Instantons and ring-polymers

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Department of Chemistry
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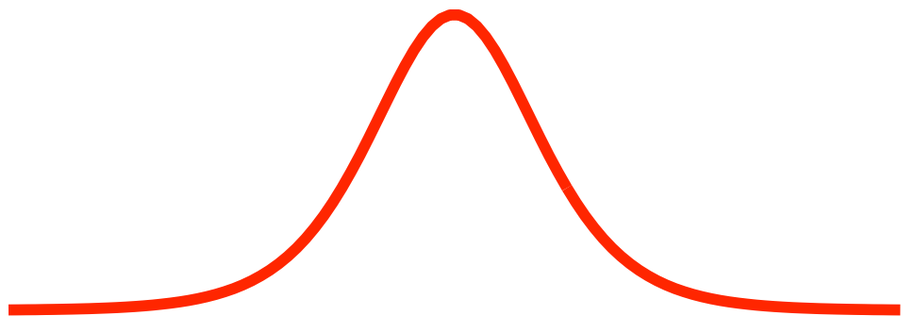
Semiclassical limit of quantum mechanical transition state theory for nonseparable systems*

William H. Miller†

Department of Chemistry, and Inorganic Materials Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
(Received 26 November 1974)

The semiclassical limit of quantum mechanical transition state theory is derived by invoking the classical path approximation for the Boltzmann density operator and making use of the stationary phase approximation; separability of motion along a reaction coordinate is not assumed. The resulting expression for the rate constant bears an interesting similarity to that of conventional transition state theory, although all quantities in it refer to the full classical dynamics on the potential energy surface. In place of the vibrational frequencies of the "activated complex" which appear in the conventional theory, for example, the semiclassical expression contains characteristic frequencies related to the stability properties of a periodic classical trajectory. Conservation of total angular momentum is easily accounted for in a rigorous manner so that the semiclassical model can be applied to three-dimensional dynamical systems.

J Chem Phys 62, 1899 (1975)



instanton

(i.e. periodic orbit)

$$e^{-\beta\hat{H}} \equiv e^{-i\tau\hat{H}/\hbar}$$

$$\tau = -i\beta\hbar$$

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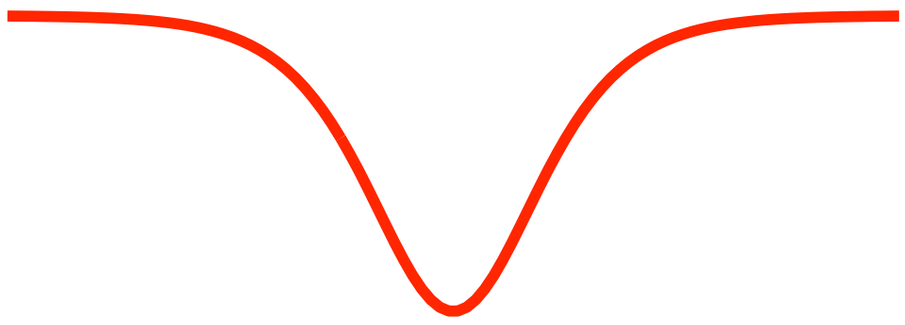

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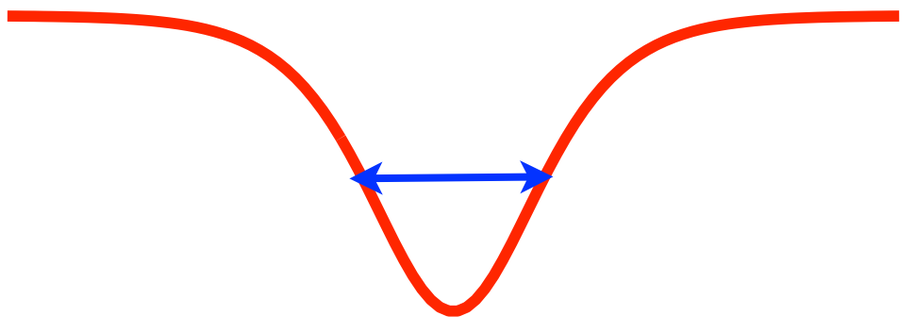

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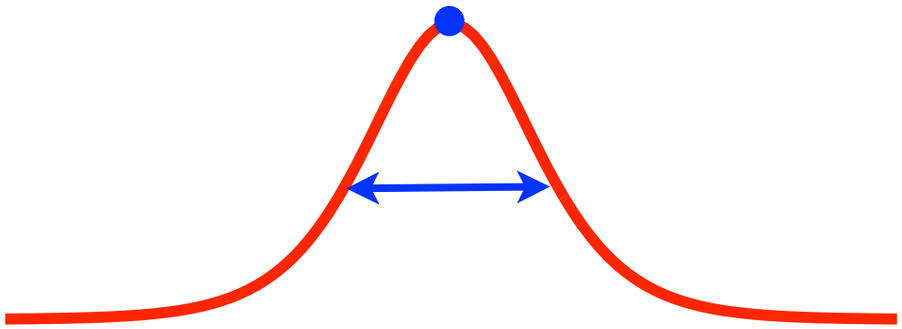
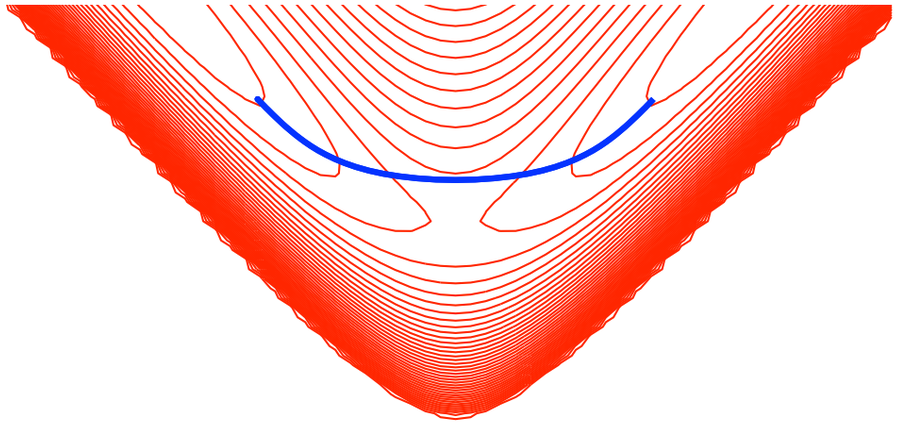
Instantons

cross-over temperature

$$\beta\hbar > \frac{2\pi}{\omega}$$

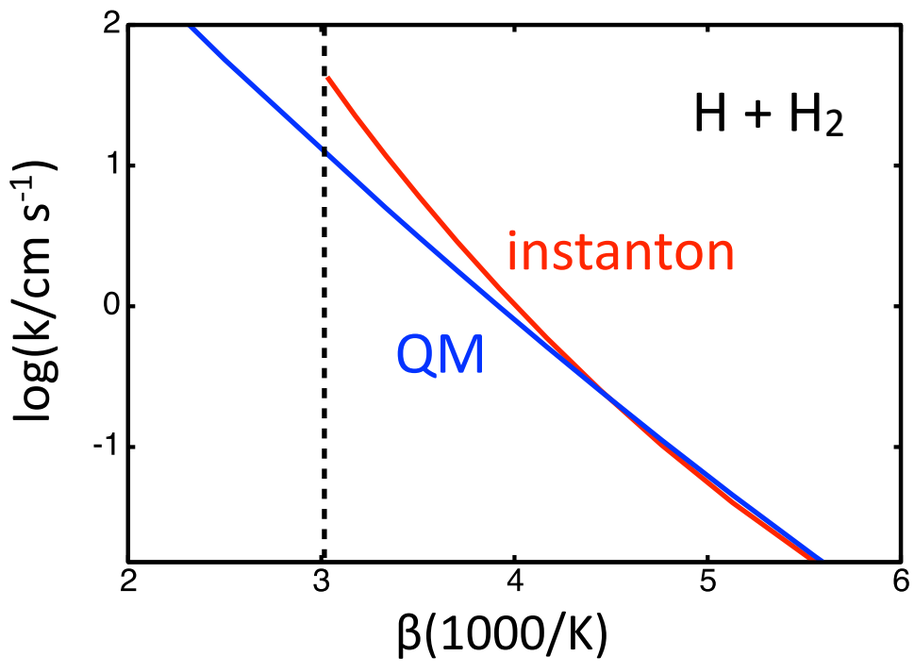




corner-cutting

cf Marcus & Coltrin 1977

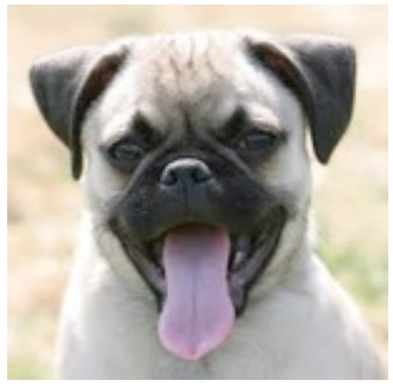
$$k(\beta)Q_{\mathrm{r}}(\beta) = A(\beta)e^{-S_{\mathrm{inst}}(\beta)/\hbar}$$



Two breeds of instanton theory

Im F (Coleman)

$$k^{(\mathrm{imf})}(\beta) Q_r(\beta) = P(\beta)\, e^{-\widetilde{A}(\beta)/\hbar},$$



Semi-classical (Miller)

$$k^{(\mathrm{fs})}(\beta) Q_r(\beta) = (2\pi\hbar^3)^{-1/2} \left| \frac{d^2 \widetilde{A}(\beta)}{d\beta^2} \right|^{1/2}$$

$$\times \prod_{i=1}^{f-1} \frac{1}{2\sinh(u_i/2)}\, e^{-\widetilde{A}(\beta)/\hbar},$$

4

Two breeds of instanton theory

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ENTIRELY EQUIVALENT!!!

Hänggi, 1987; Benderskii 1987
SCA, 2011

Two breeds of instanton theory

Im F (Coleman)

instanton action

$$k^{(\mathrm{imf})}(\beta) Q_r(\beta) = P(\beta)\, e^{-\widetilde{A}(\beta)/\hbar},$$

thermal fluctuations

Semi-classical (Miller)

$$k^{(\mathrm{fs})}(\beta) Q_r(\beta) = (2\pi\hbar^3)^{-1/2} \left| \frac{d^2 \widetilde{A}(\beta)}{d\beta^2} \right|^{1/2}$$

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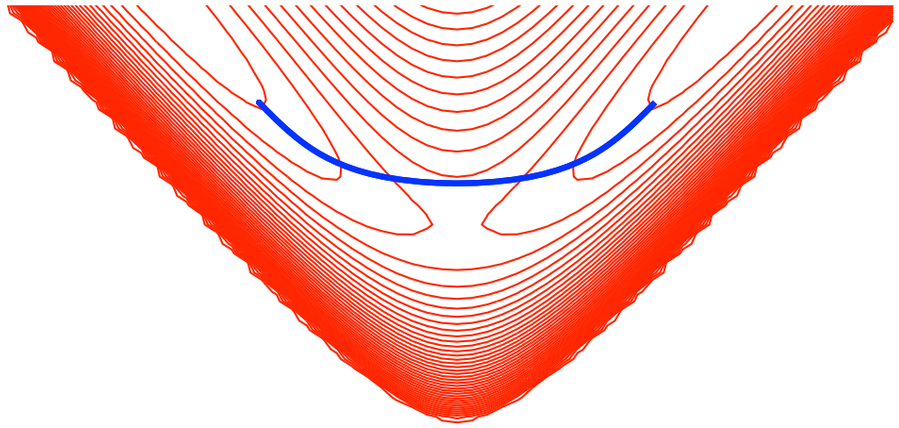
Finding instantons



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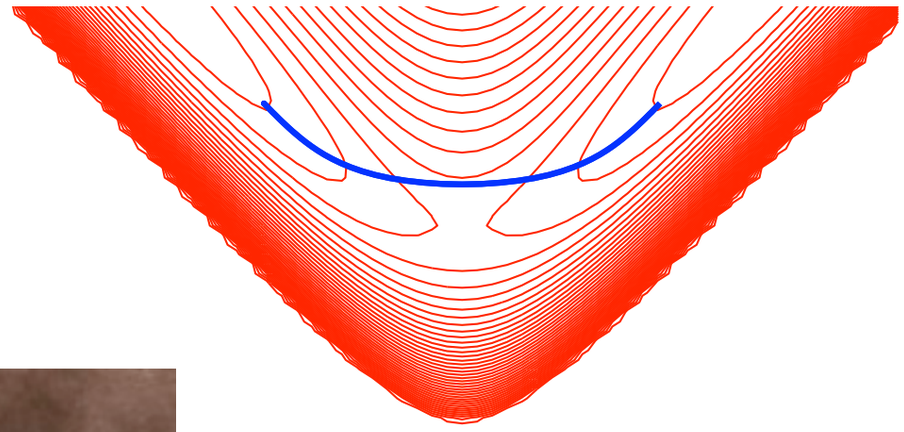
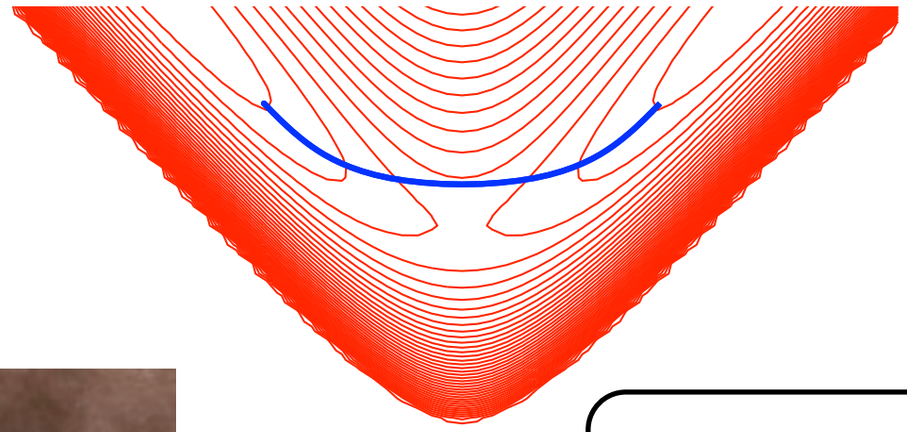


shooting

Finding instantons



shooting

$$\frac{\partial U_N(\beta, \mathbf{x})}{\partial x_n} = 0$$

stationary points on ring-polymer surface

S. Andersson, H. Jónsson & coworkers, JPCA 2009

J.O. Richardson & SCA, JCP 2009

Romell, Goumens and Kästner, JCTC 2011

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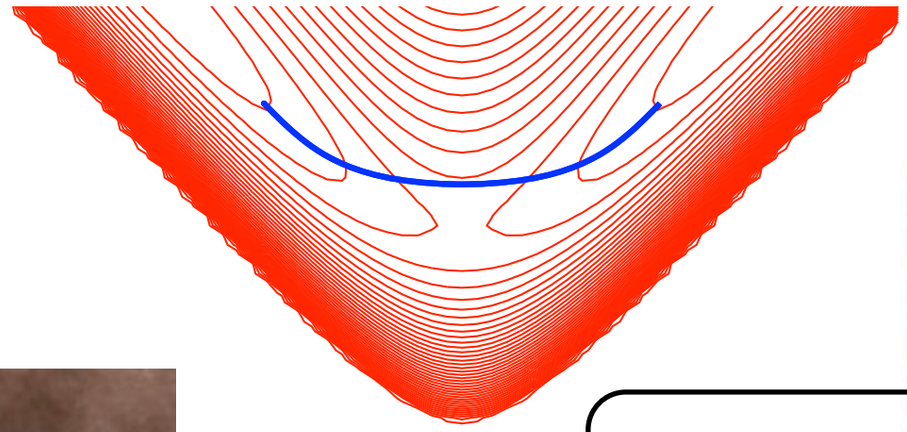

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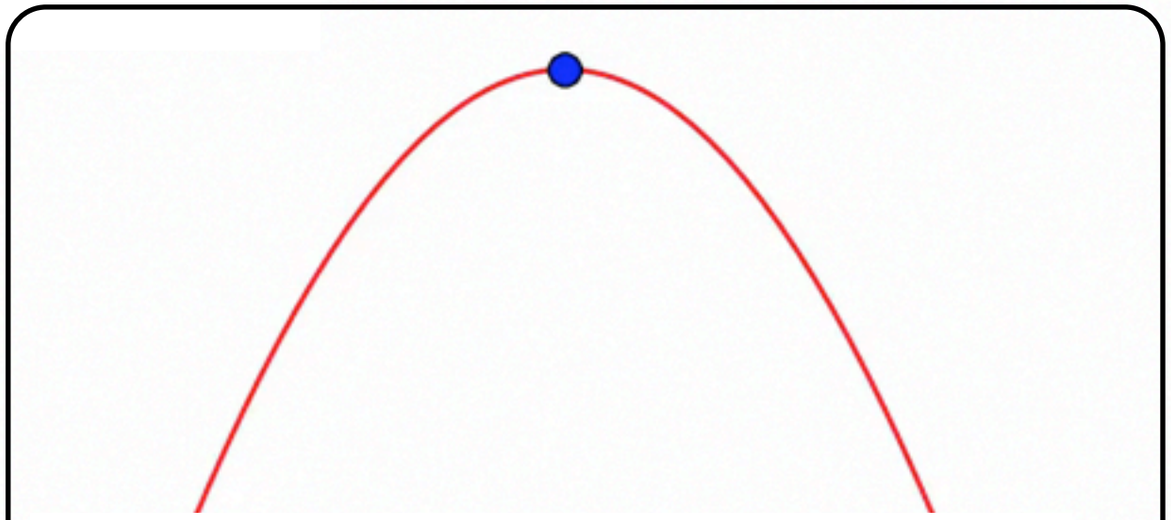

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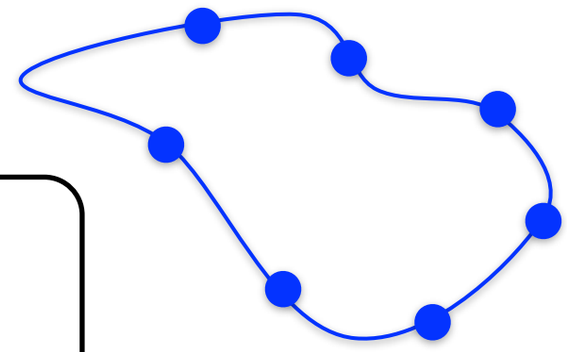
Ring Polymers



Chandler & Wolynes
Ceperley

$$Q(\beta) \simeq \left(\frac{m}{2\pi\epsilon\hbar^2}\right)^{N/2} \int d\mathbf{x}\, e^{-\epsilon U_N(\beta,\mathbf{x})}$$

$$U_N(\beta,\mathbf{x}) = \sum_{n=1}^{N} V(x_n) + \frac{m}{2(\epsilon\hbar)^2} \sum_{n=1}^{N} (x_{n+1} - x_n)^2$$

$$\epsilon = \beta/N$$

Ring Polymers

$$e^{-\beta\hat{H}} \equiv e^{-\epsilon\hat{H}} e^{-\epsilon\hat{H}} \ldots e^{-\epsilon\hat{H}}$$

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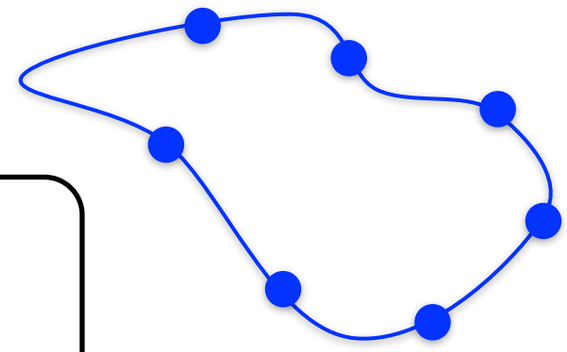

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Ceperley

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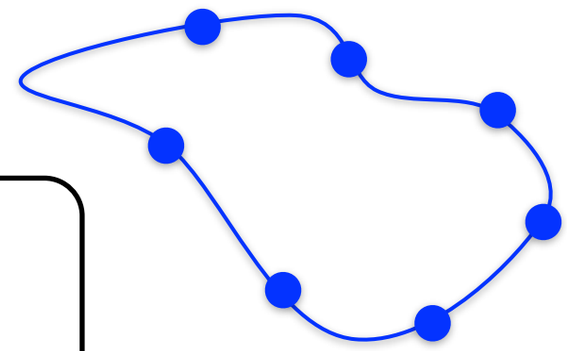

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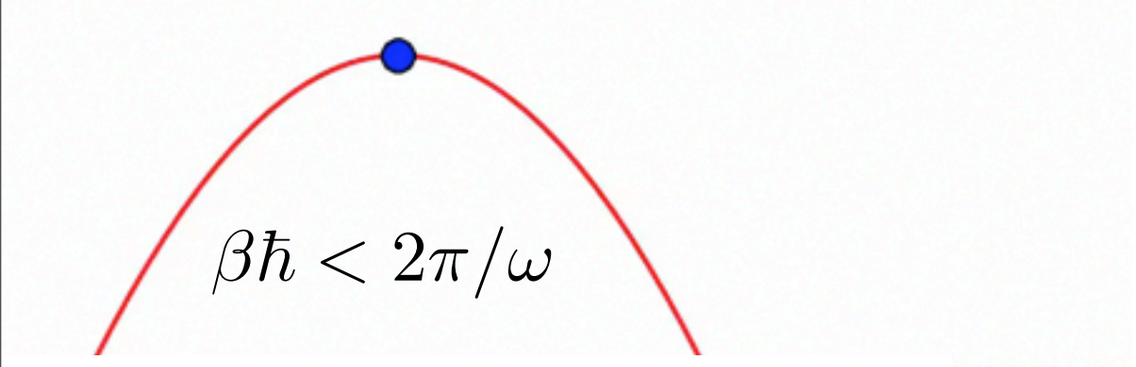

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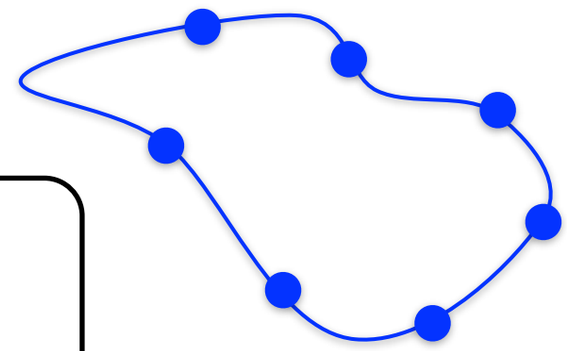

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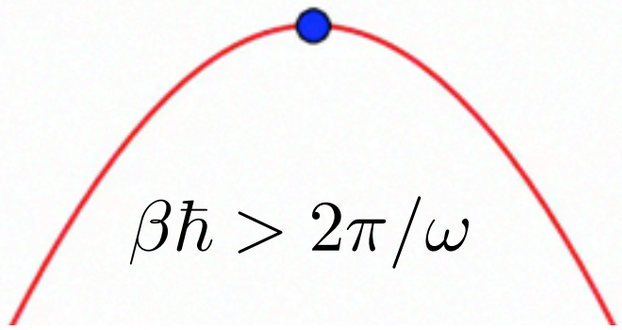
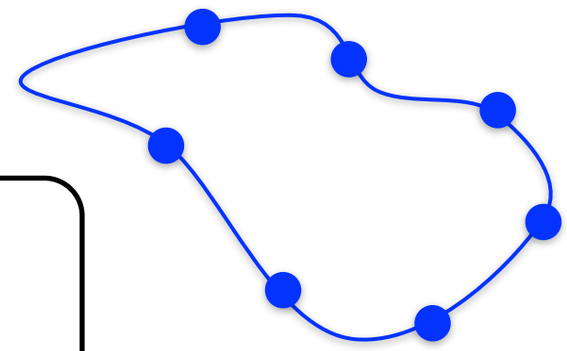


