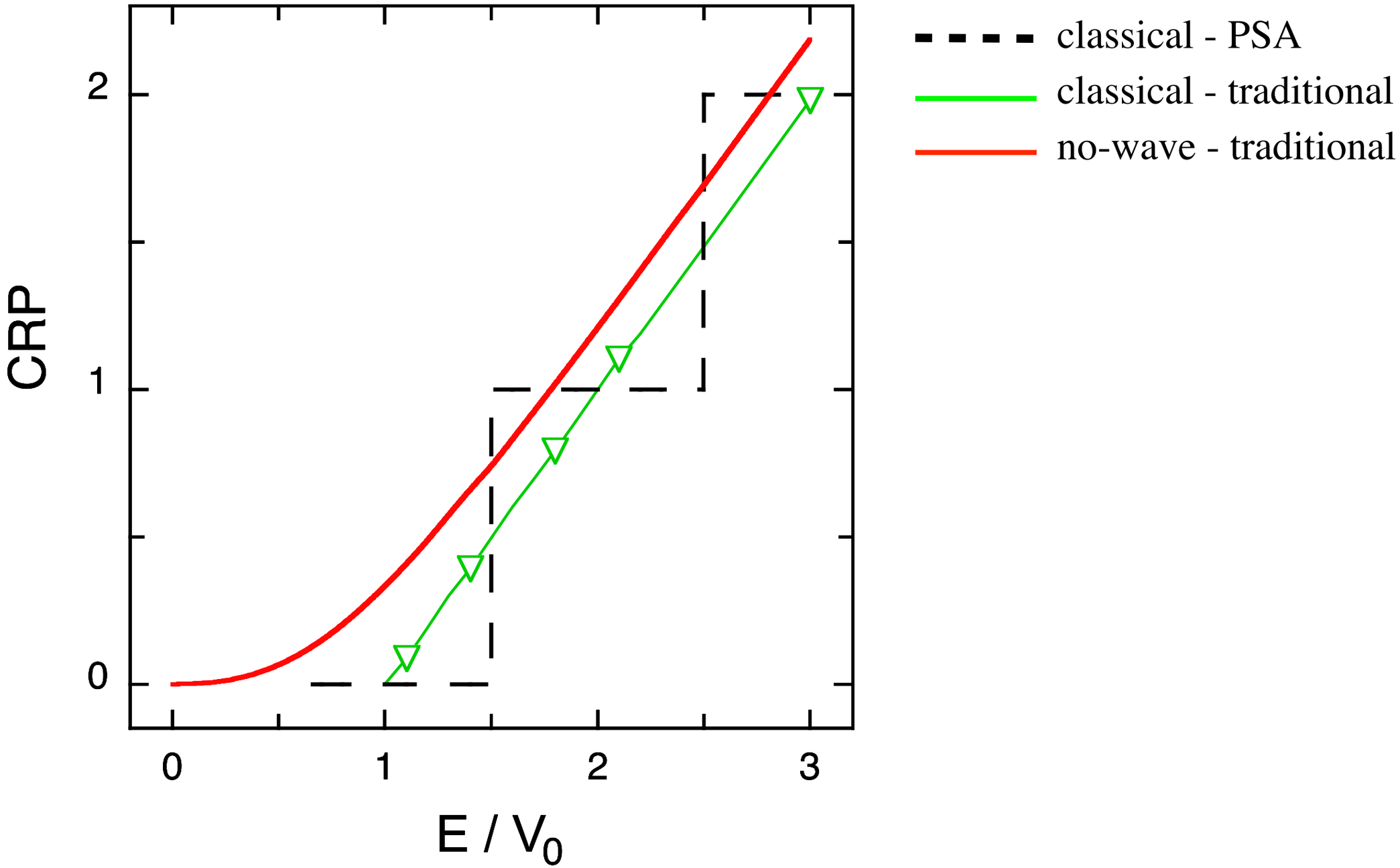