Ring-polymer instanton

Ring Polymers



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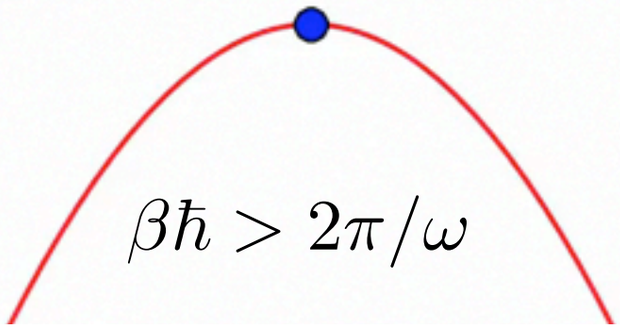
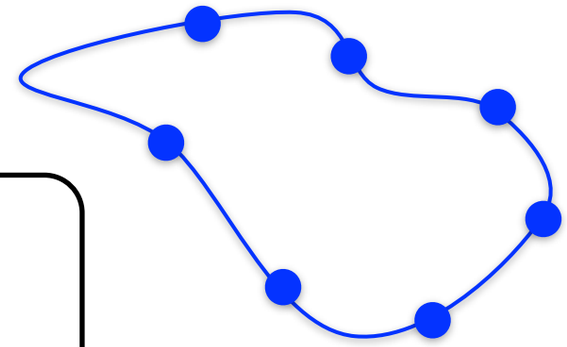


Ring-polymer instanton

Ring Polymers



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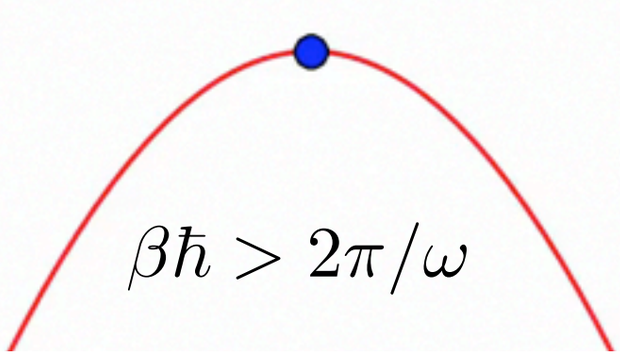
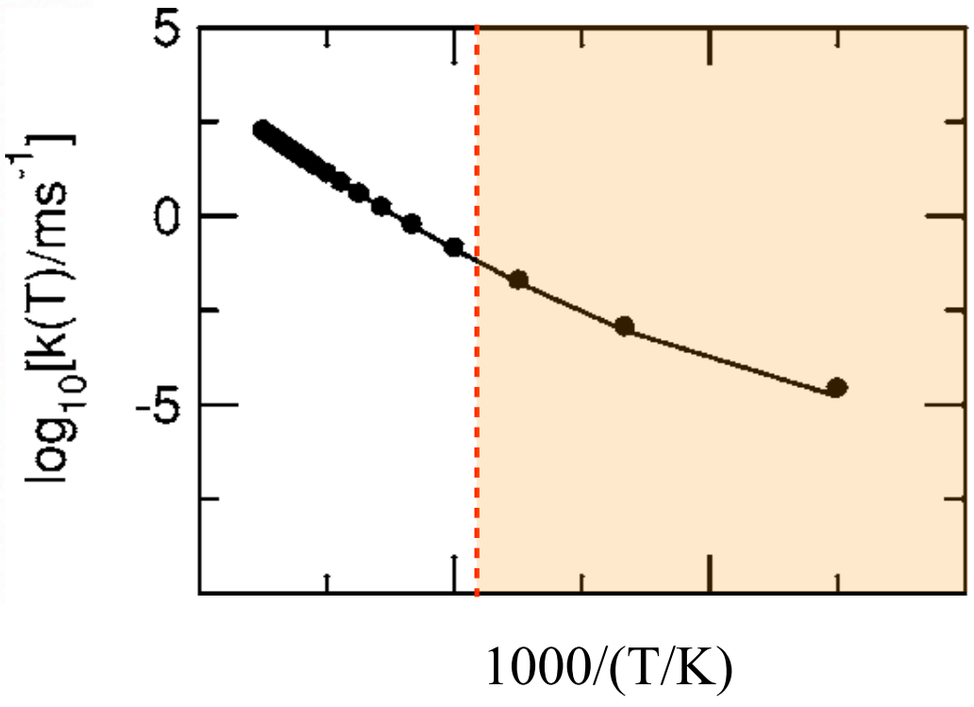


$$\beta\hbar > 2\pi/\omega$$

Ring-polymer instanton

RPMD

Manolopoulos & co
T. Miller, Markland



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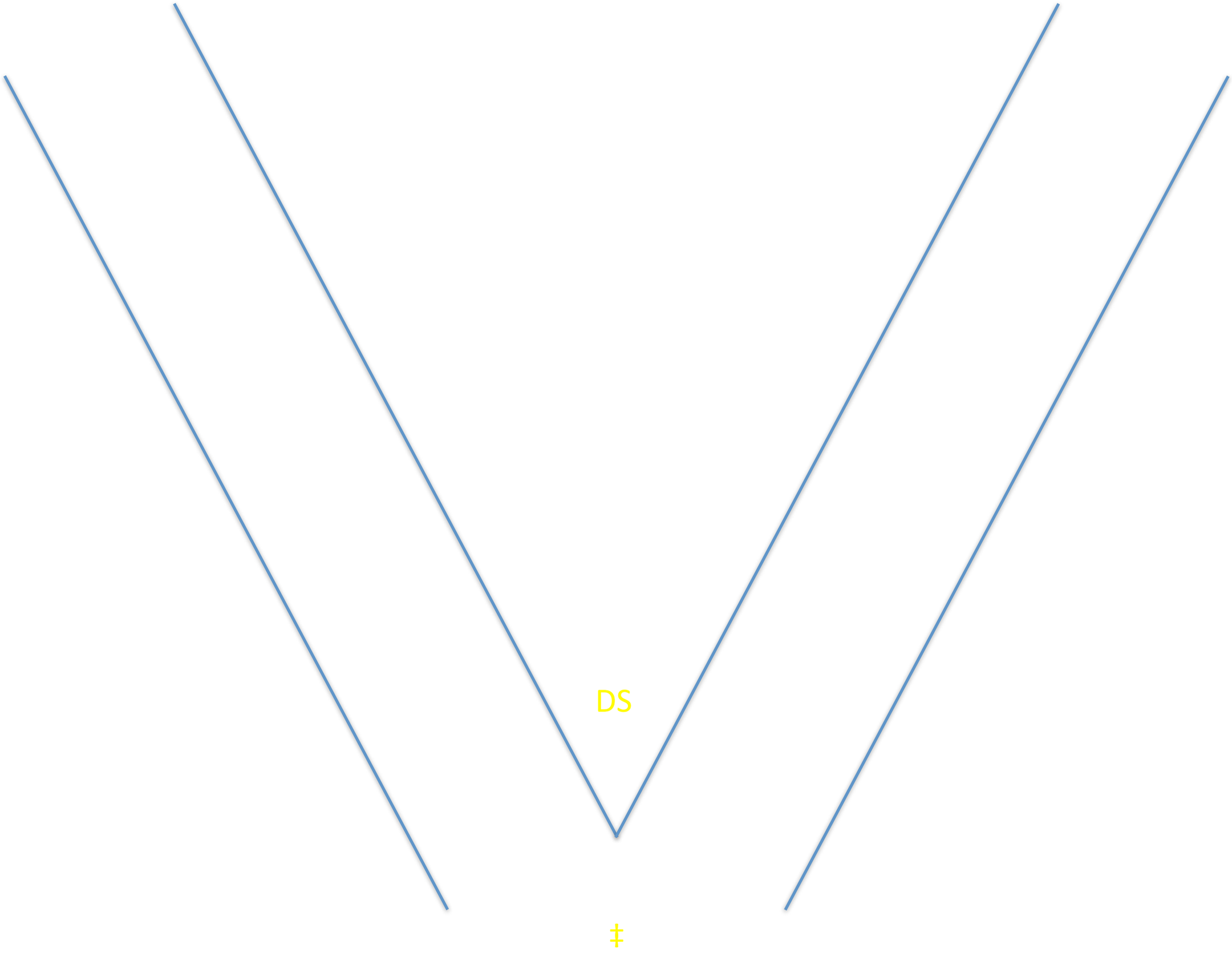
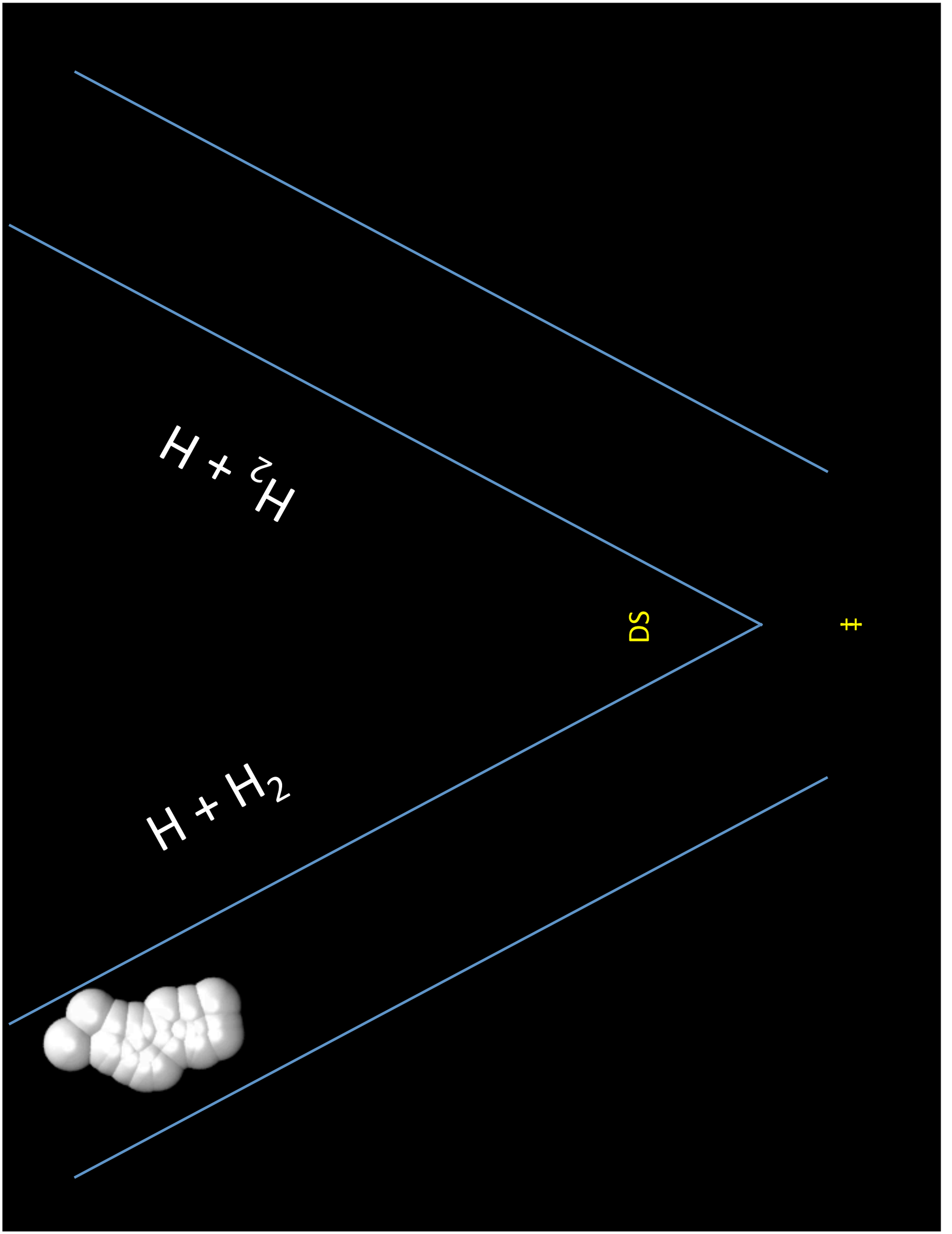
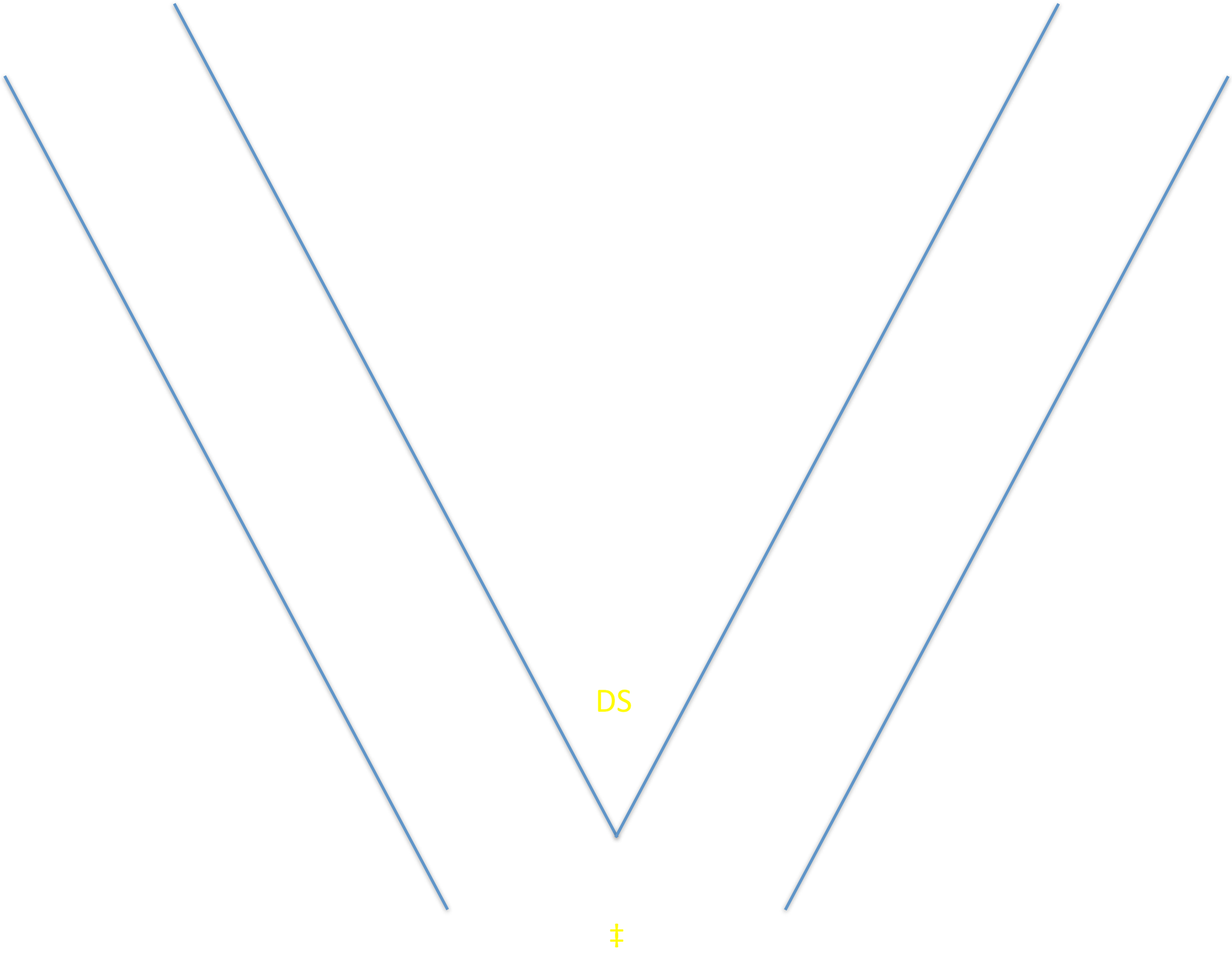