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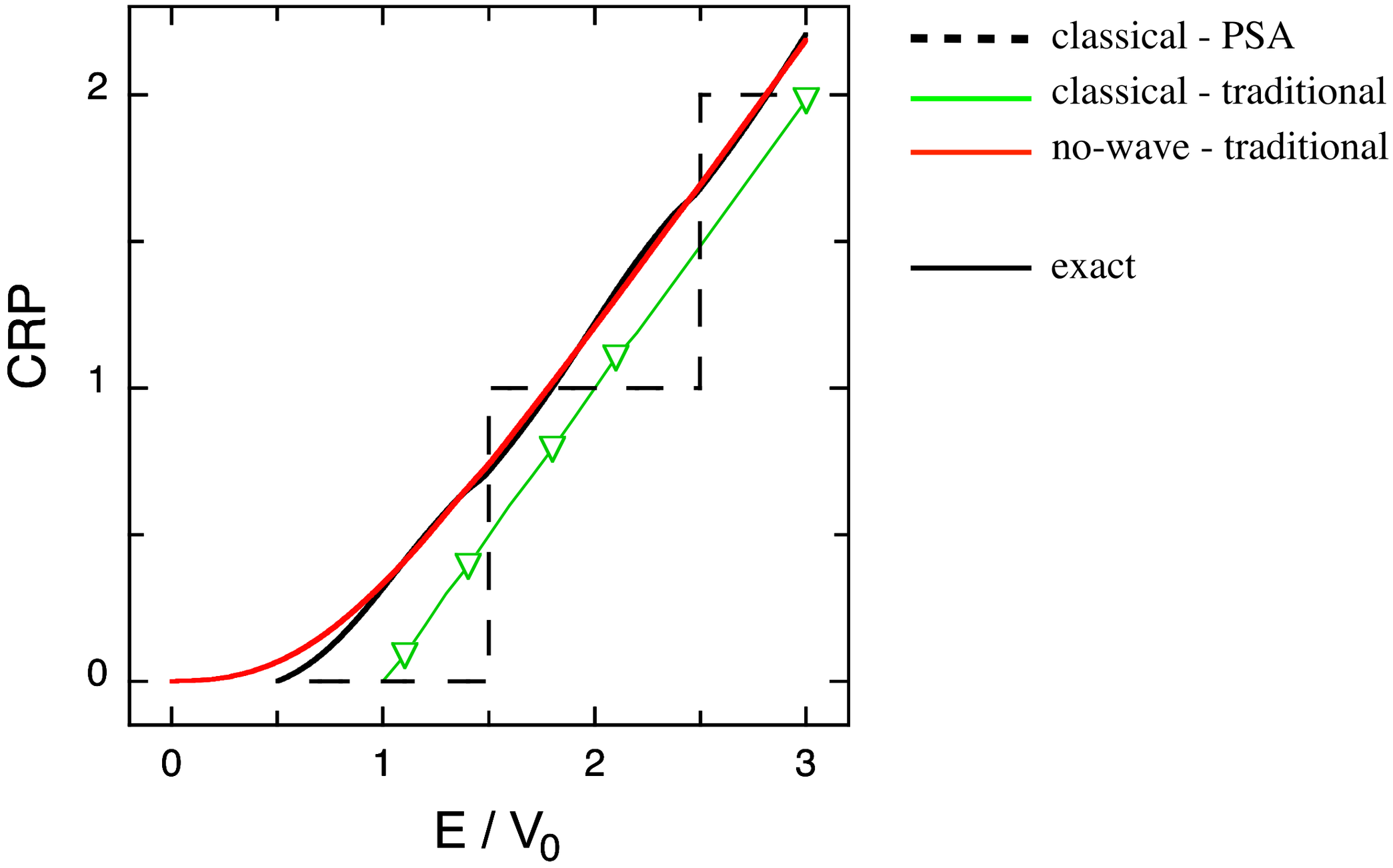