DS
‡


H + H2
DS
+
H + H2


DS
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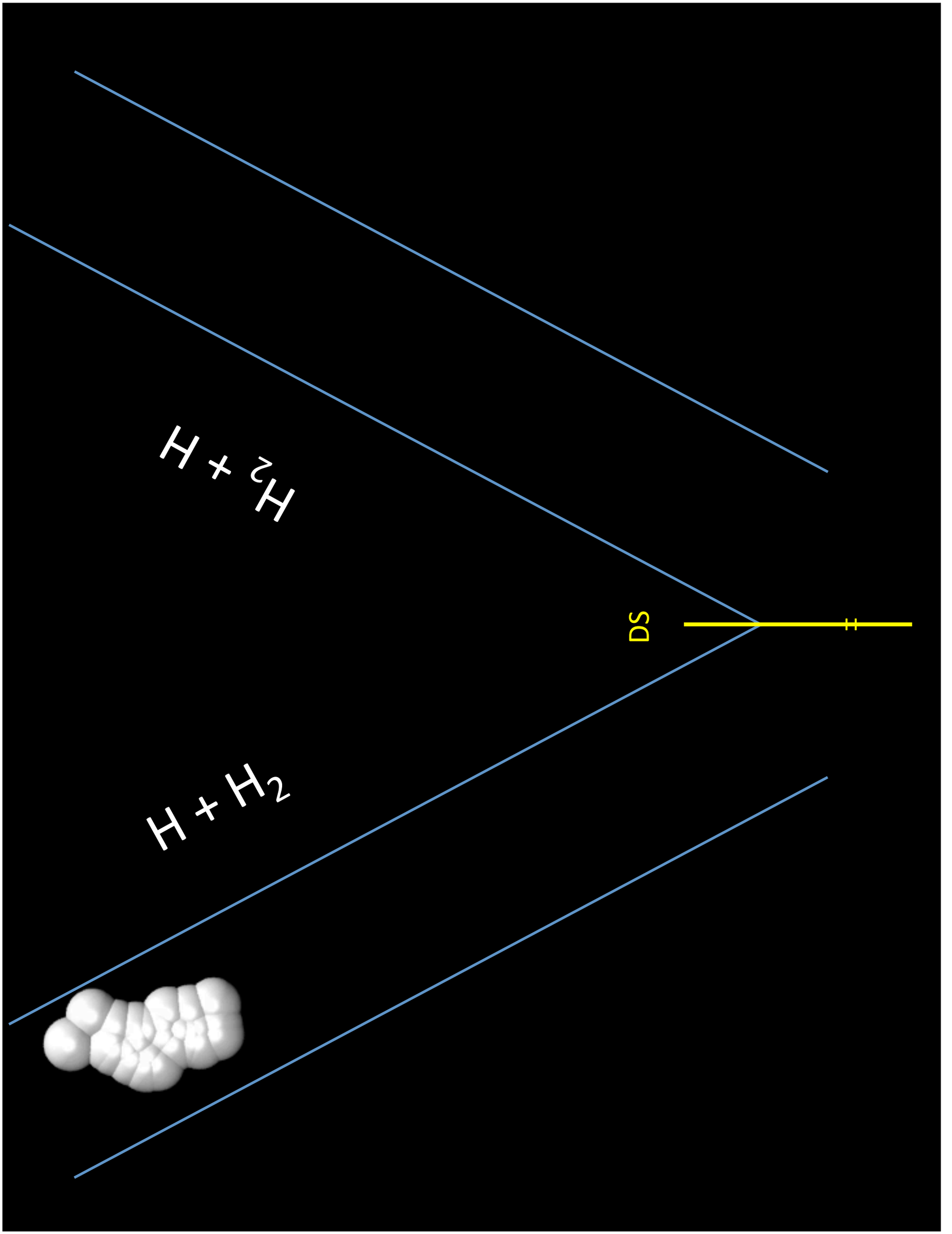
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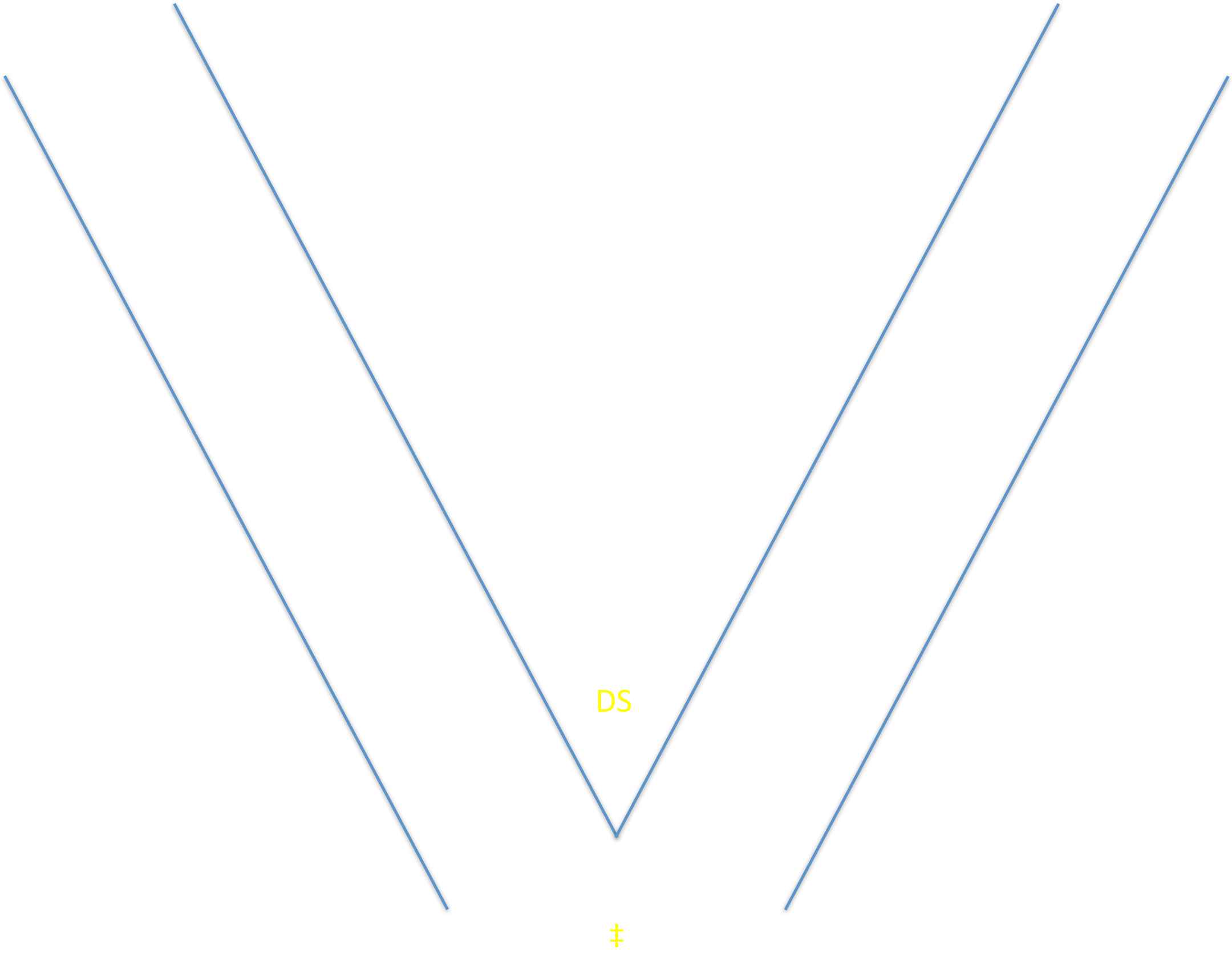
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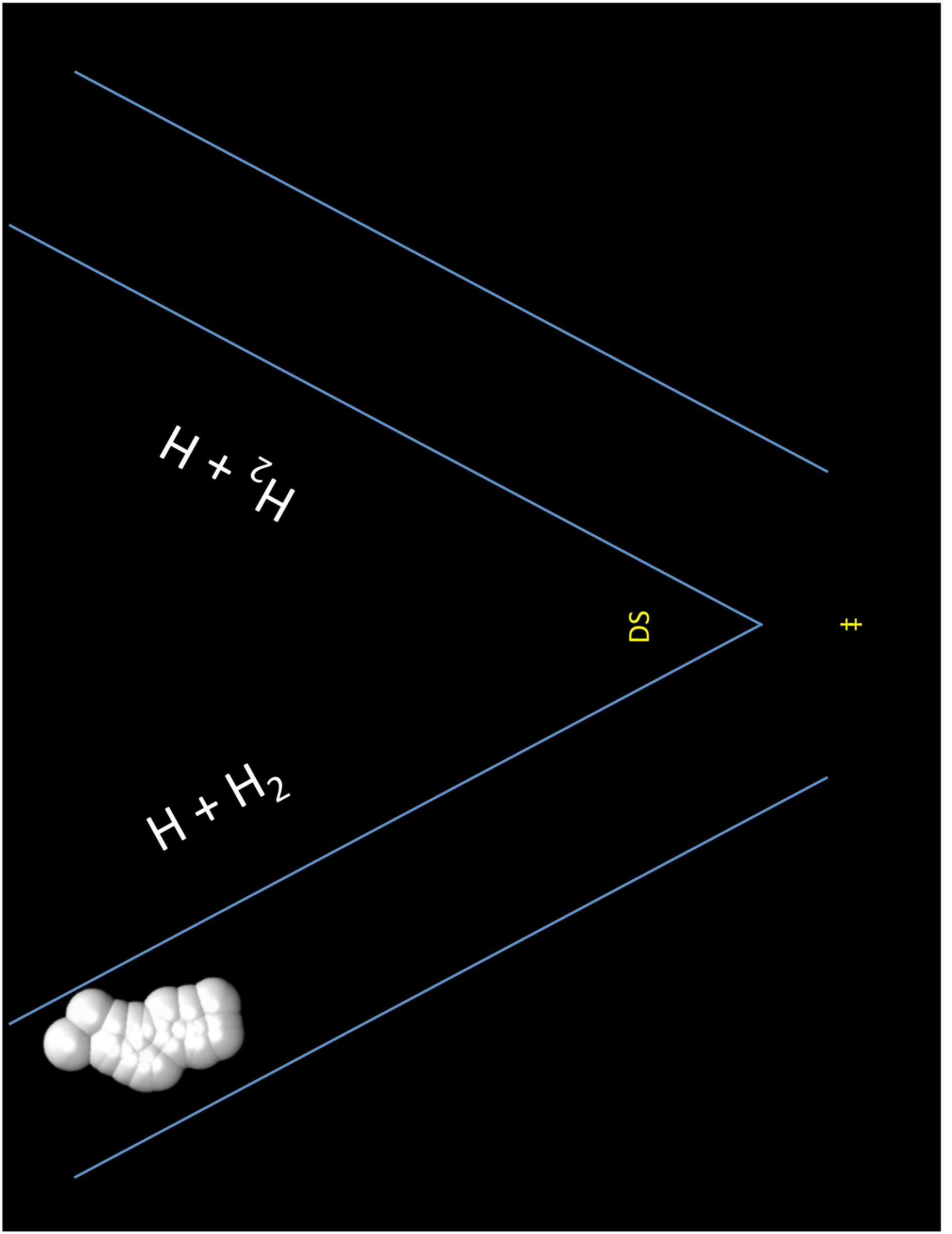
H + H2
DS
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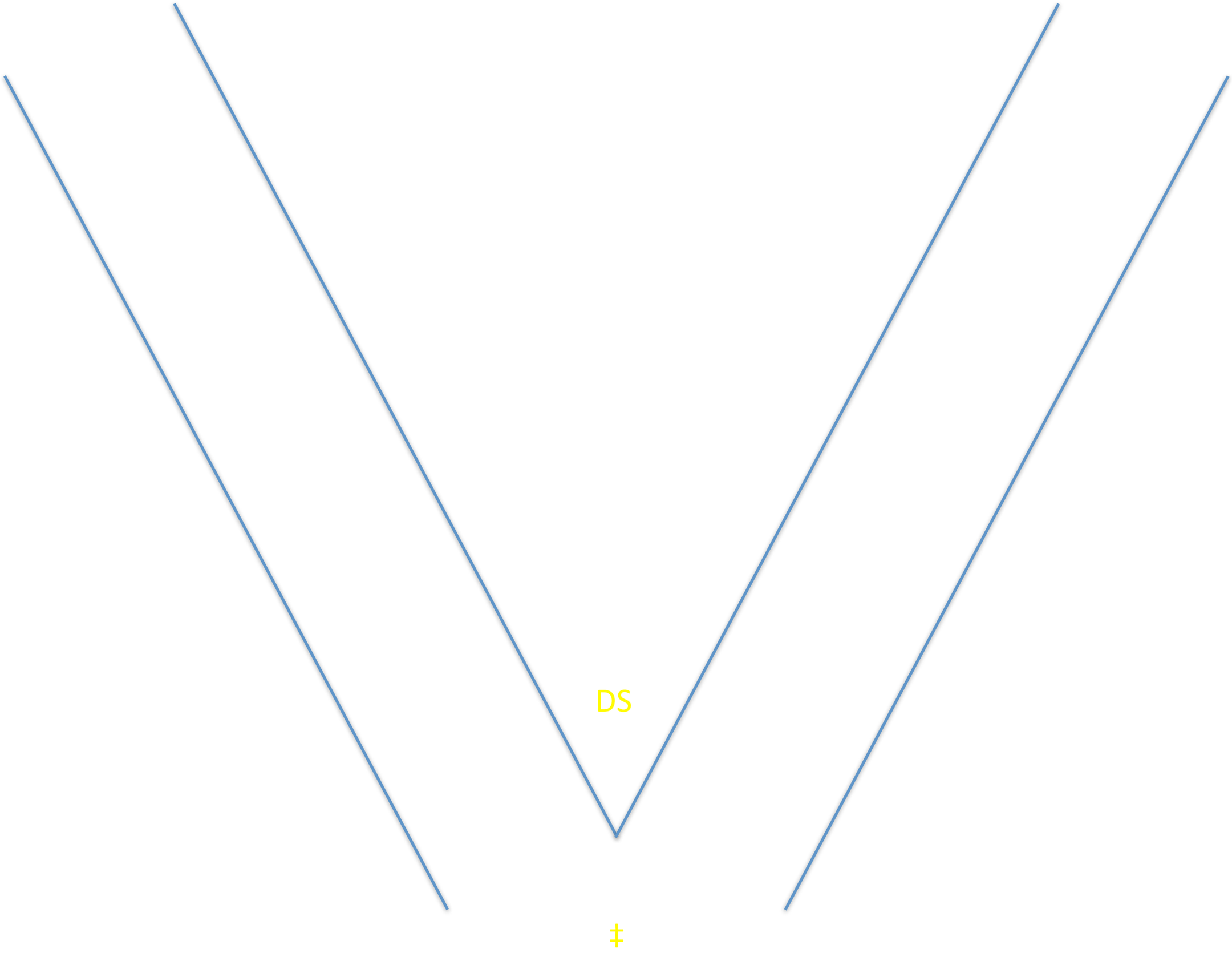
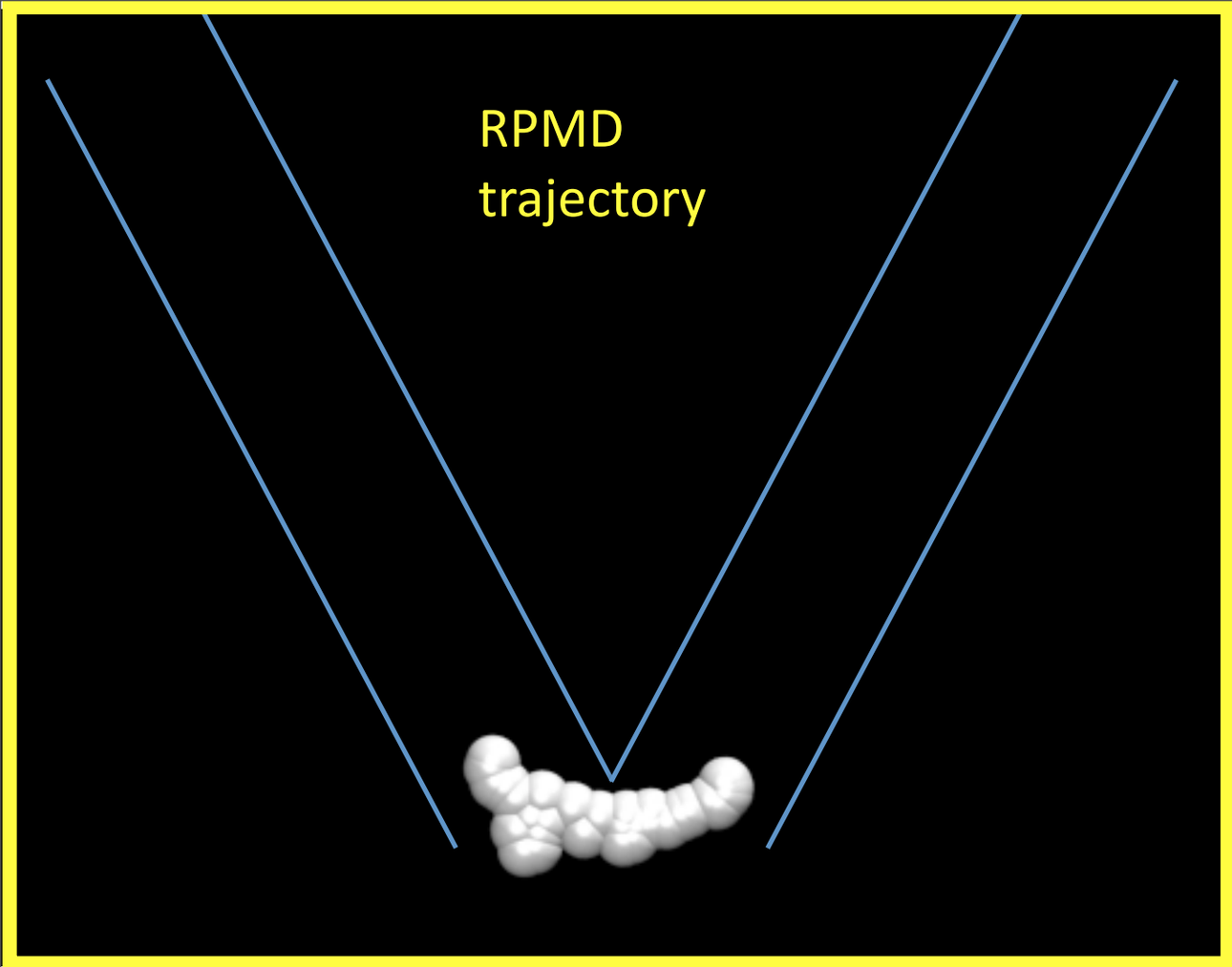
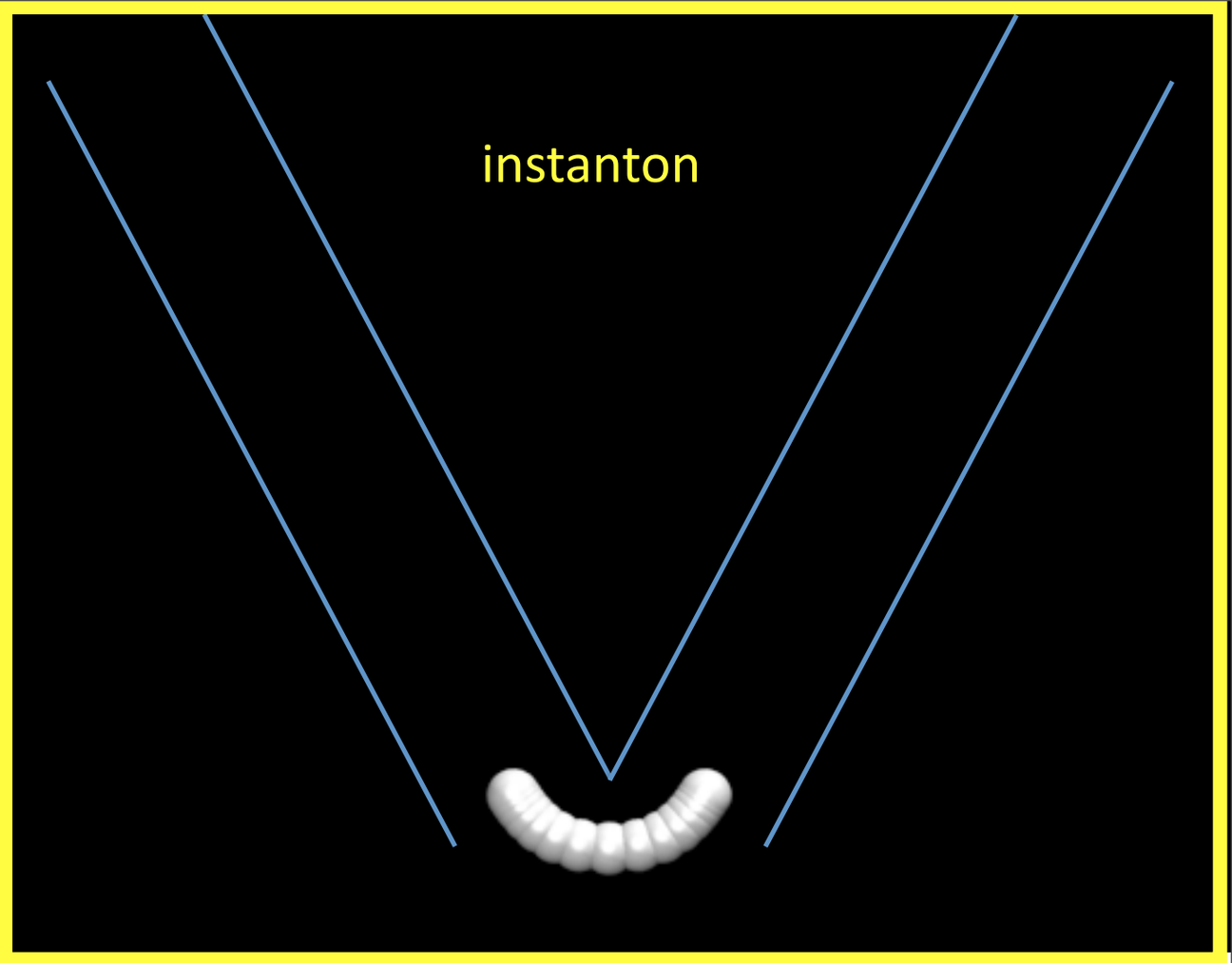