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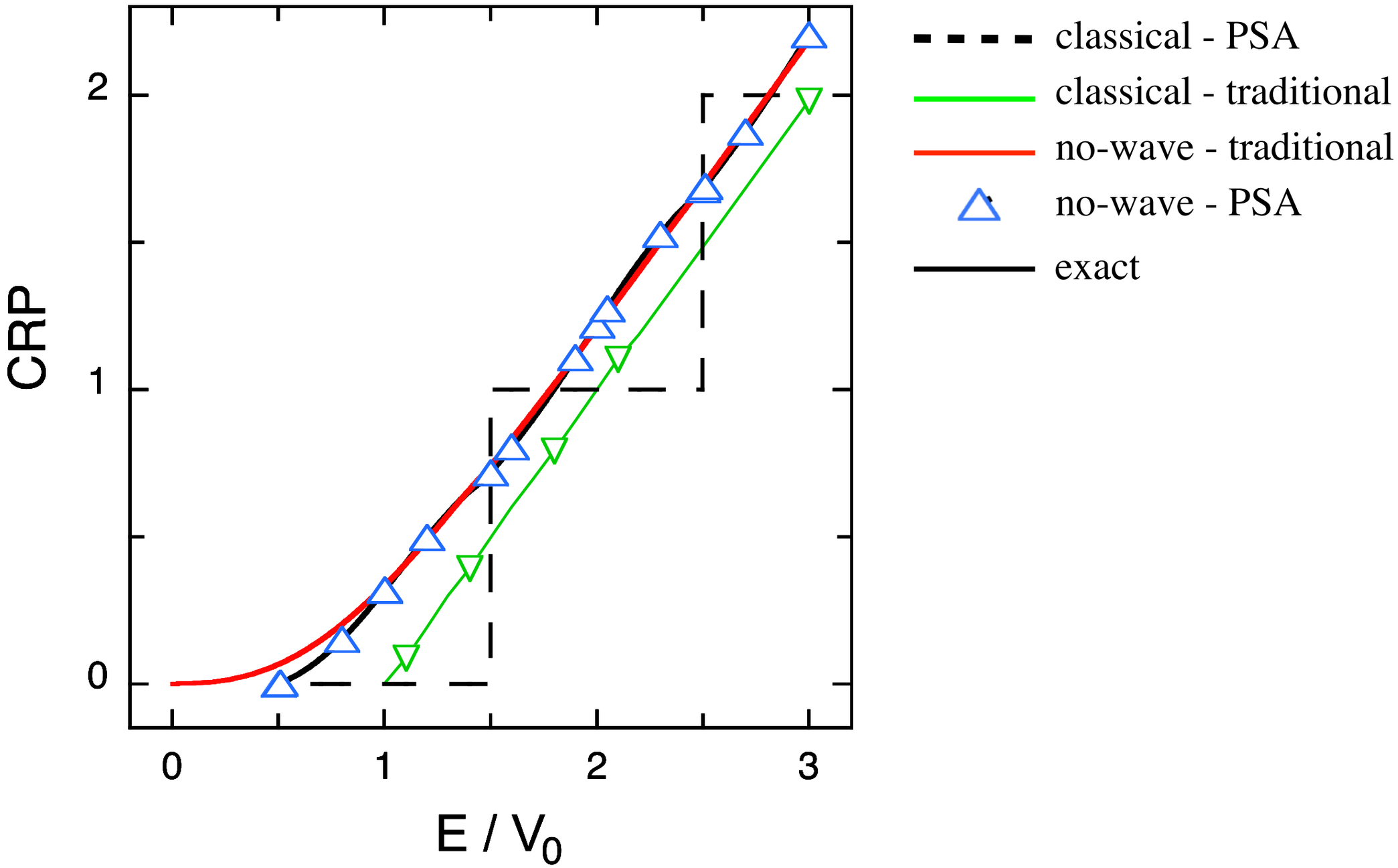