DS
‡

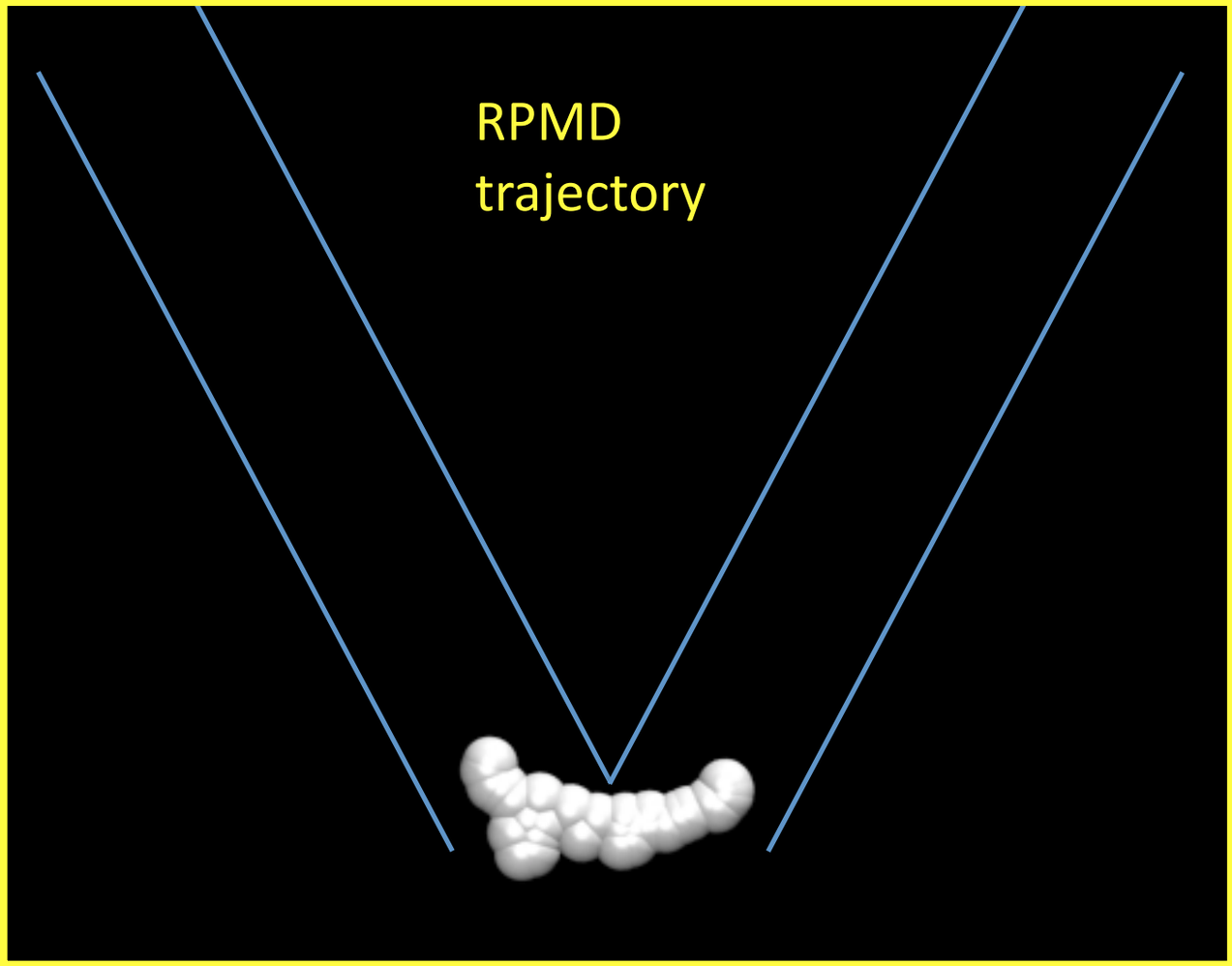
$H + H_2$

DS

$H + H_2$


RPMD
trajectory


instanton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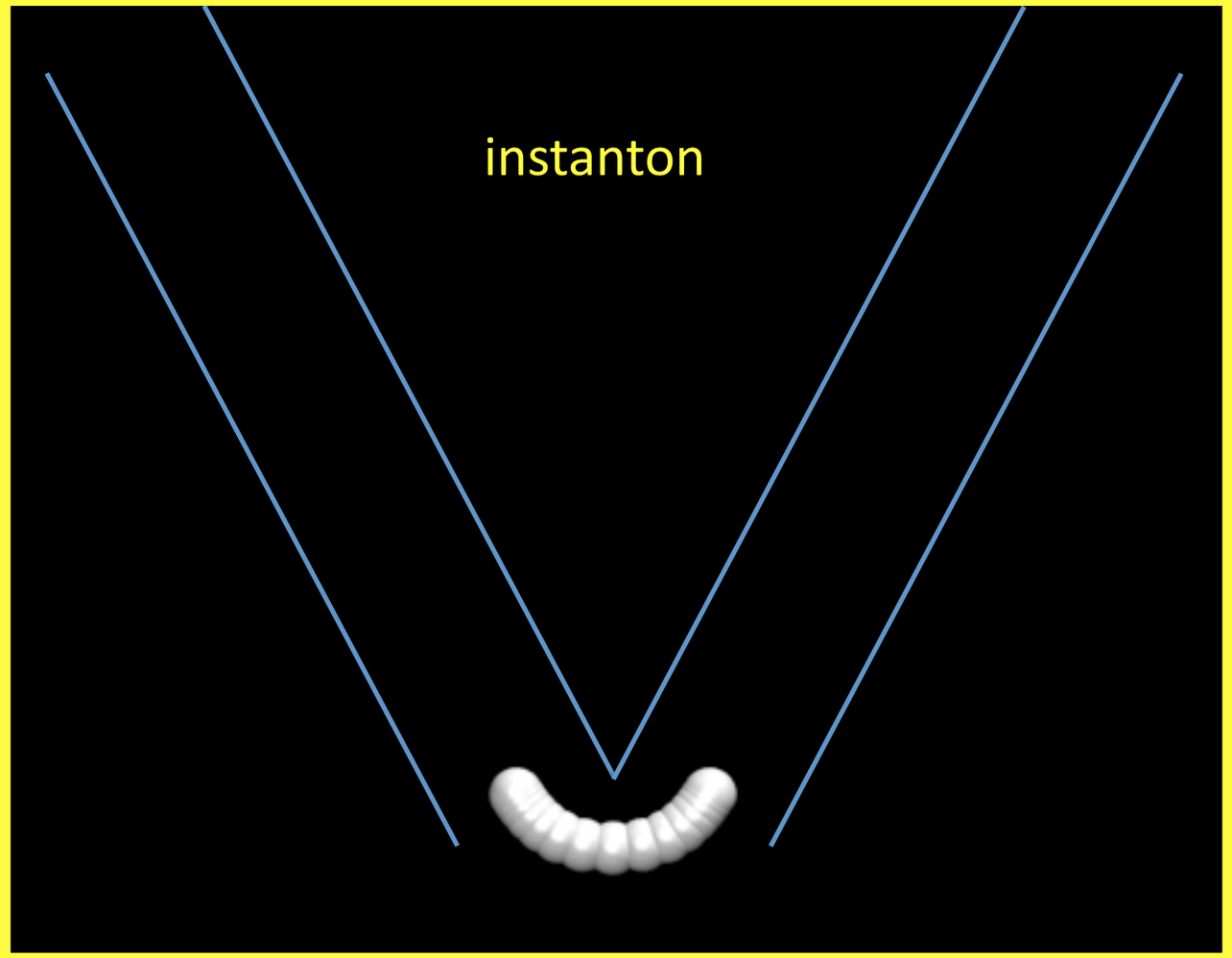
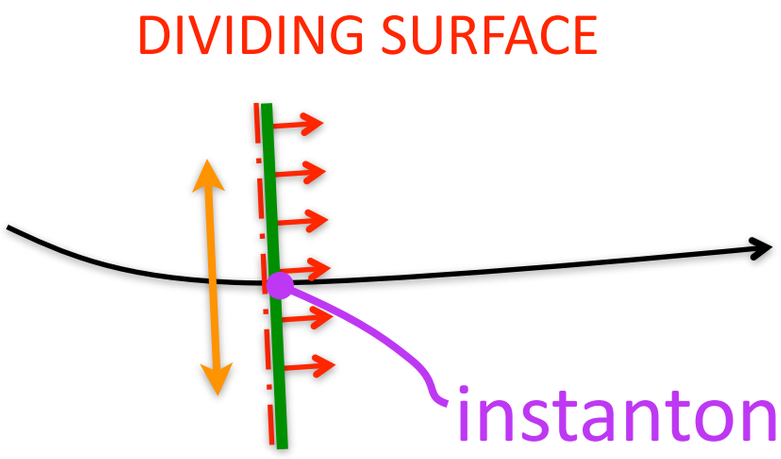
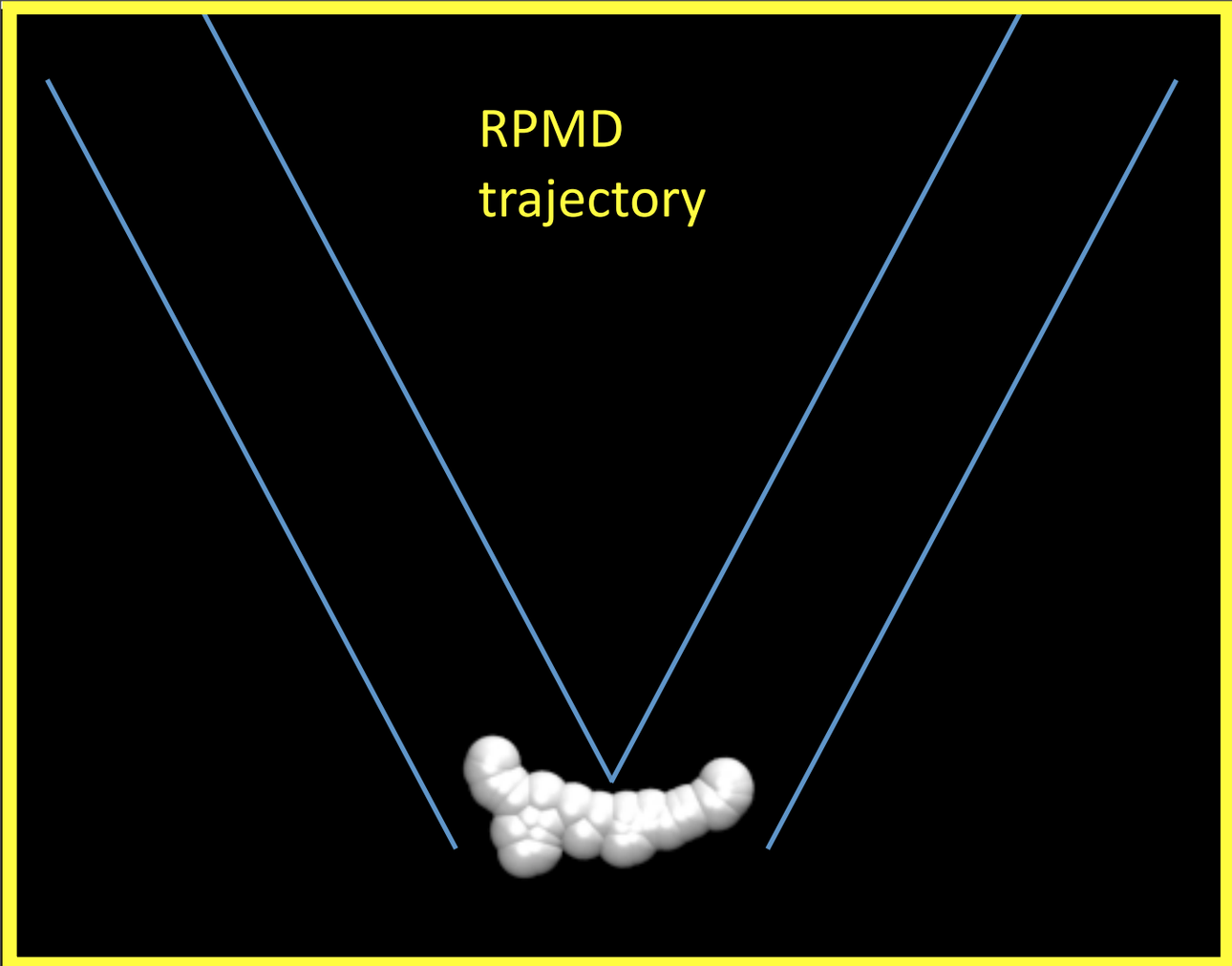
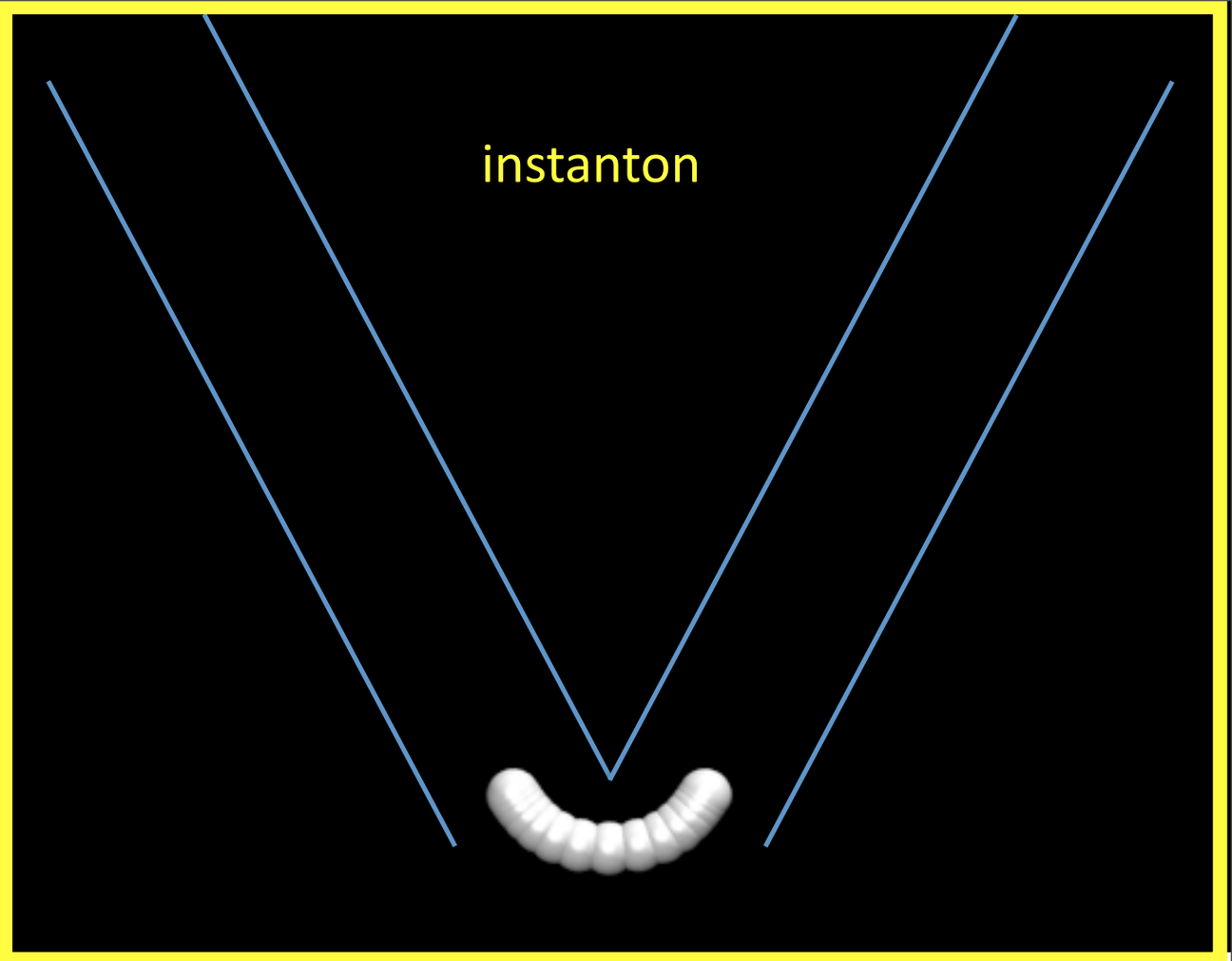
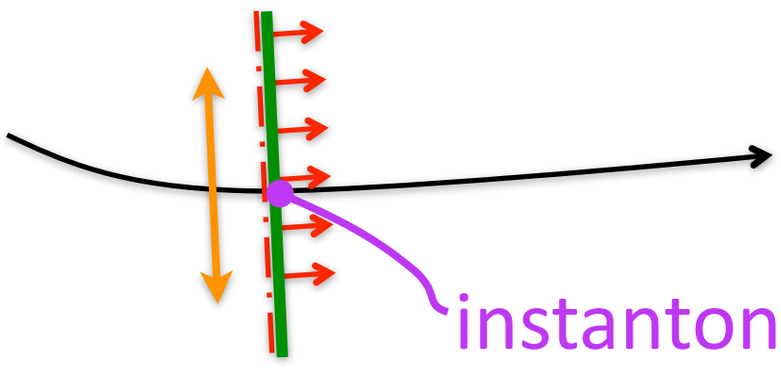

instanton


DIVIDING SURFACE
instanton

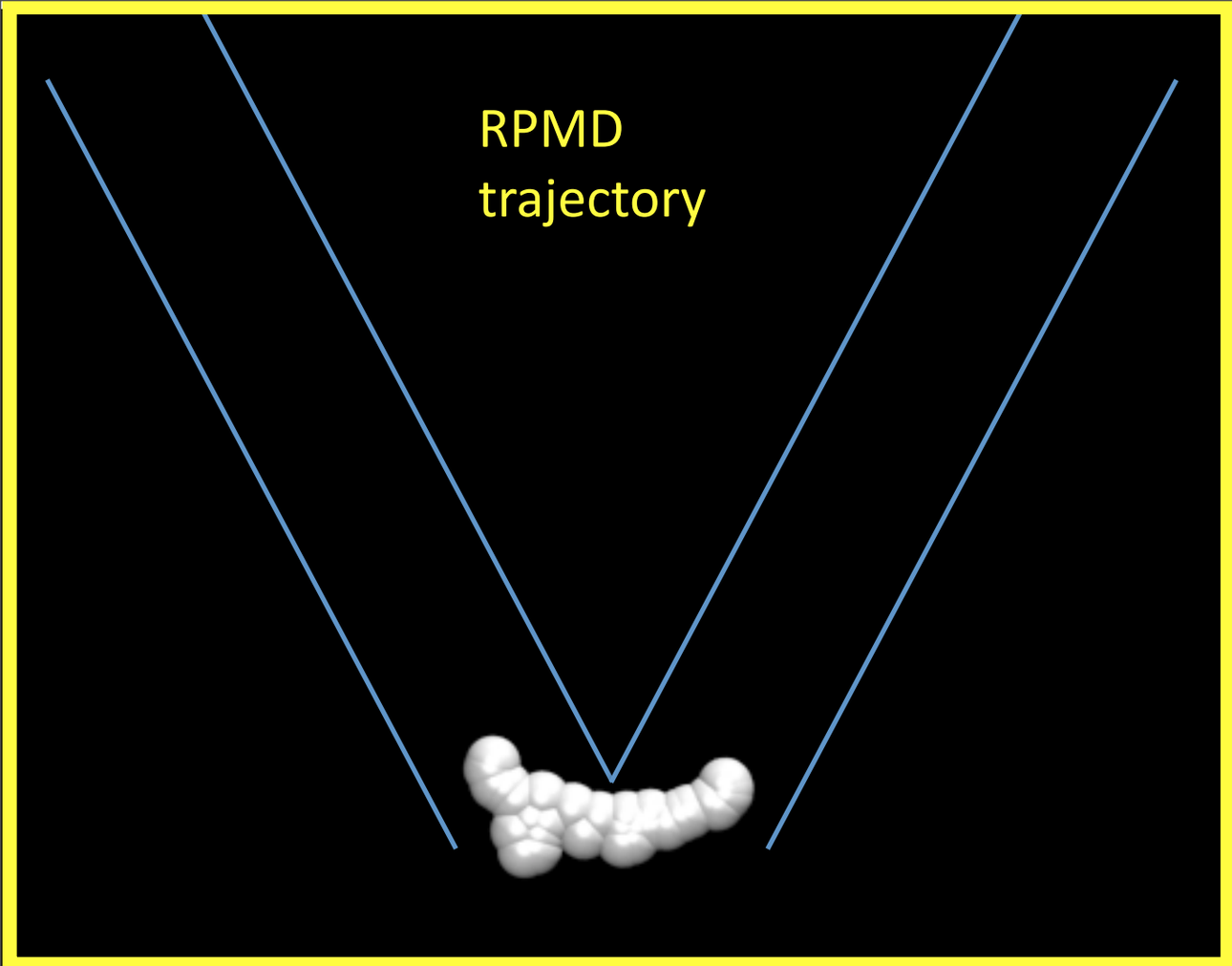


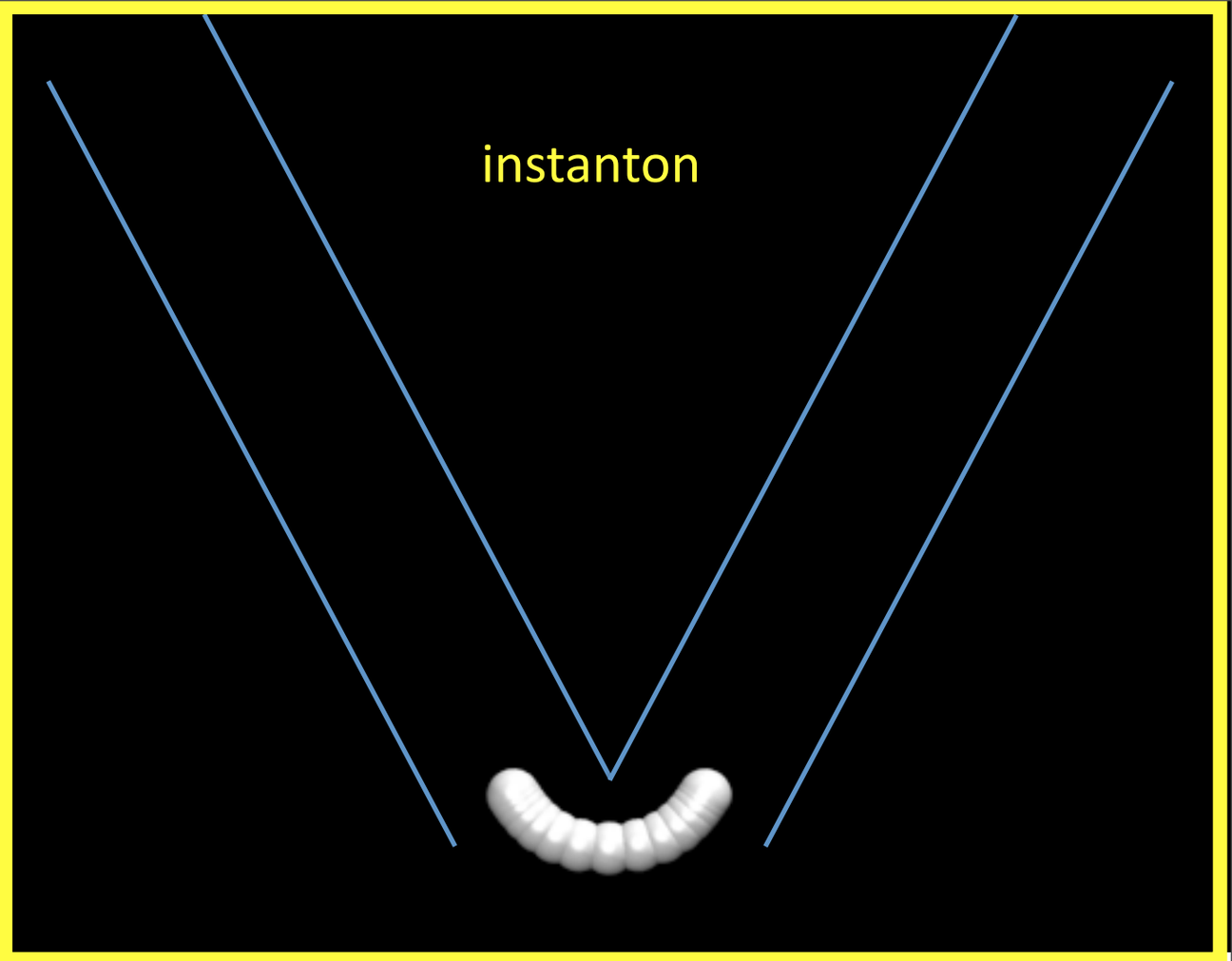


DIVIDING SURFACE



$$k(\beta)Q_{\mathrm{r}}(\beta) \simeq A(\beta)e^{-S(\beta)/\hbar}$$





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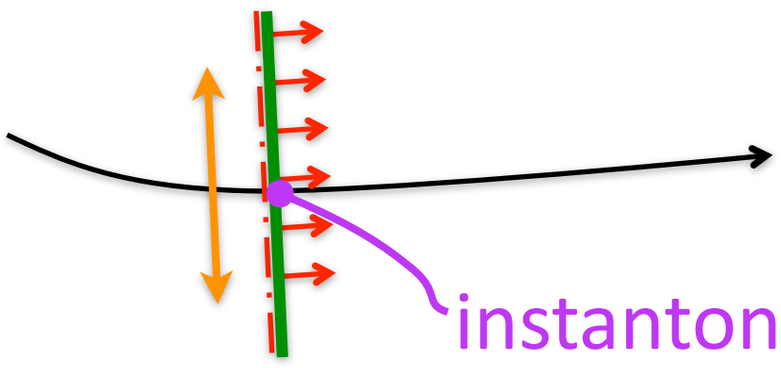
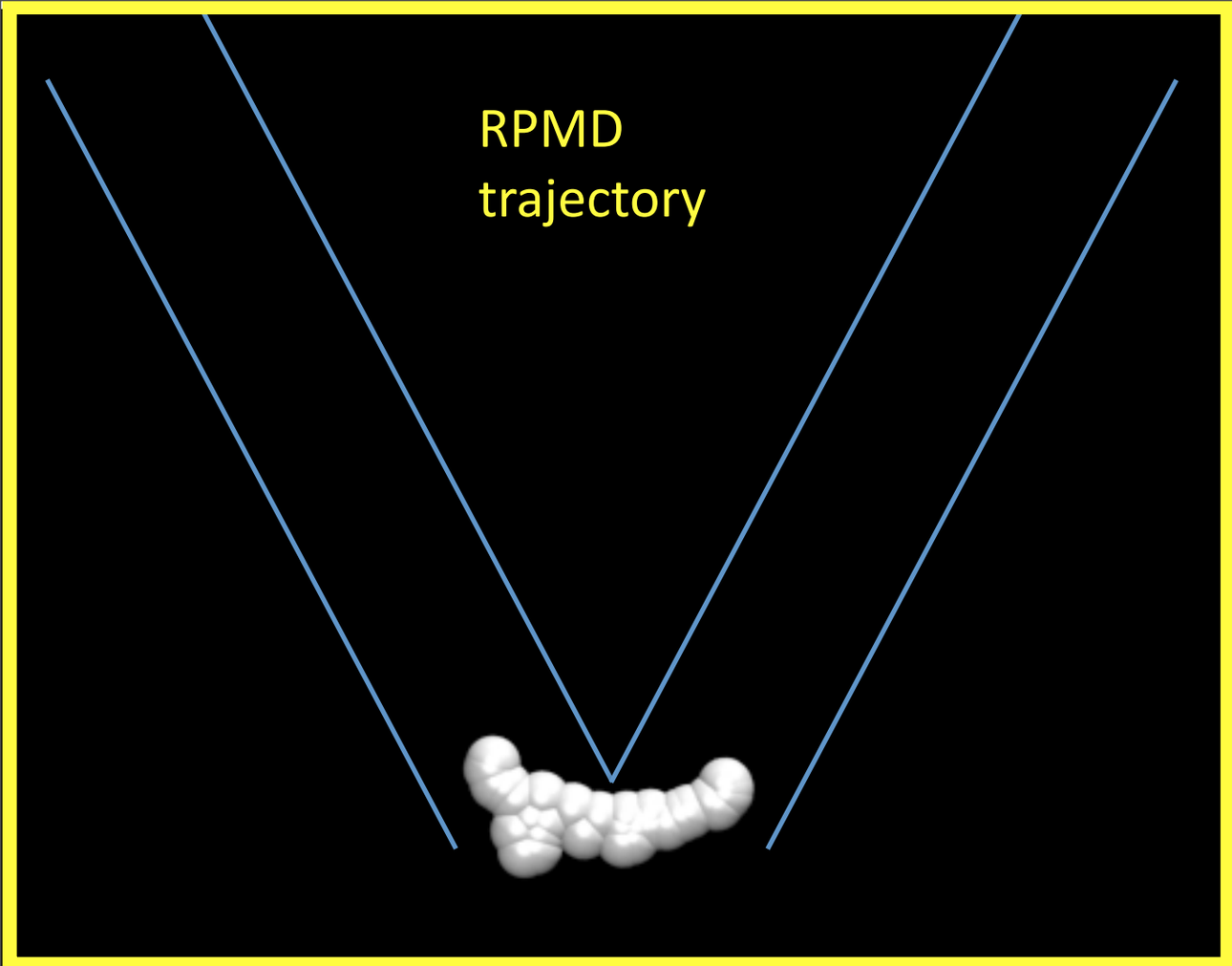
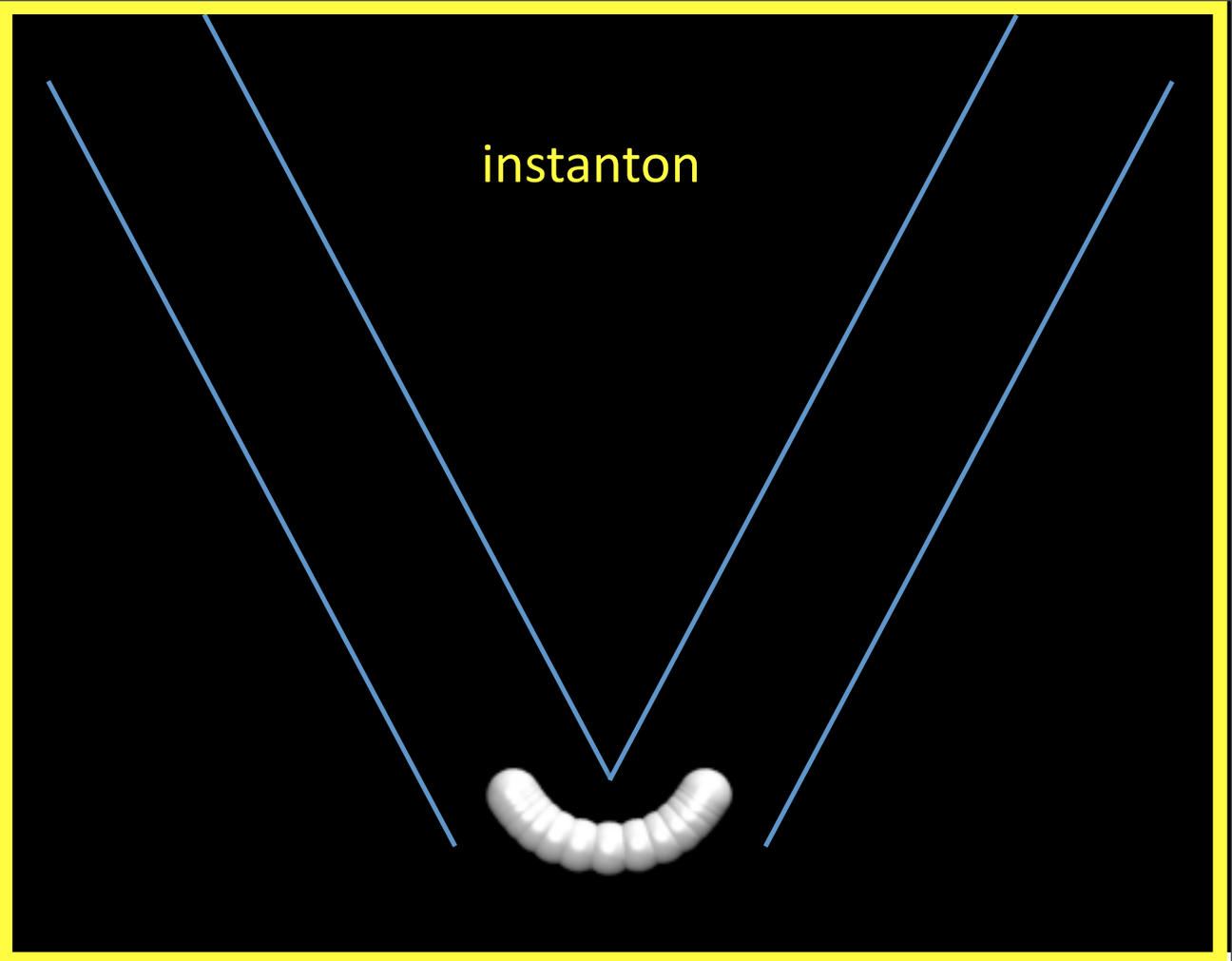


$$k(\beta)Q_{\mathrm{r}}(\beta) \simeq A(\beta)e^{-S(\beta)/\hbar}$$

cf: Voth-Chandler-Miller TST
Quantum instanton: Miller, Ceotto, Vanicek
PACMD: Rossky, Voth
RAW-TST: Schenter, Jonsson