cumulative reaction probabilities - CRPs

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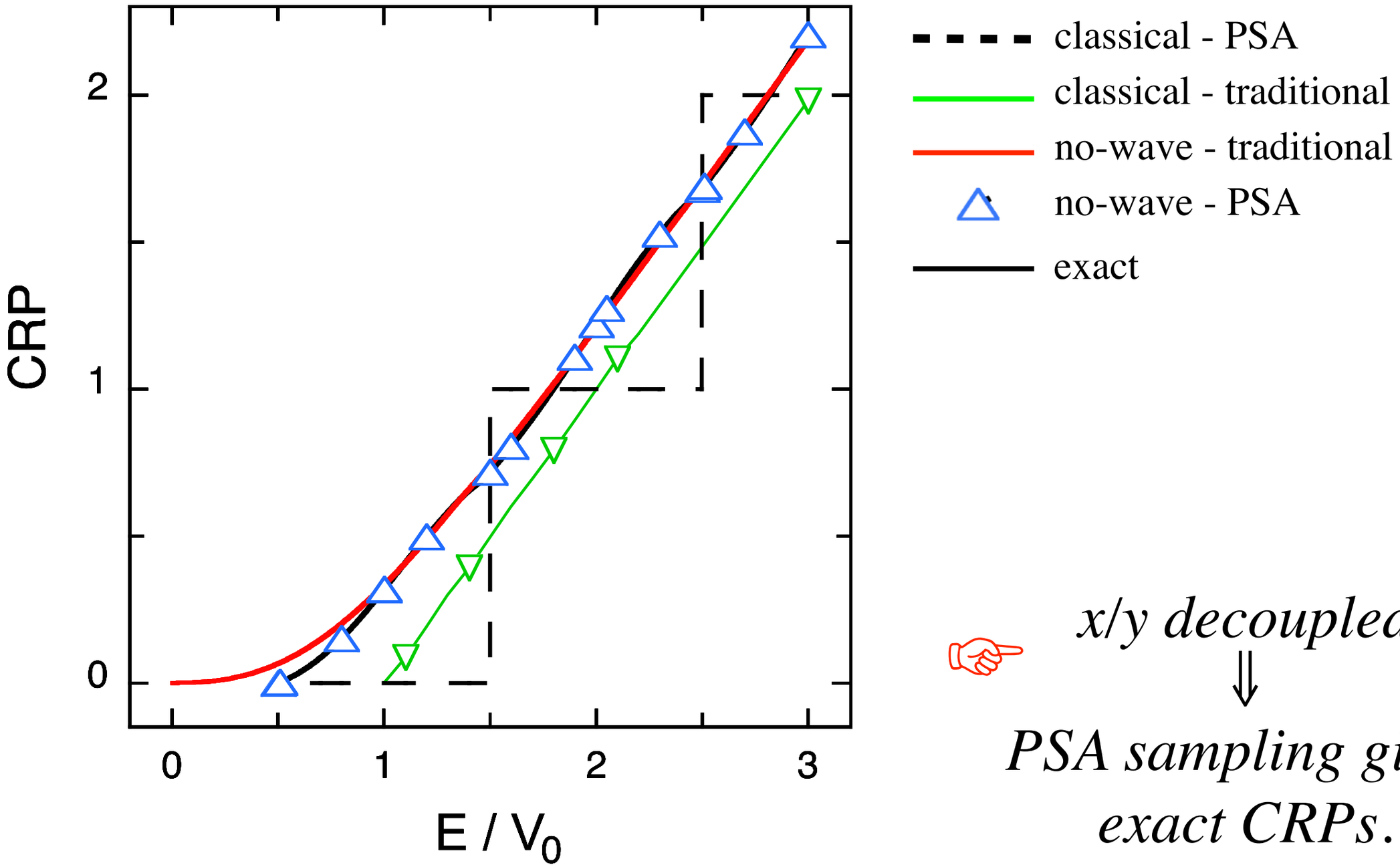