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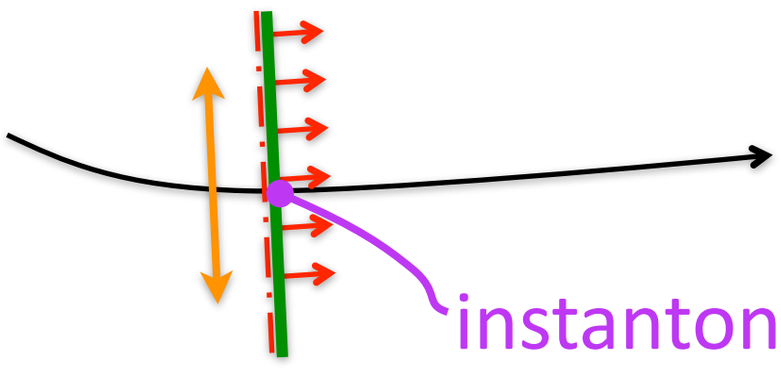


$$k(\beta)Q_{\mathrm{r}}(\beta) \simeq A(\beta)e^{-S(\beta)/\hbar}$$

RPMD masses → asymmetric barriers

cf: Voth-Chandler-Miller TST
Quantum instanton: Miller, Ceotto, Vanicek
PACMD: Rossky, Voth
RAW-TST: Schenter, Jonsson

THE JOURNAL OF CHEMICAL PHYSICS **131**, 214106 (2009)

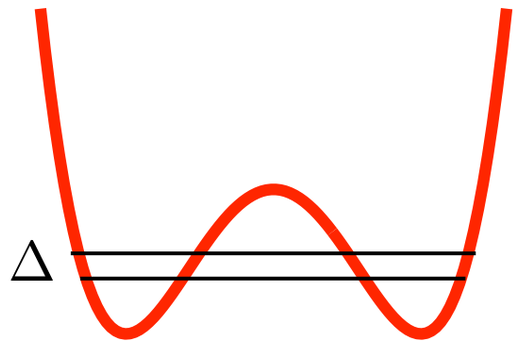
Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory

Jeremy O. Richardson and Stuart C. Althorpe
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

(Received 14 October 2009; accepted 4 November 2009; published online 3 December 2009)

We demonstrate that the ring-polymer molecular dynamics (RPMD) method is equivalent to an automated and approximate implementation of the "Im F" version of semiclassical instanton theory when used to calculate reaction rates in the deep-tunneling regime. This explains why the RPMD method is often reliable in this regime and also shows how it can be systematically improved. The geometry of the beads at the transition state on the ring-polymer potential surface describes a finite-difference approximation to the "instanton" trajectory (a periodic orbit in imaginary time $\beta\hbar$ on the inverted potential surface). The deep-tunneling RPMD rate is an approximation to the rate obtained by applying classical transition-state theory (TST) in ring-polymer phase-space using the optimal dividing surface; this TST rate is in turn an approximation to a free-energy version of the Im F instanton rate. The optimal dividing surface is in general a function of several modes of the ring polymer, which explains why centroid-based quantum-TSTs break down at low temperatures for asymmetric reaction barriers. Numerical tests on one-dimensional models show that the RPMD rate tends to overestimate deep-tunneling rates for asymmetric barriers and underestimate them for symmetric barriers, and we explain that this is likely to be a general trend. The ability of the RPMD method to give a dividing-surface-independent rate in the deep-tunneling regime is shown to be a consequence of setting the bead-masses equal to the physical mass. [doi:10.1063/1.3267318]

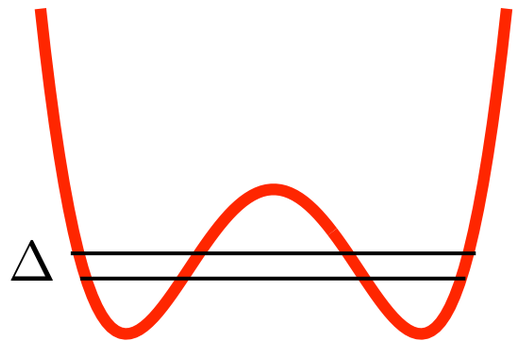
Tunnelling splittings



$$\cosh\left(\frac{\beta\Delta}{2}\right) = \lim_{\beta\to\infty}\frac{Q(\beta)}{Q_0(\beta)}$$

Vainshtein et al. 1982
Mil'nikov & Nakamura 2001
Ceperley 1987; Marchi & Chandler 1991

Tunnelling splittings



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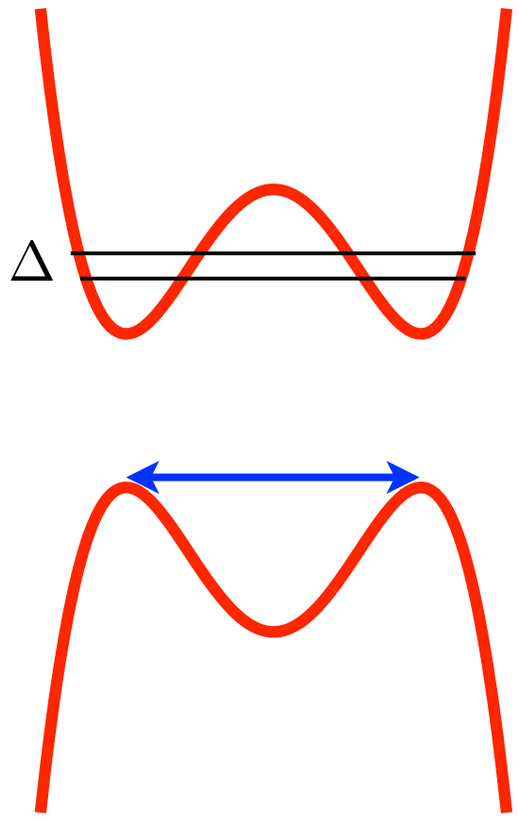
Vainshtein et al. 1982
Mil'nikov & Nakamura 2001
Ceperley 1987; Marchi & Chan

$$= \frac{\exp[-\beta(E_0+\Delta)] + \exp[-\beta(E_0-\Delta)]}{2\exp(-\beta E_0)}$$

Tunnelling splittings

$$\cosh\left(\frac{\beta\Delta}{2}\right) = \lim_{\beta\to\infty}\frac{Q(\beta)}{Q_0(\beta)}$$

Vainshtein et al. 1982
Mil'nikov & Nakamura 2001
Ceperley 1987; Marchi & Chandler 1991



Tunnelling splittings

$$\cosh\left(\frac{\beta\Delta}{2}\right) = \lim_{\beta\to\infty}\frac{Q(\beta)}{Q_0(\beta)}$$

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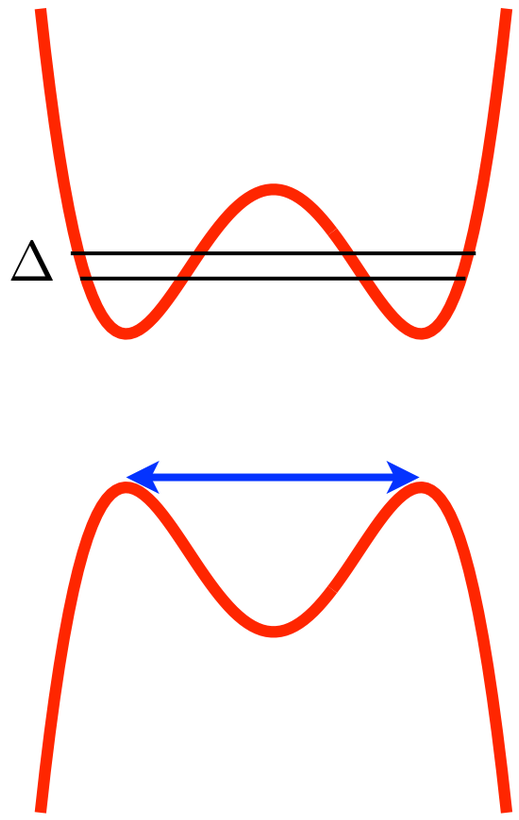
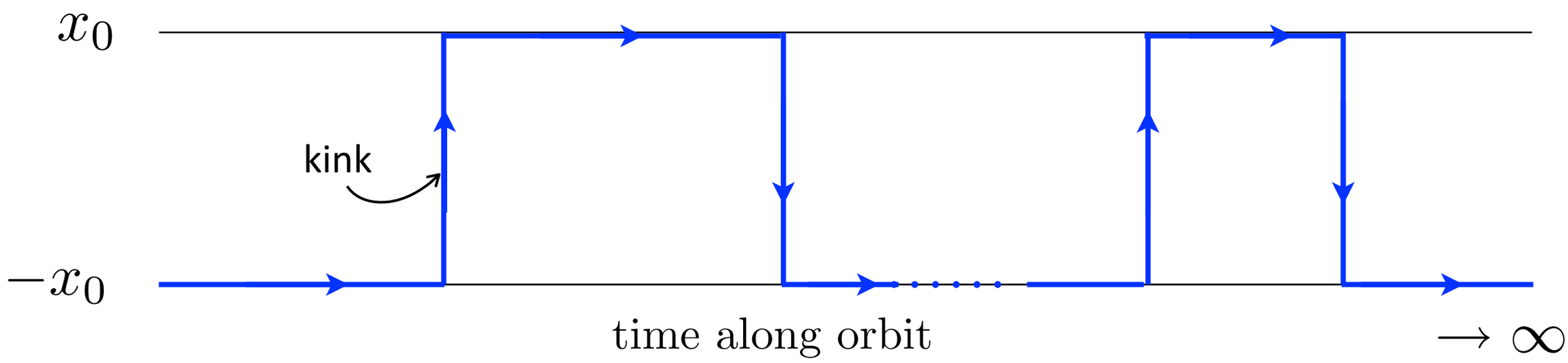




$$\Delta = A_{\rm kink} e^{-S_{\rm kink}/\hbar}$$

THE JOURNAL OF CHEMICAL PHYSICS **134**, 054109 (2011)

Ring-polymer instanton method for calculating tunneling splittings

Jeremy O. Richardson and Stuart C. Althorpe
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

(Received 9 November 2010; accepted 3 December 2010; published online 1 February 2011)

The semiclassical instanton expression for the tunneling splitting between two symmetric wells is rederived, starting from the ring-polymer representation of the quantum partition function. This leads to simpler mathematics by replacing functional determinants with matrix determinants. By exploiting the simple Hückel-like structure of the matrices, we derive an expression for the instanton tunneling splitting in terms of a minimum on the potential surface of a *linear* polymer. The latter is a section cut out of a ring polymer, consisting of an infinite number of beads, which describes a periodic orbit on the inverted potential surface. The approach is straightforward to generalize to multiple dimensions, and we demonstrate that it is computationally practical by carrying out instanton calculations of tunneling splittings in HO_2 and malonaldehyde in full dimensionality. [doi:10.1063/1.3530589]

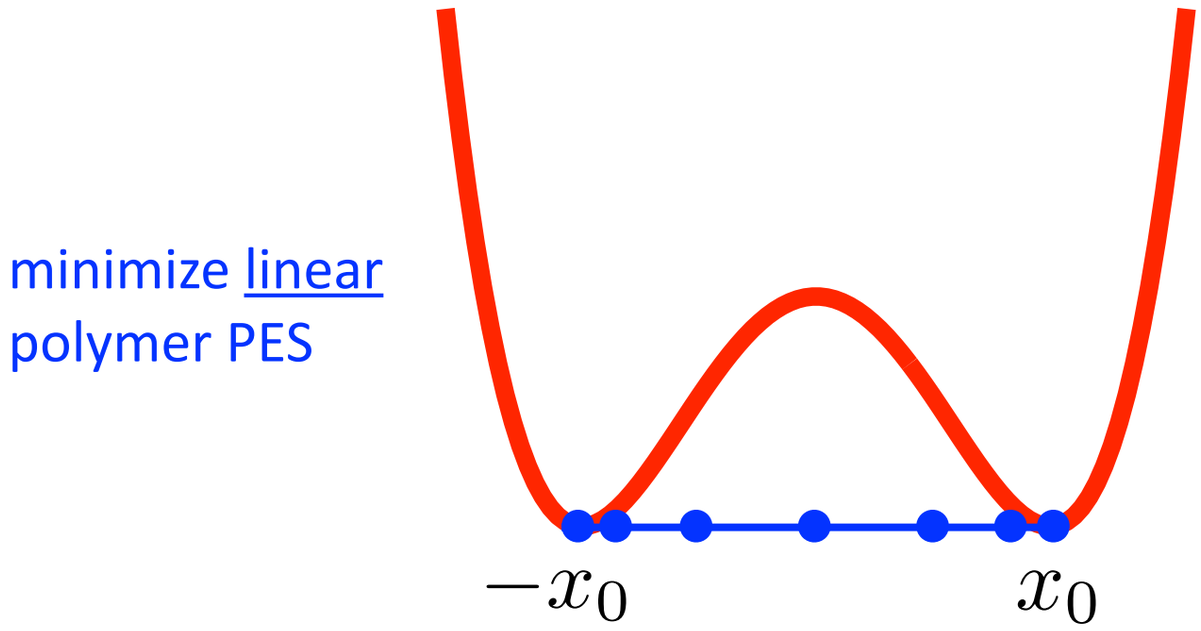
$$\frac{\partial U_N(\beta, \mathbf{x})}{\partial x_n} = 0$$

find stationary points on ring-polymer surface

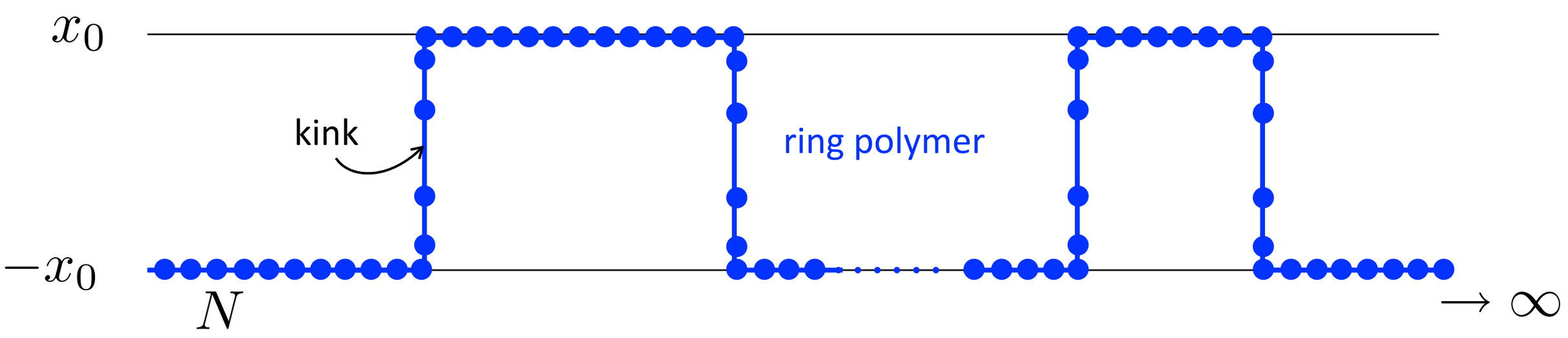
14

Ring-polymer instanton (RPI) method

J.O. Richardson & SCA, JCP 2011



$$\beta\hbar \to \infty$$



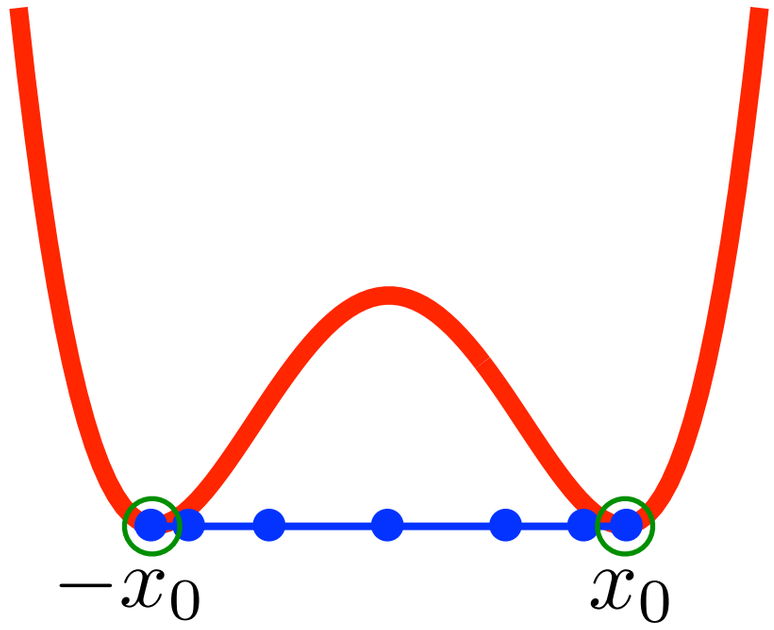
$$\Delta = A_{\mathrm{linear}} e^{-S_{\mathrm{linear}}/\hbar}$$

15

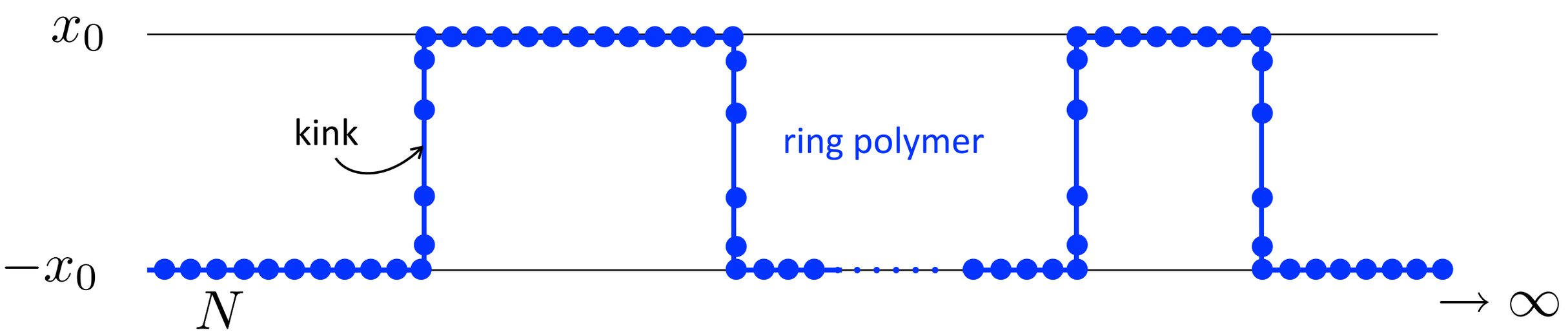
Ring-polymer instanton (RPI) method

J.O. Richardson & SCA, JCP 2011

minimize linear polymer PES



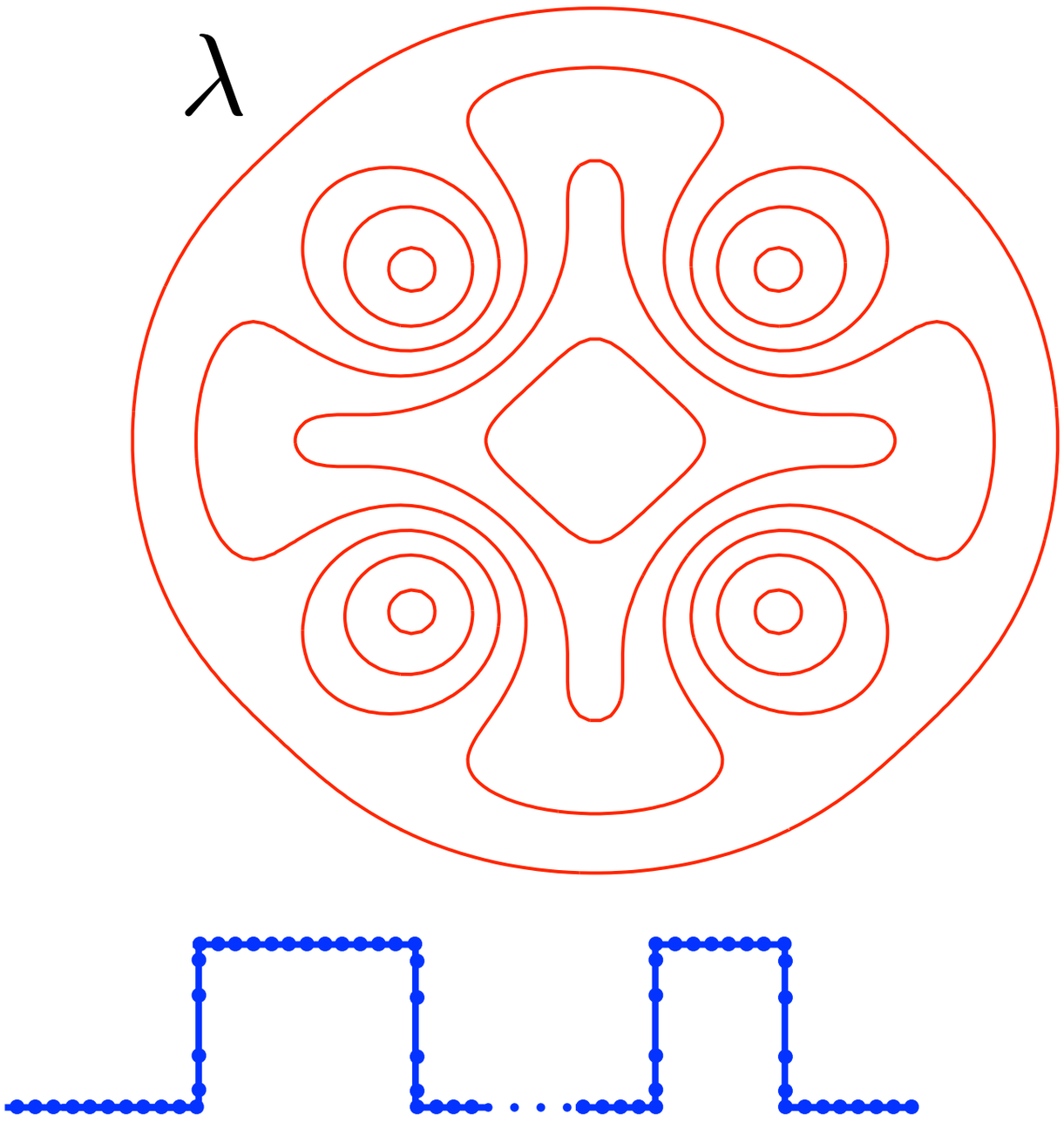
$$\beta\hbar \to \infty$$



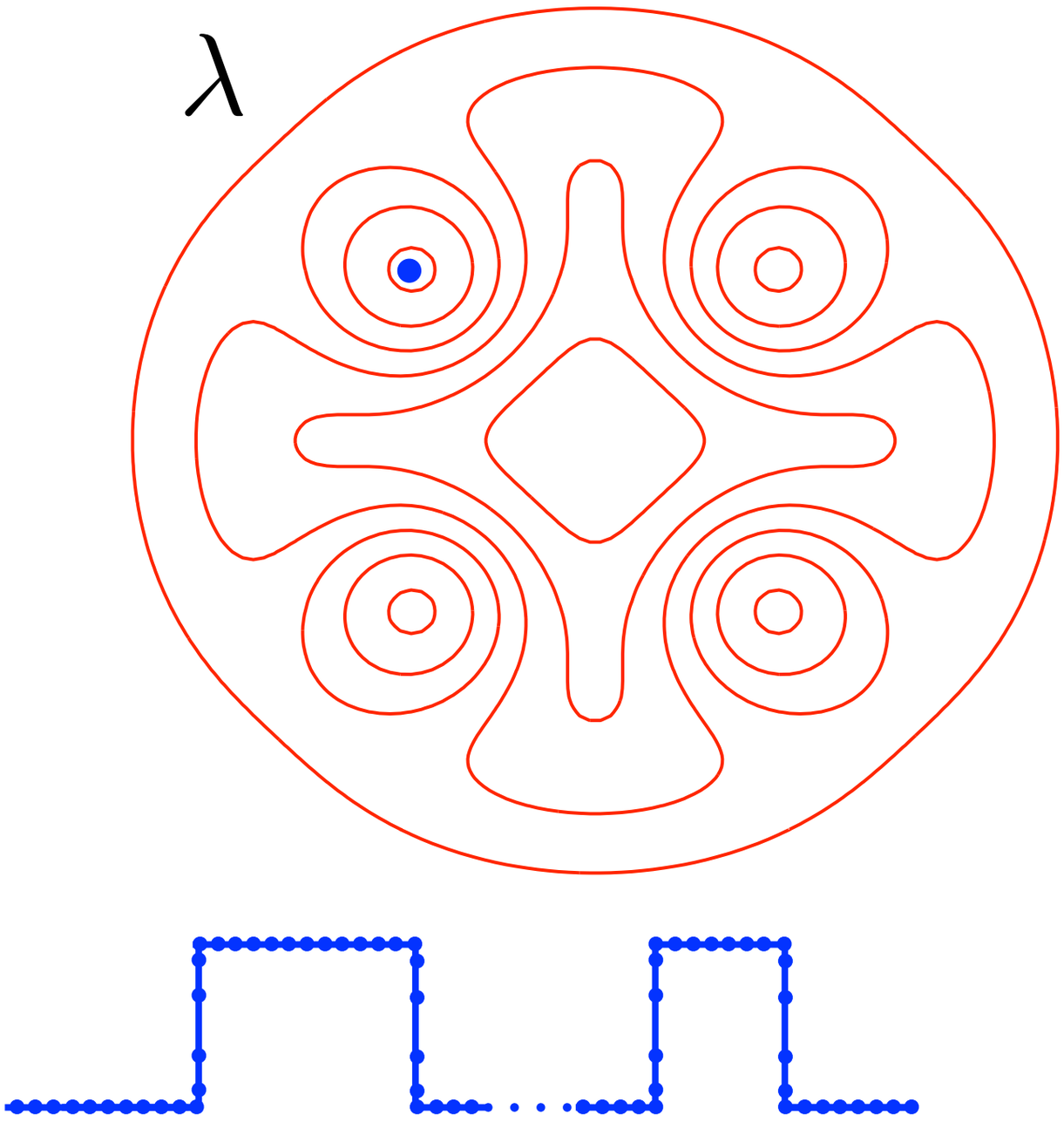
$$\Delta = A_{\mathrm{linear}} e^{-S_{\mathrm{linear}}/\hbar}$$

15

Tunnelling between multiple minima



Tunnelling between multiple minima



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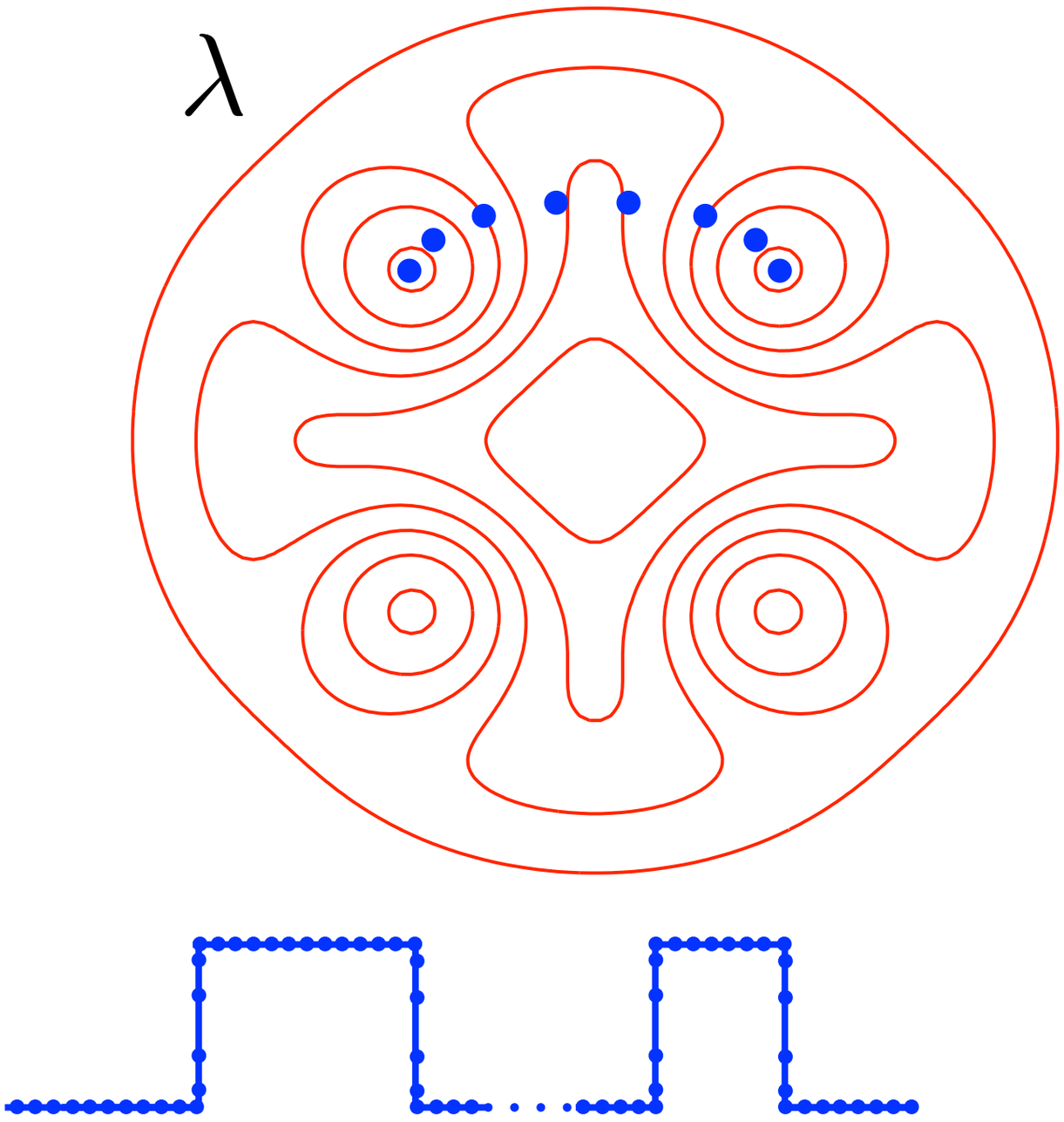
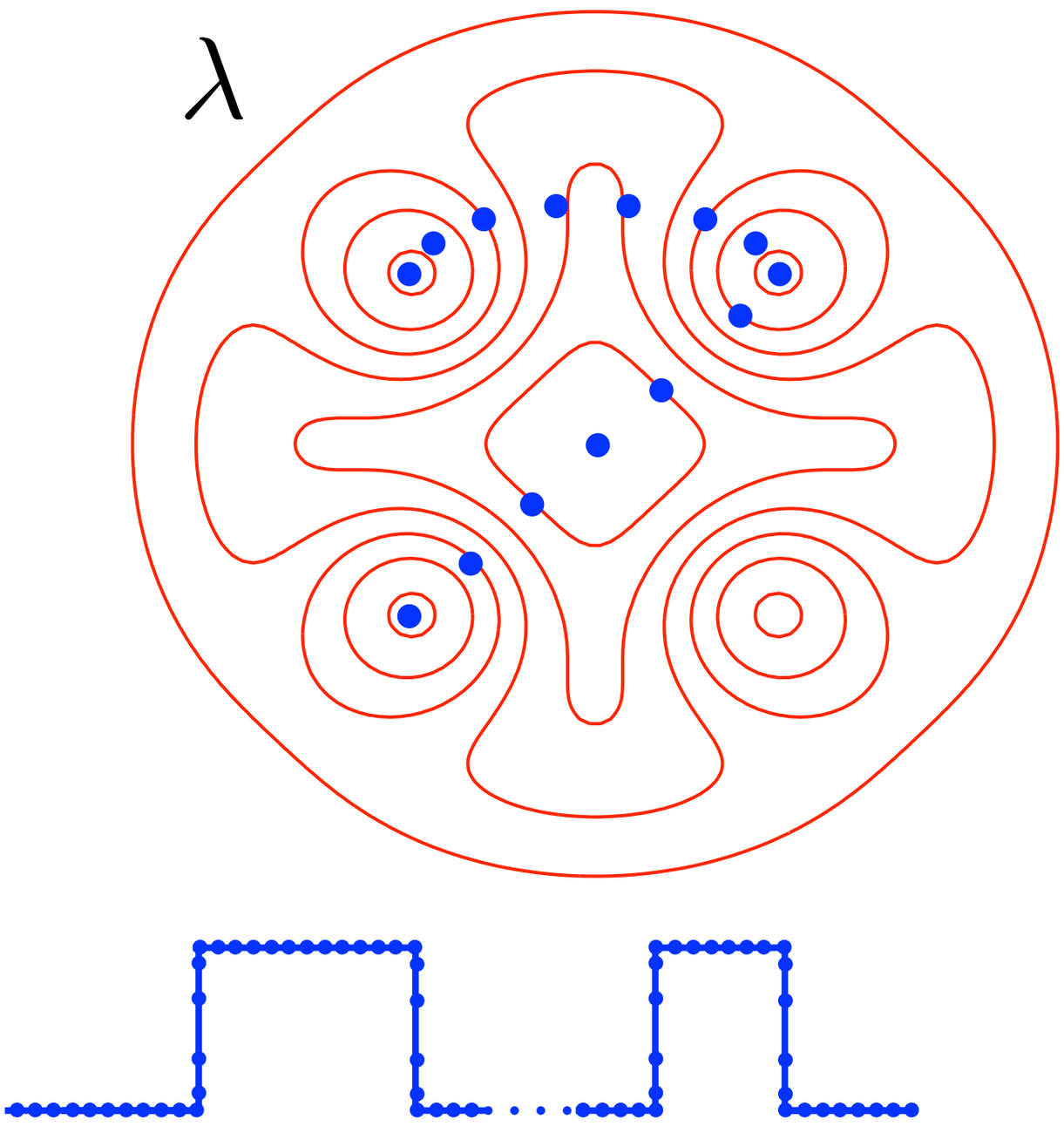
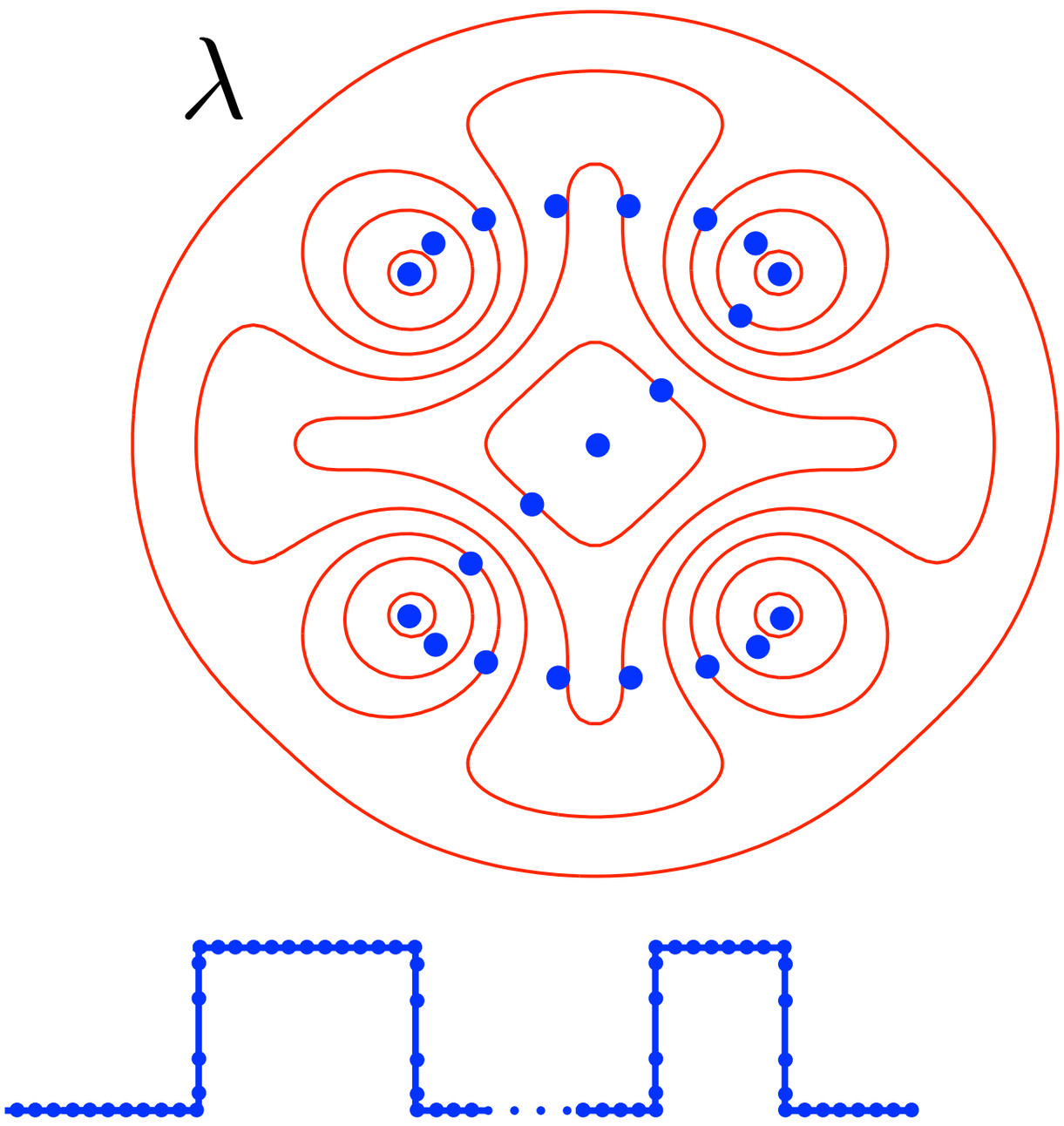
Tunnelling between multiple minima