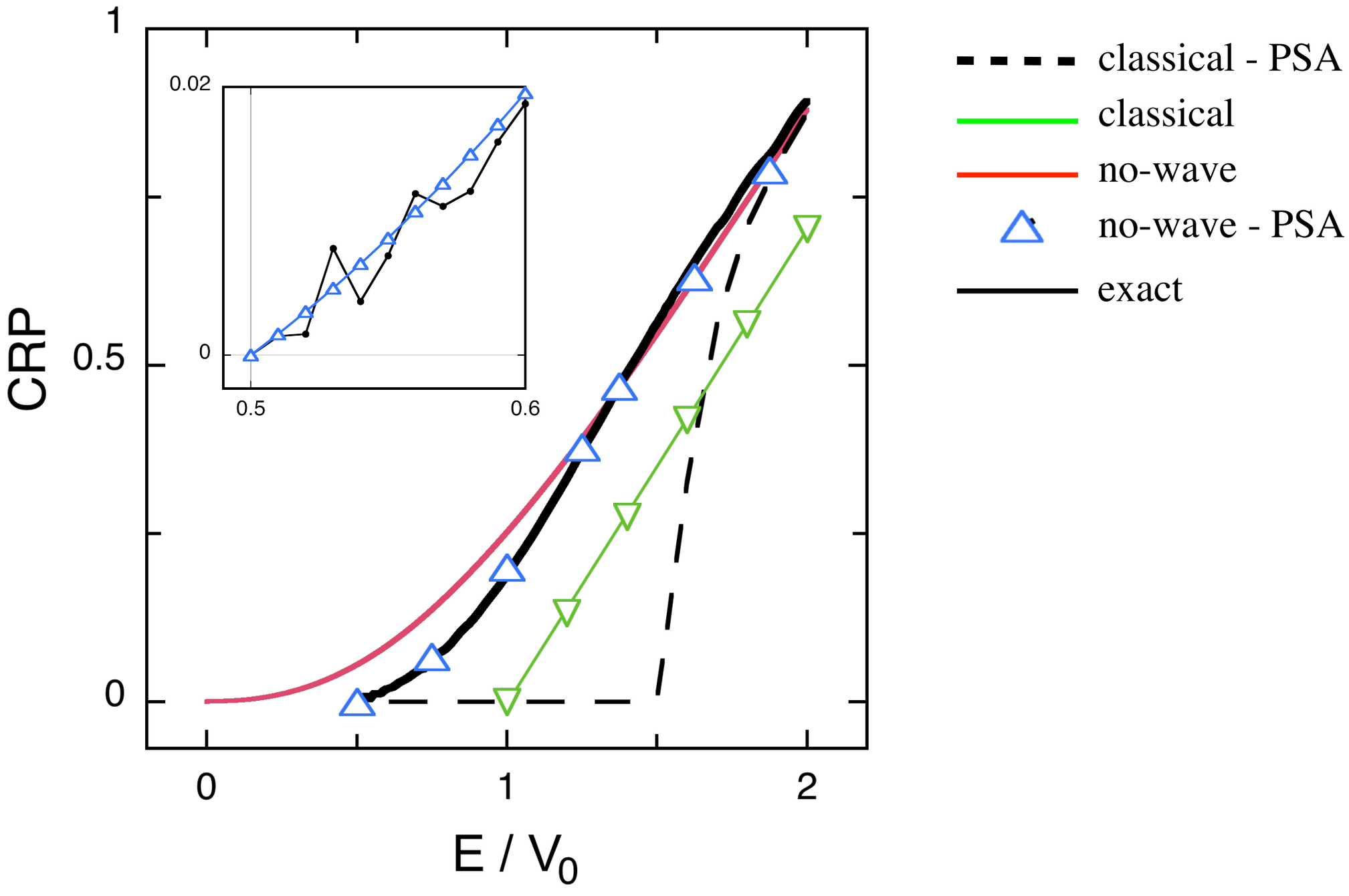
x/y decoupled

⇓

PSA sampling gives exact CRPs.