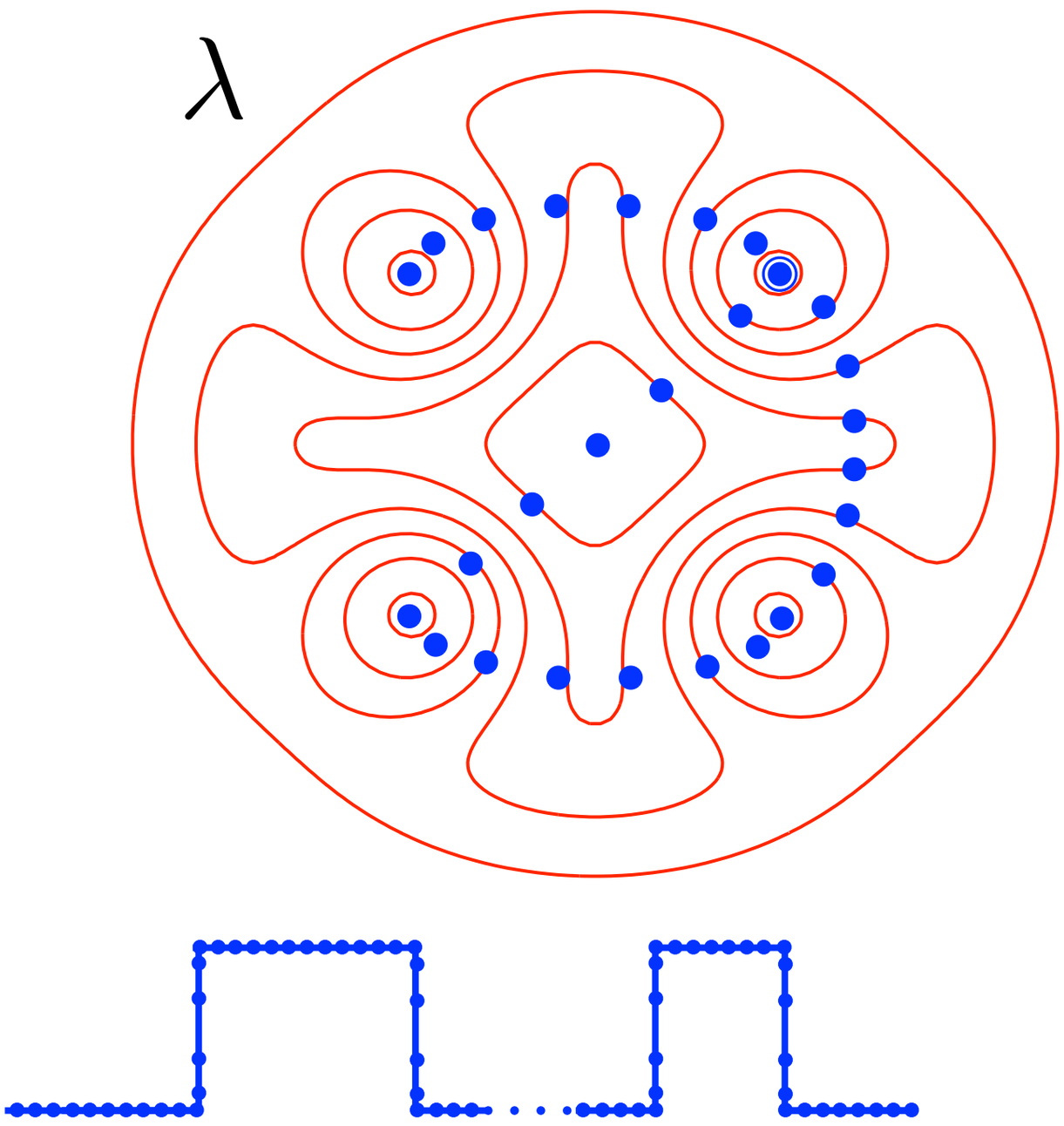
Tunnelling between multiple minima



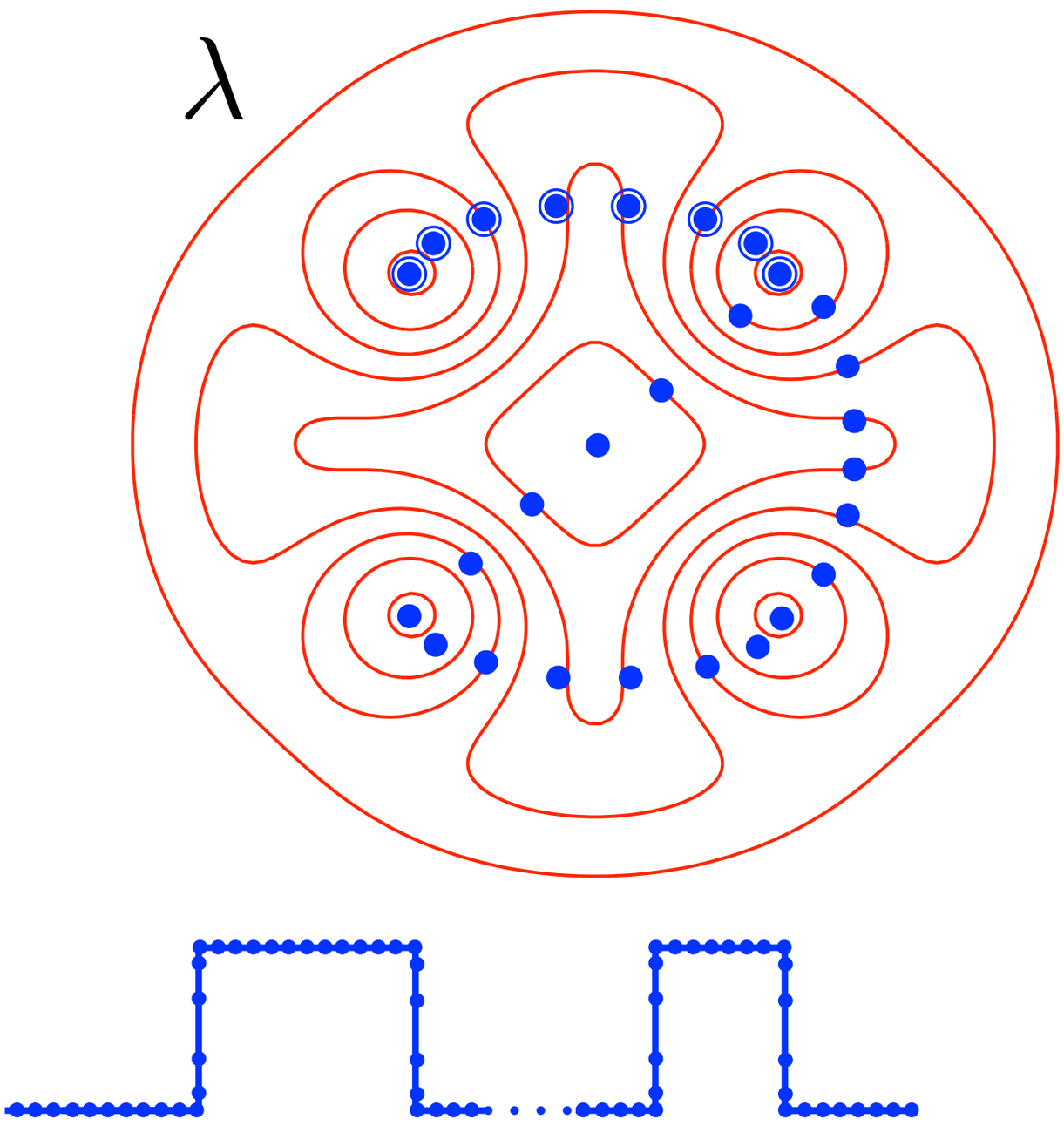
Tunnelling between multiple minima



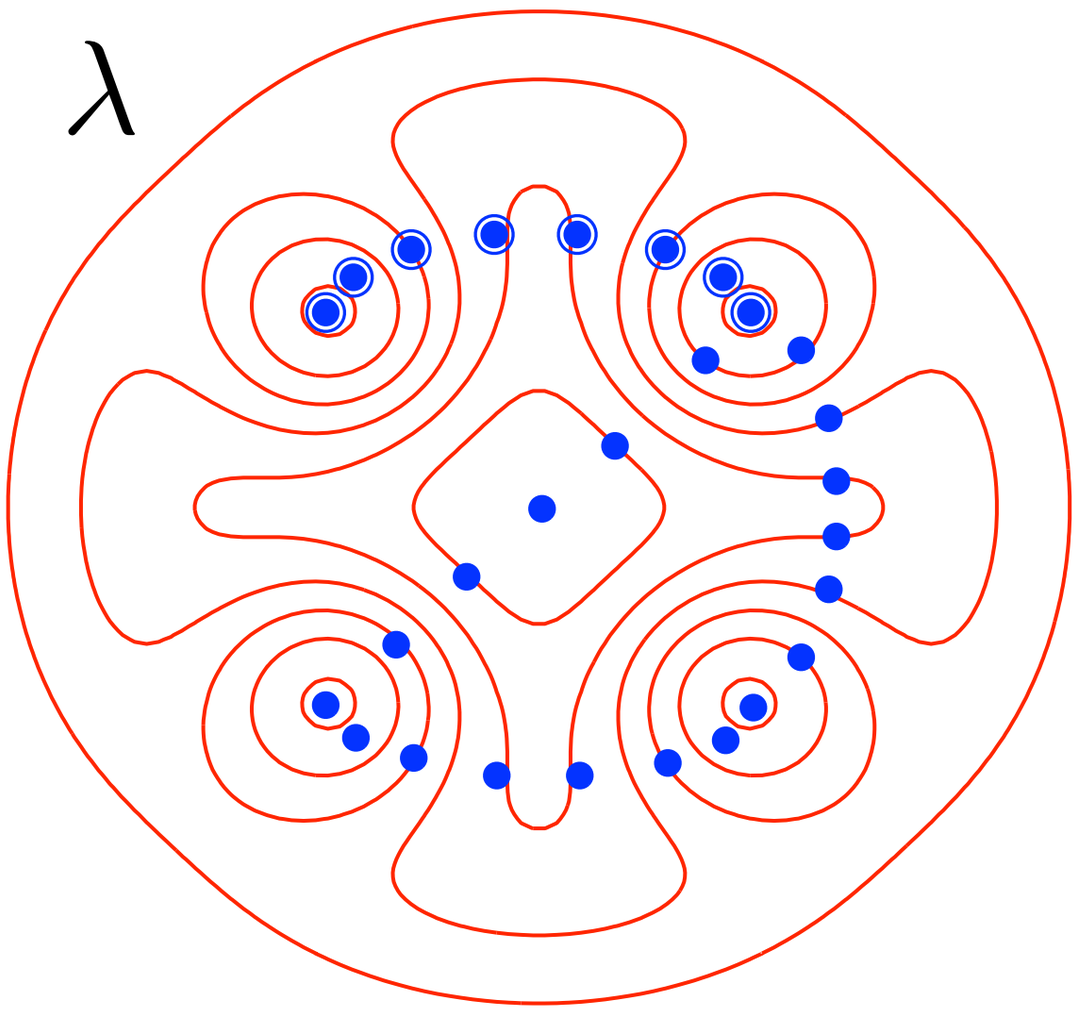
Tunnelling between multiple minima

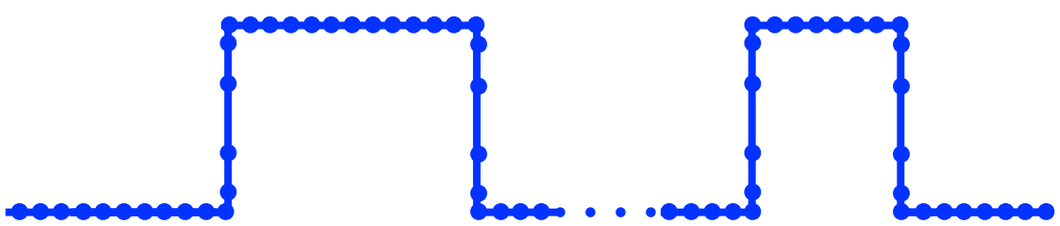


Tunnelling between multiple minima



Tunnelling between multiple minima

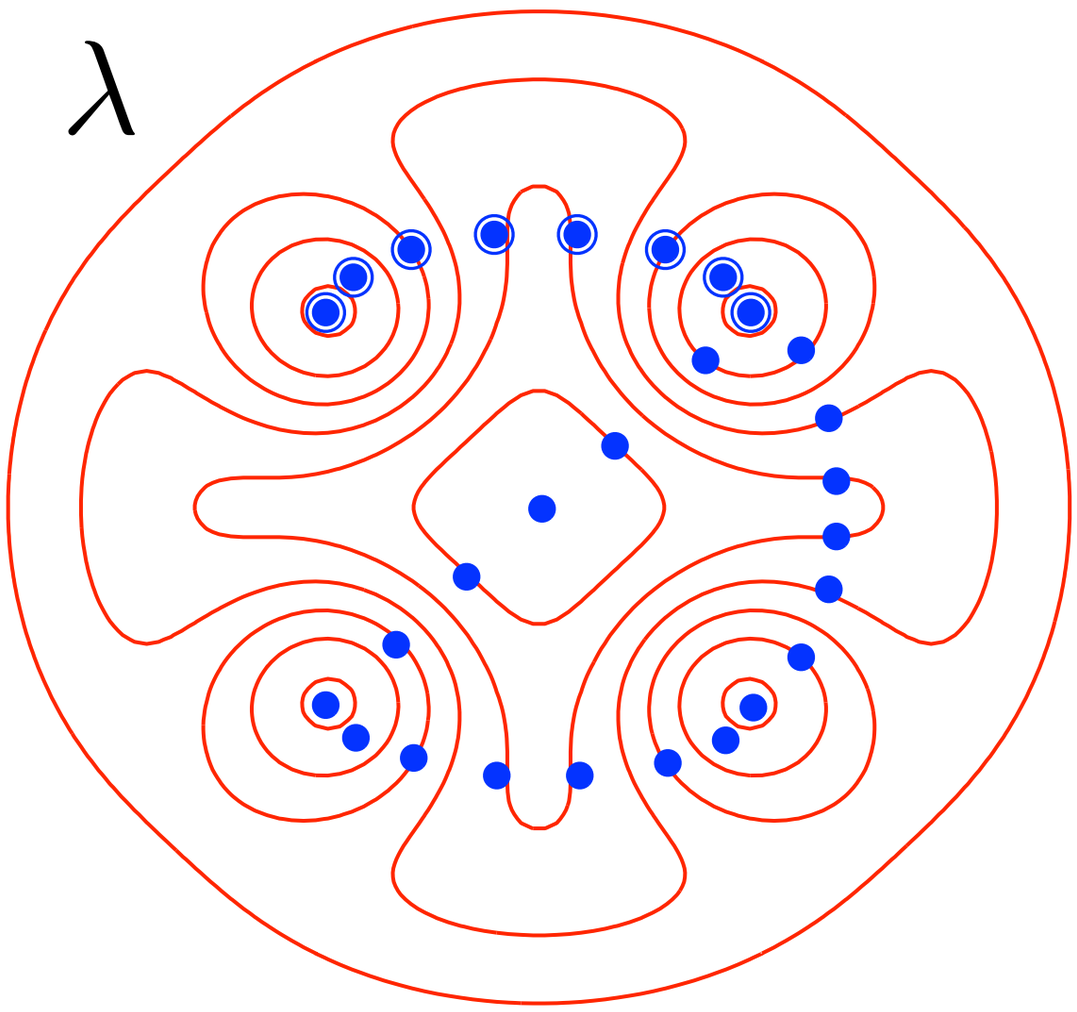


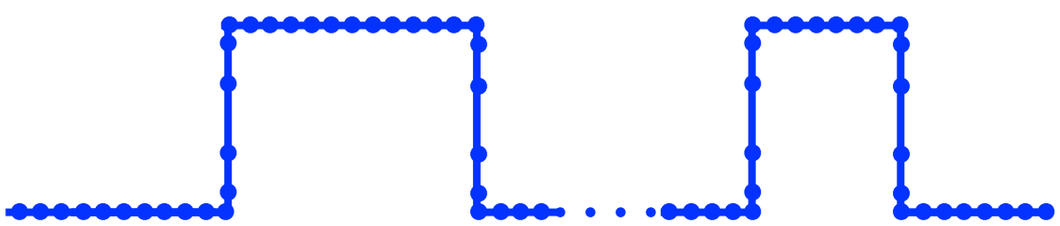


Adjacency matrix $\mathbf{A}$

$\lambda \to \lambda$ paths $(\mathbf{A}^n)_{\lambda\lambda}$

Tunnelling between multiple minima





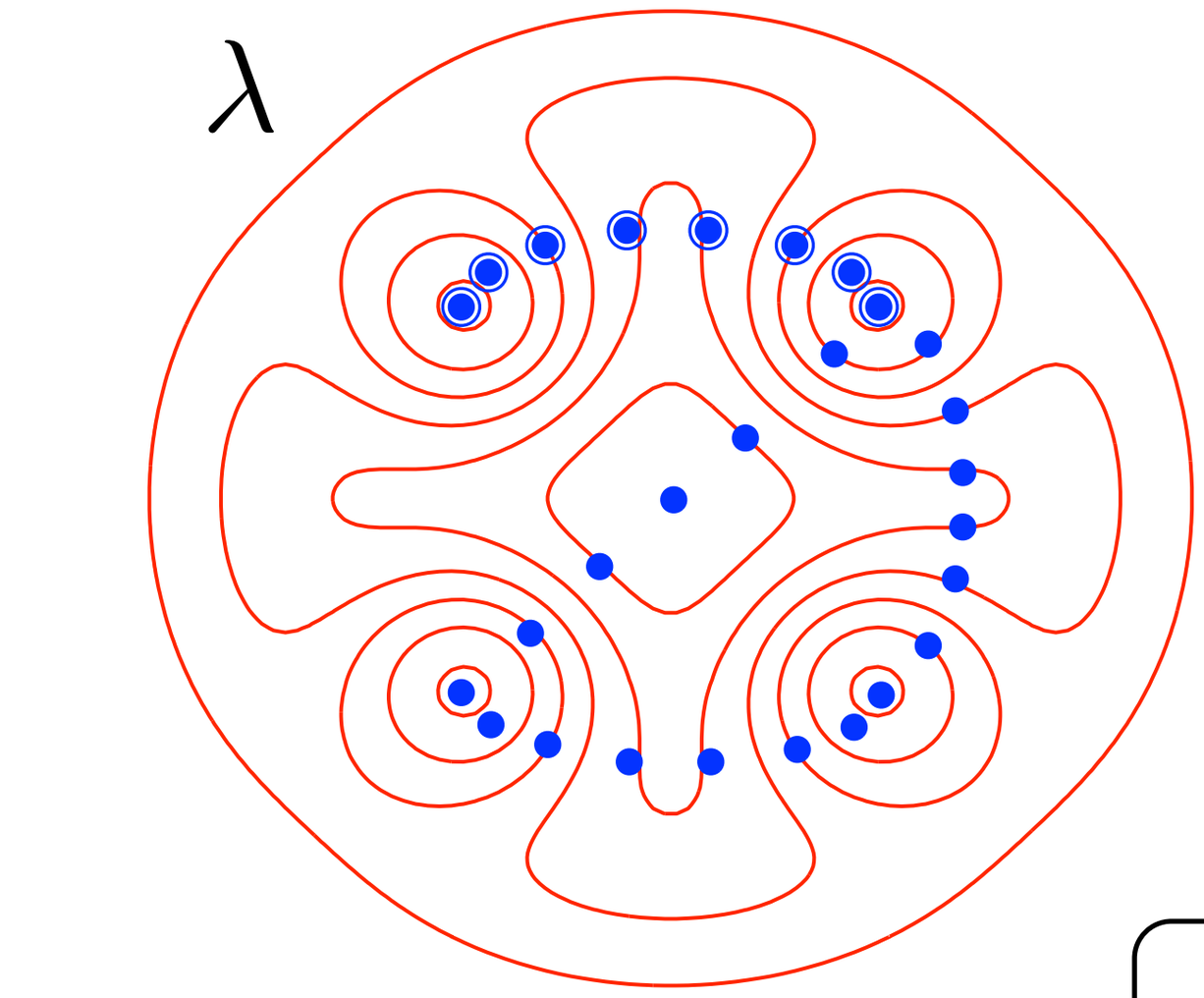
Adjacency matrix $\mathbf{A}$

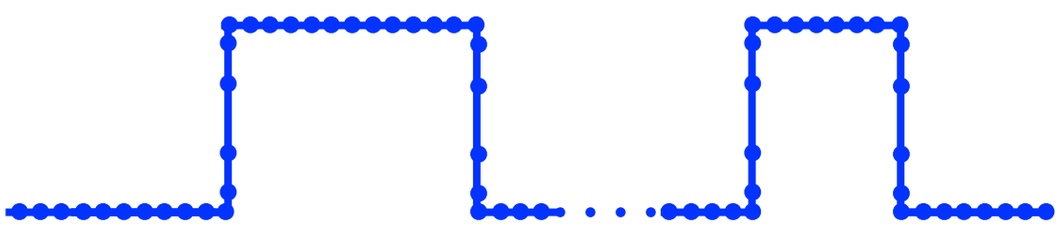
$\lambda \to \lambda$ paths $(\mathbf{A}^n)_{\lambda\lambda}$

$$W_{\lambda\mu} = A_{\lambda\mu}\, A_{\rm kink} e^{-S_{\rm kink}/\hbar}$$

16

Tunnelling between multiple minima





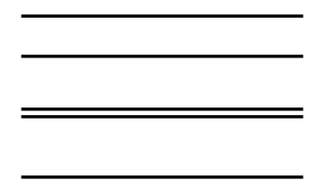
Adjacency matrix $\mathbf{A}$

$\lambda \rightarrow \lambda$ paths $(\mathbf{A}^n)_{\lambda\lambda}$

$$W_{\lambda\mu} = A_{\lambda\mu}\, A_{\mathrm{kink}} e^{-S_{\mathrm{kink}}/\hbar}$$

splitting pattern

diagonalize $\mathbf{W}$ ⟶



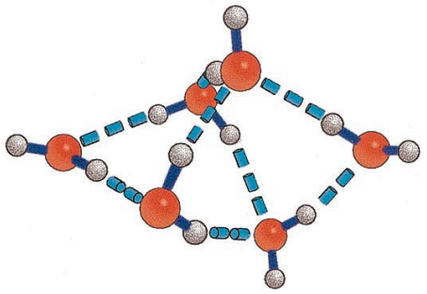
Richardson & SCA, JCP 2011

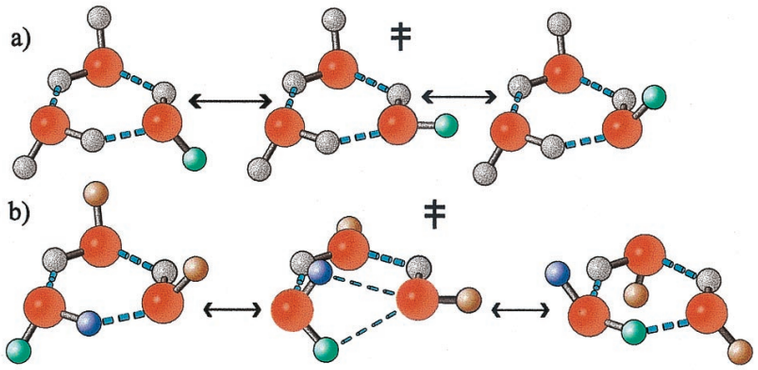
Water clusters: Untangling the mysteries of the liquid, one molecule at a time

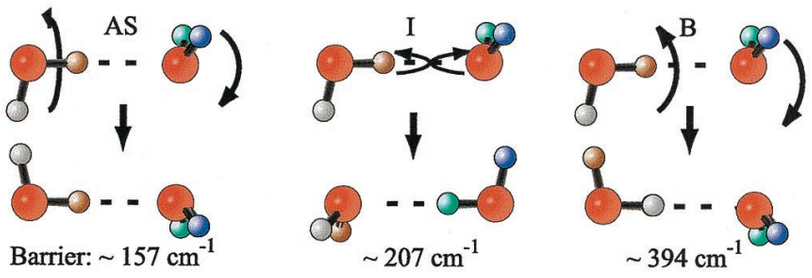
Frank N. Keutsch* and Richard J. Saykally†

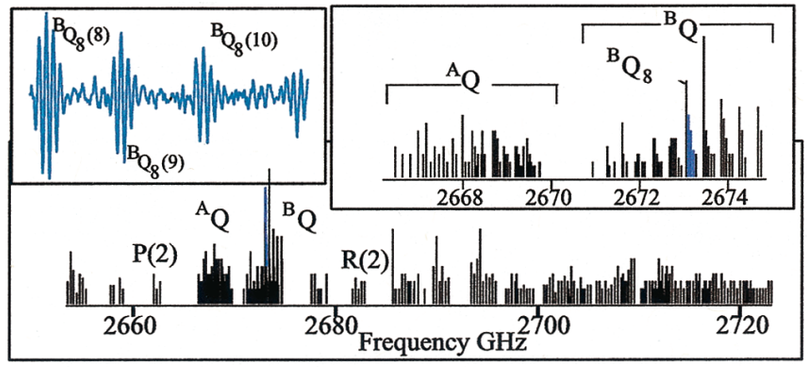
Department of Chemistry, University of California, Berkeley, CA 94720-1460

PNAS | **September 11, 2001** | vol. 98 | no. 19 | **10533–10540**









THE JOURNAL OF CHEMICAL PHYSICS **134**, 094509 (2011)

Flexible, *ab initio* potential, and dipole moment surfaces for water. I. Tests and applications for clusters up to the 22-mer

Yimin Wang,[1] Xinchuan Huang,[2,a)] Benjamin C. Shepler,[3] Bastiaan J. Braams,[4] and Joel M. Bowman[1,b)]

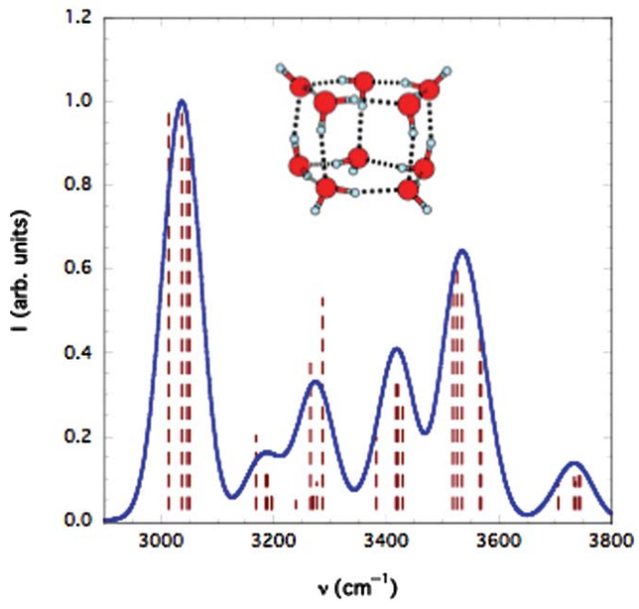
[1]*Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322, USA*

[2]*SETI Institute, 189 Bernardo Ave, Suite 100, Mountain View, California 94043,USA*

[3]*Georgia Gwinnett College, Lawrenceville, Georgia 30043, USA*

[4]*Division of Physical and Chemical Sciences, International Atomic Energy Agency, Vienna, Austria*

(Received 29 December 2010; accepted 26 January 2011; published online 3 March 2011)



also cf: Gregory & Clary 1996
Whaley 2000
Leforestier 2002

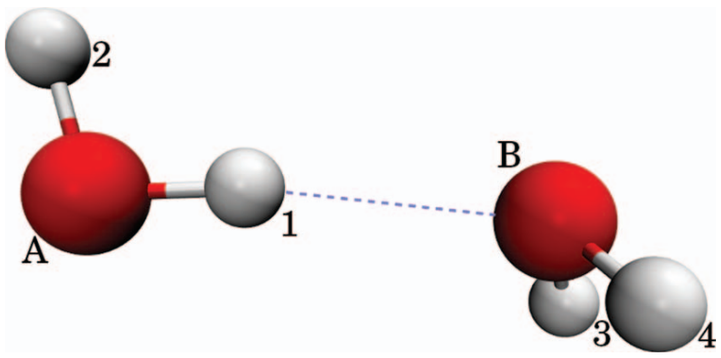
THE JOURNAL OF CHEMICAL PHYSICS **135**, 124109 (2011)

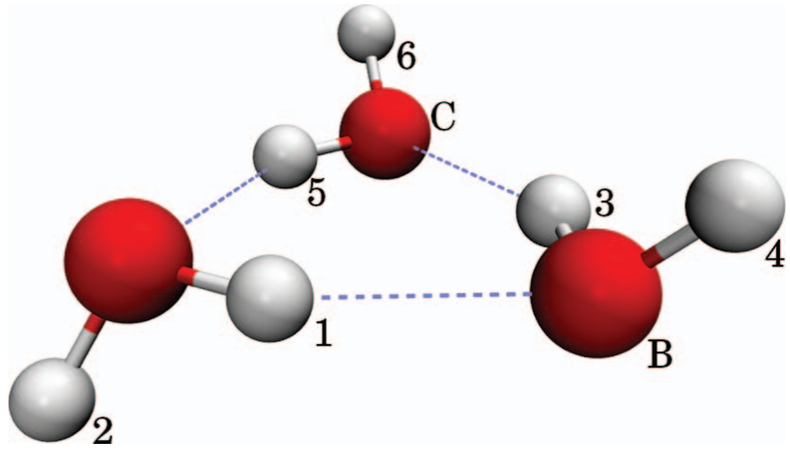
Instanton calculations of tunneling splittings for water dimer and trimer

Jeremy O. Richardson, Stuart C. Althorpe,[a)] and David J. Wales
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom

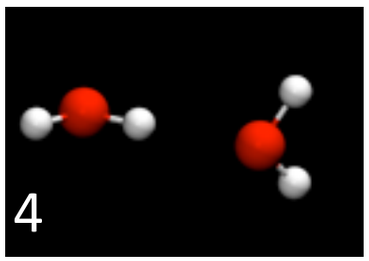
(Received 15 August 2011; accepted 30 August 2011; published online 30 September 2011)

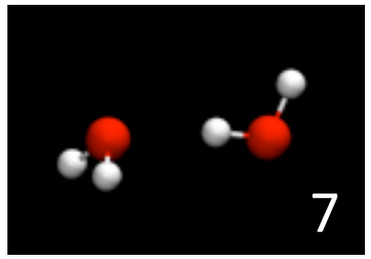
We investigate the ability of the recently developed ring-polymer instanton (RPI) method [J. O. Richardson and S. C. Althorpe, J. Chem. Phys. **134**, 054109 (2011)] to treat tunneling in water clusters. We show that the RPI method is easy to extend to treat tunneling between more than two minima, using elementary graph theory. Tests of the method on water dimer and trimer yield a set of instanton periodic orbits which correspond to all known tunneling pathways in these systems. Splitting patterns obtained from the orbits are in good overall agreement with experiment. The agreement is closer for the deuterated than for the protonated clusters, almost certainly because the main approximation in the calculations is neglect of anharmonicity perpendicular to the tunneling path. All the calculations were performed on a desktop computer, which suggests that similar calculations will be possible on much larger clusters. © *2011 American Institute of Physics*. [doi:10.1063/1.3640429]

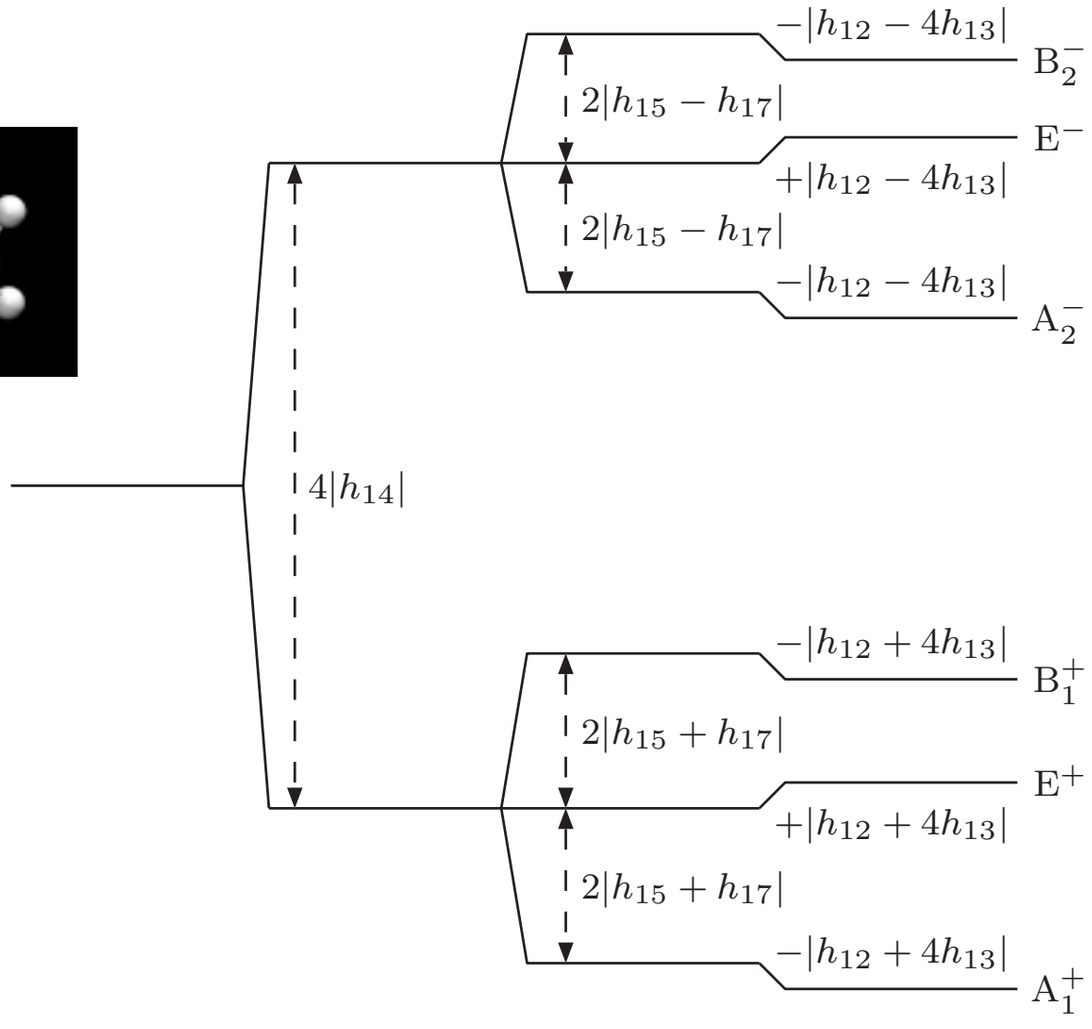




$$W_{\lambda\mu} = A_{\lambda\mu} \overbrace{A_{\text{kink}} e^{-S_{\text{kink}}/\hbar}}^{h_{ij}}$$