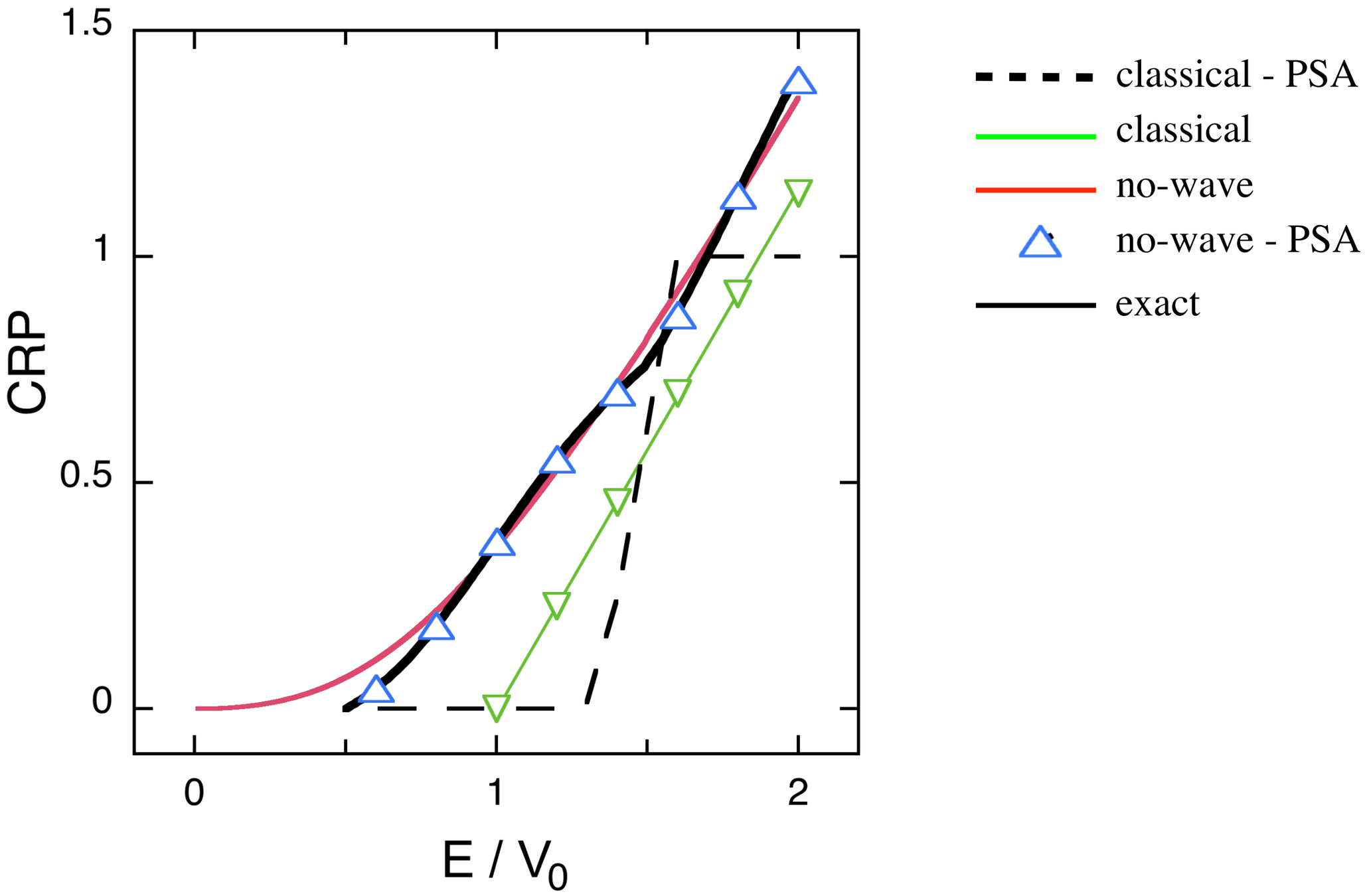
cumulative reaction probabilities - CRPs

narrower bottleneck (*b=1*)



cumulative reaction probabilities - CRPs

wider bottleneck (b= –0.25)



Conclusions

- New trajectory sampling procedure.
- Correct quantum state thresholds.
- Easy to use.
- Would be interesting to investigate for fully classical systems.
- Try to use it all along trajectories to avoid “energy leak”?