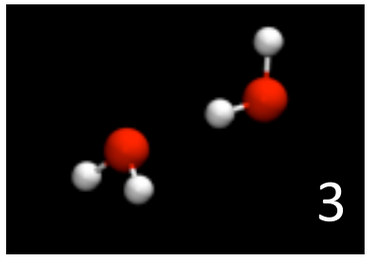


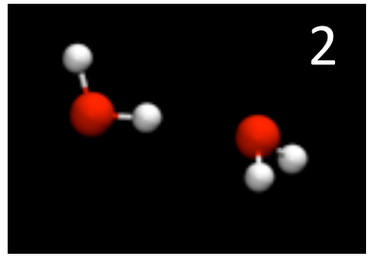




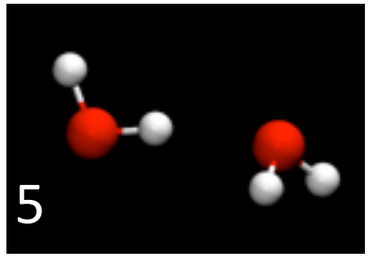
$(H_2O)_2$

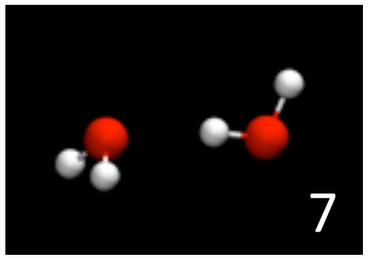
Richardson, SCA, Wales 2011

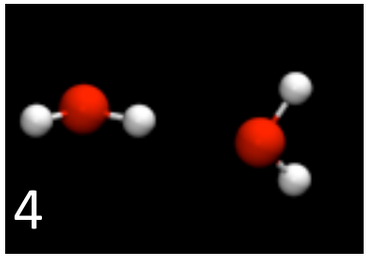


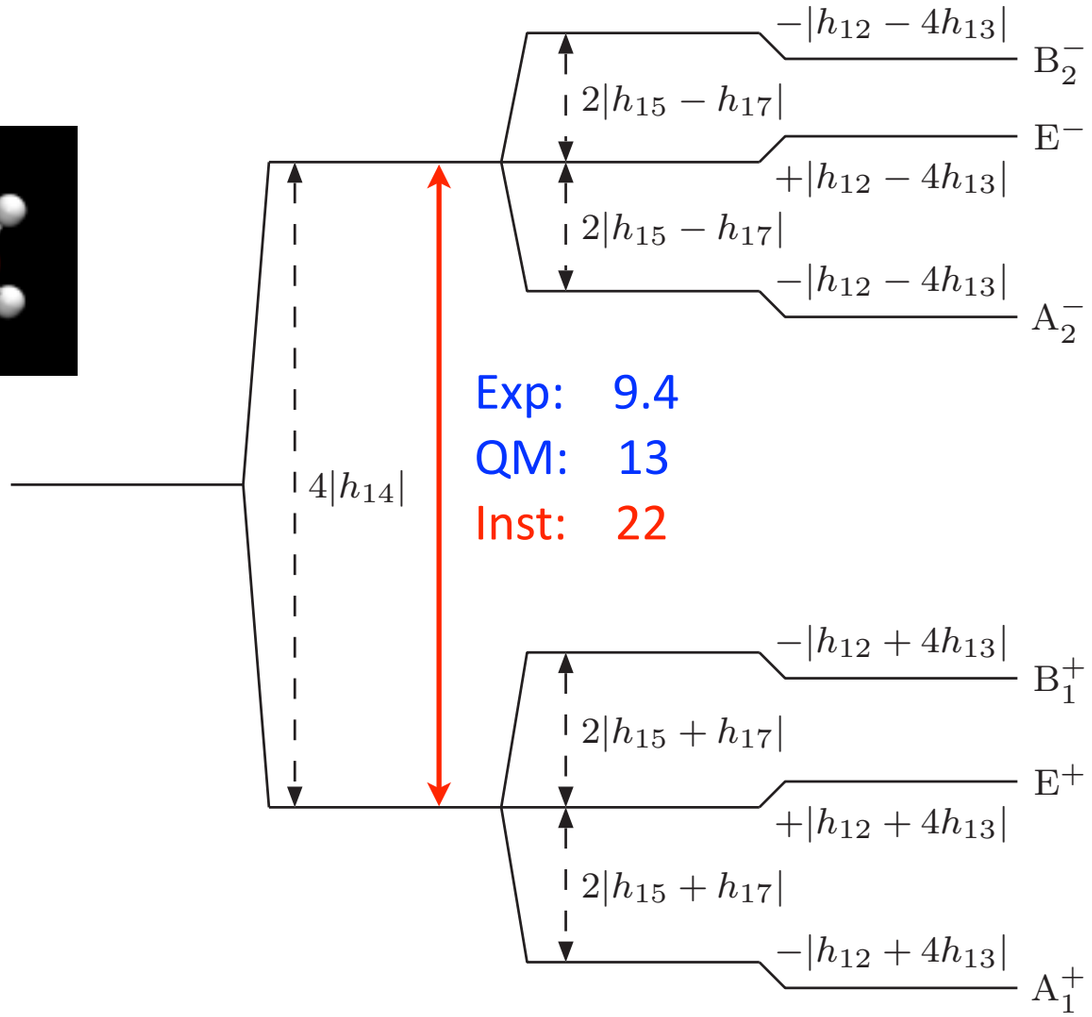


$$W_{\lambda\mu} = A_{\lambda\mu} \overbrace{A_{\text{kink}} e^{-S_{\text{kink}}/\hbar}}^{h_{ij}}$$







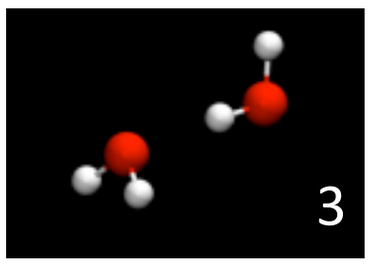


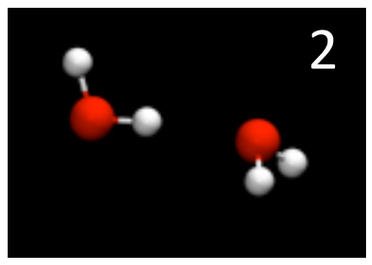
Exp: 9.4
QM: 13
Inst: 22

cm^{-1}
Exp: 0.75
QM: 0.75
Inst: 0.86

$(H_2O)_2$

Richardson, SCA, Wales 2011



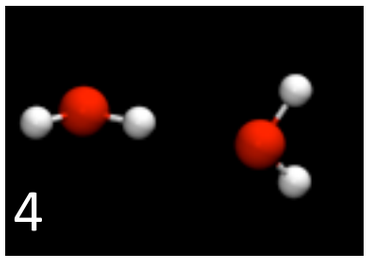


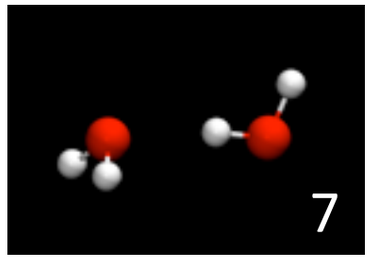
19

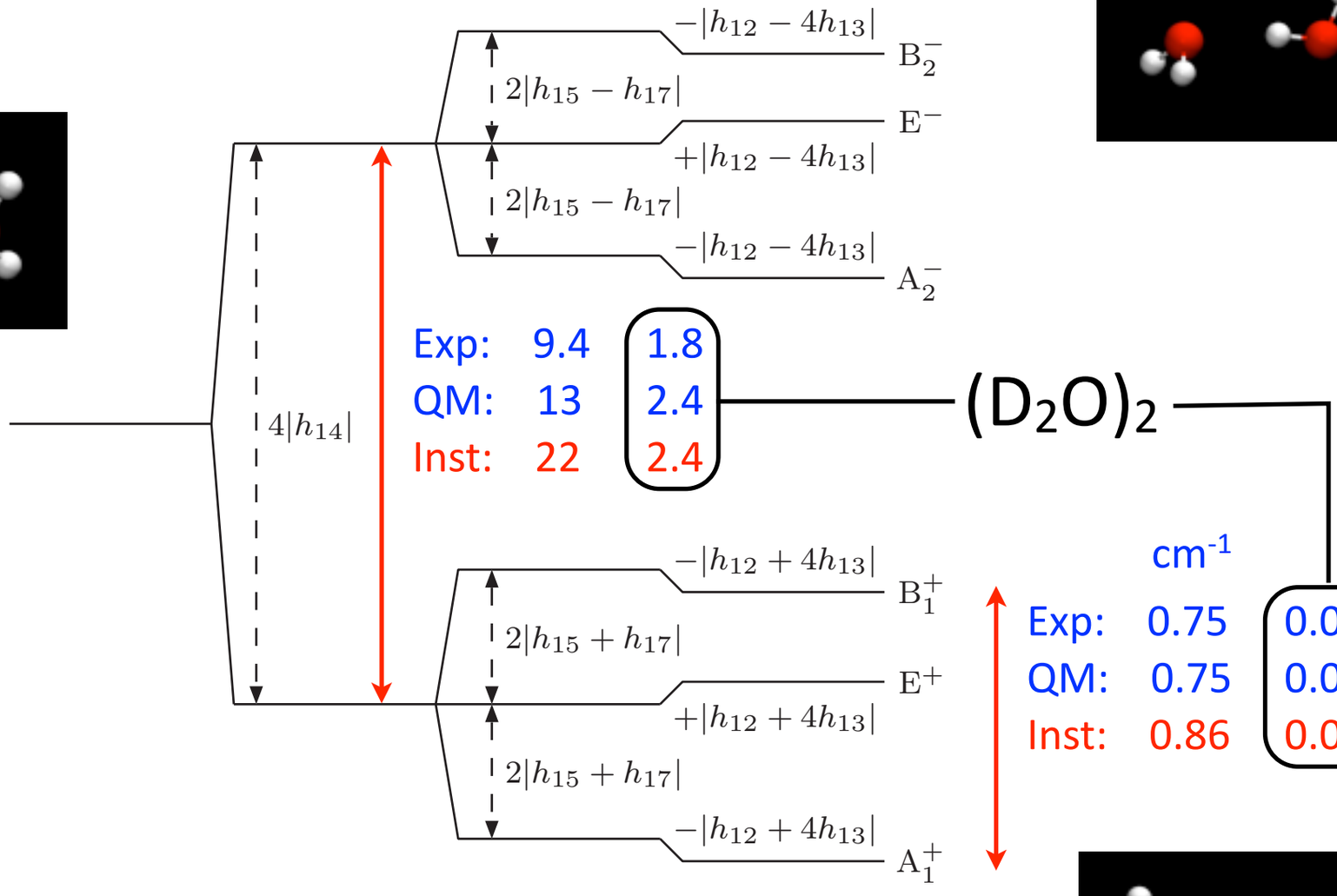
$$W_{\lambda\mu} = A_{\lambda\mu} \overbrace{A_{\text{kink}} e^{-S_{\text{kink}}/\hbar}}^{h_{ij}}$$

$(H_2O)_2$

Richardson, SCA, Wales 2011



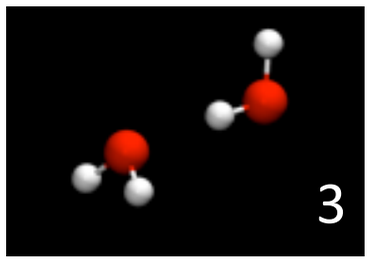


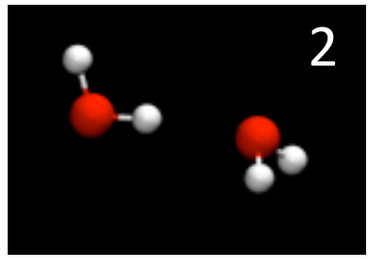


Exp:	9.4	1.8
QM:	13	2.4
Inst:	22	2.4

$(D_2O)_2$

	cm^{-1}	
Exp:	0.75	0.039
QM:	0.75	0.040
Inst:	0.86	0.037

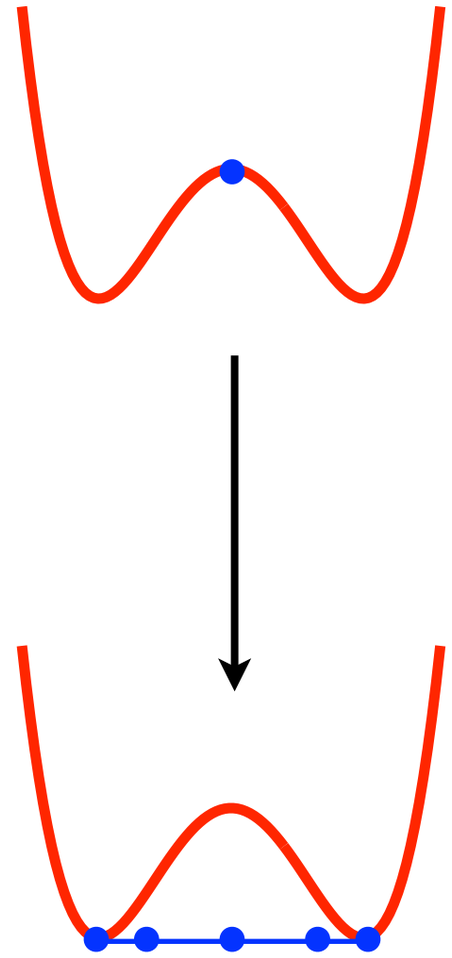




19

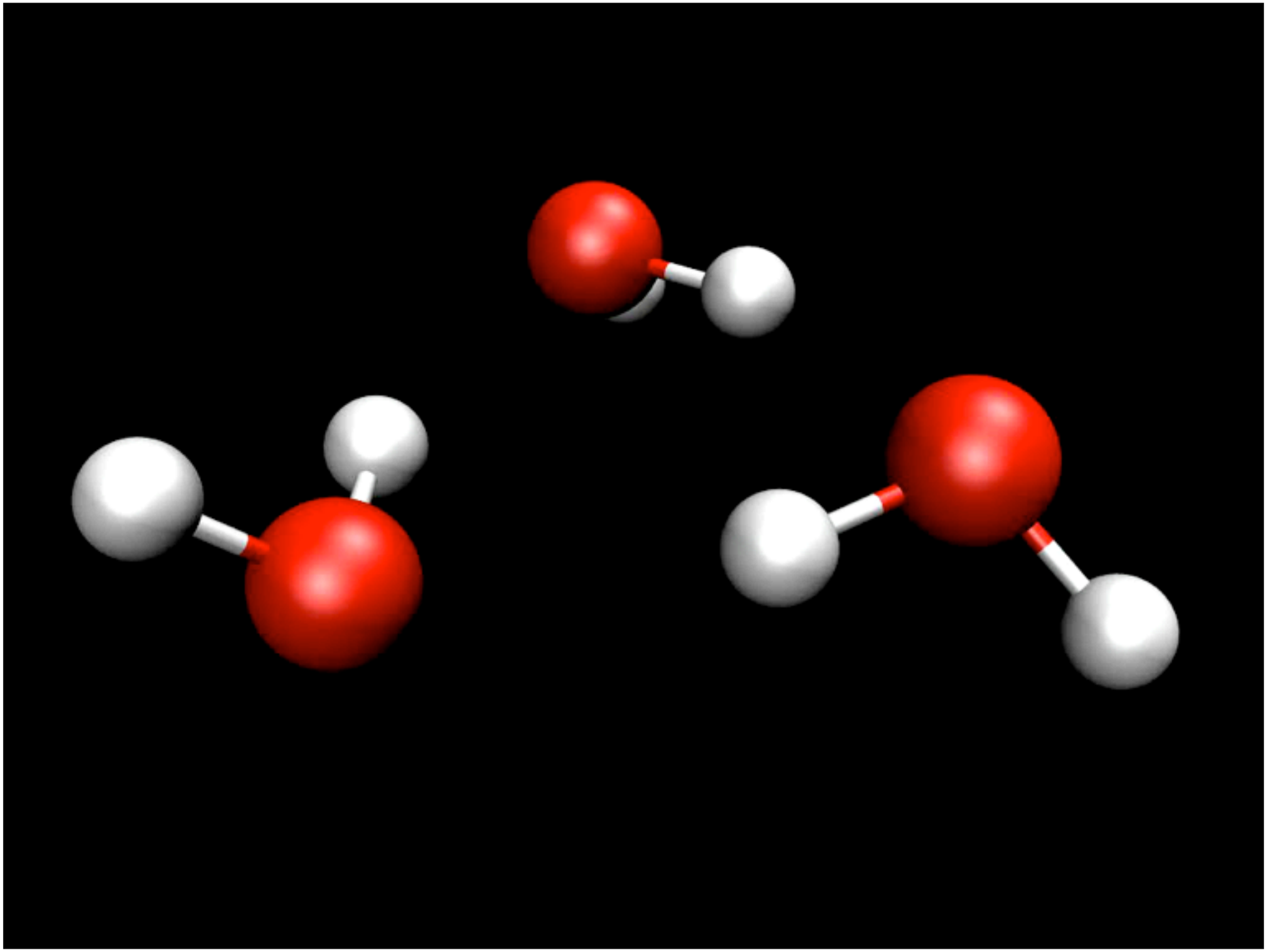
$(H_2O)_3$

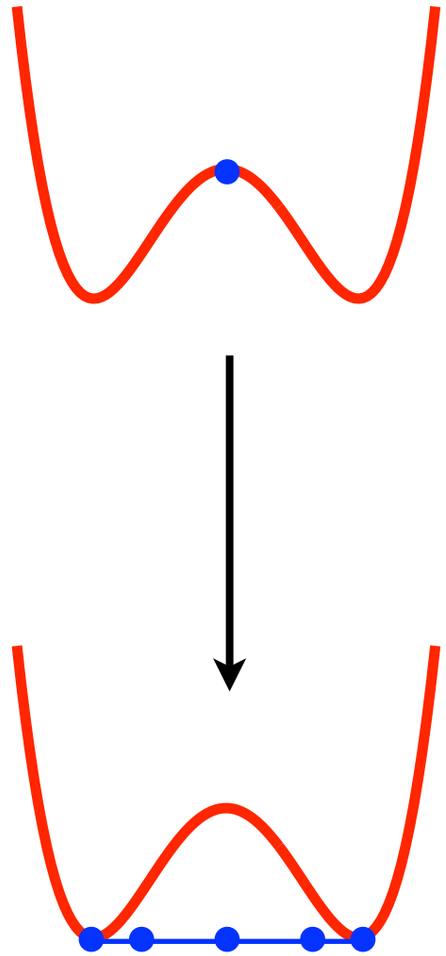
J.O. Richardson, SCA & David Wales → GMIN



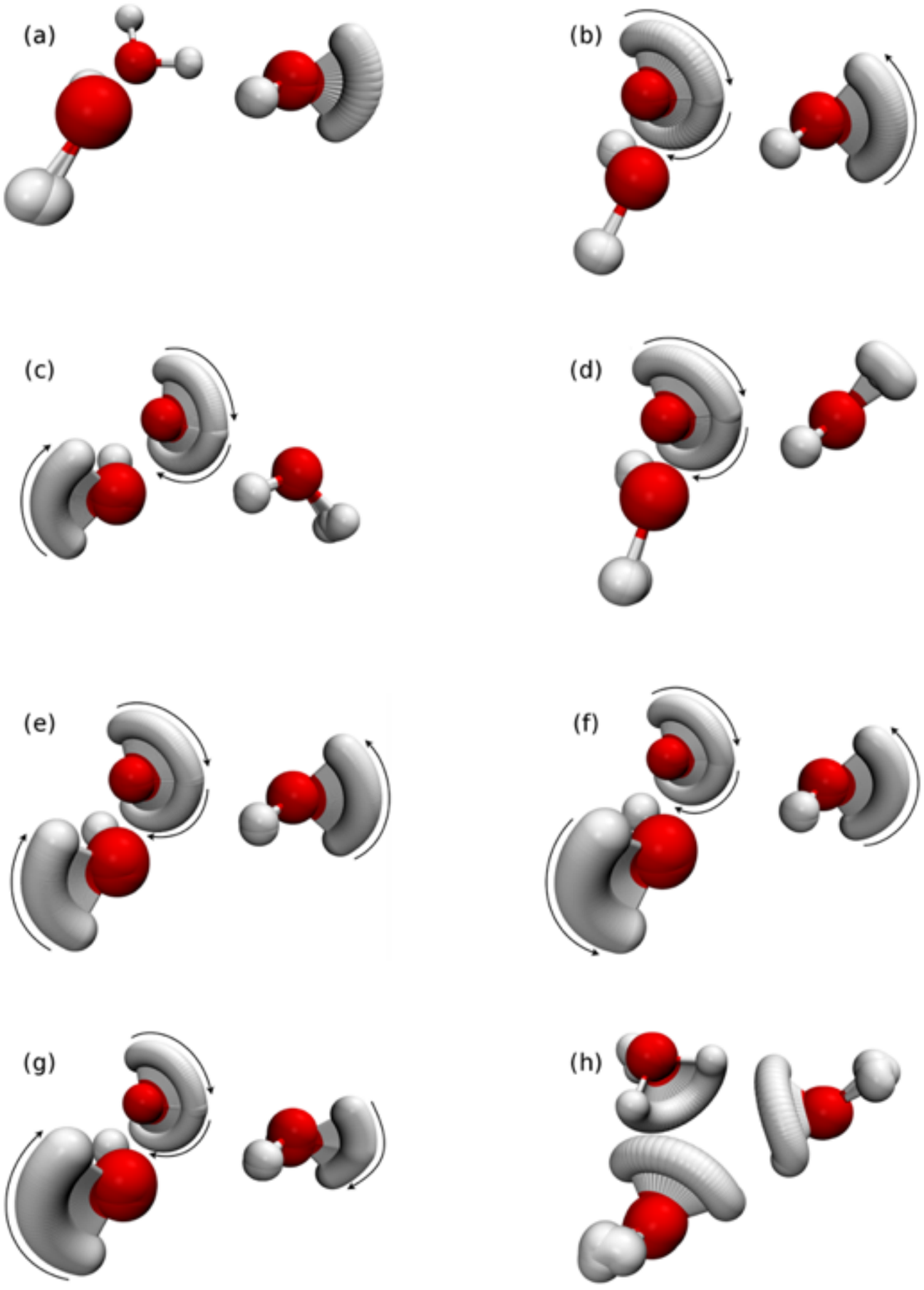
$(H_2O)_3$

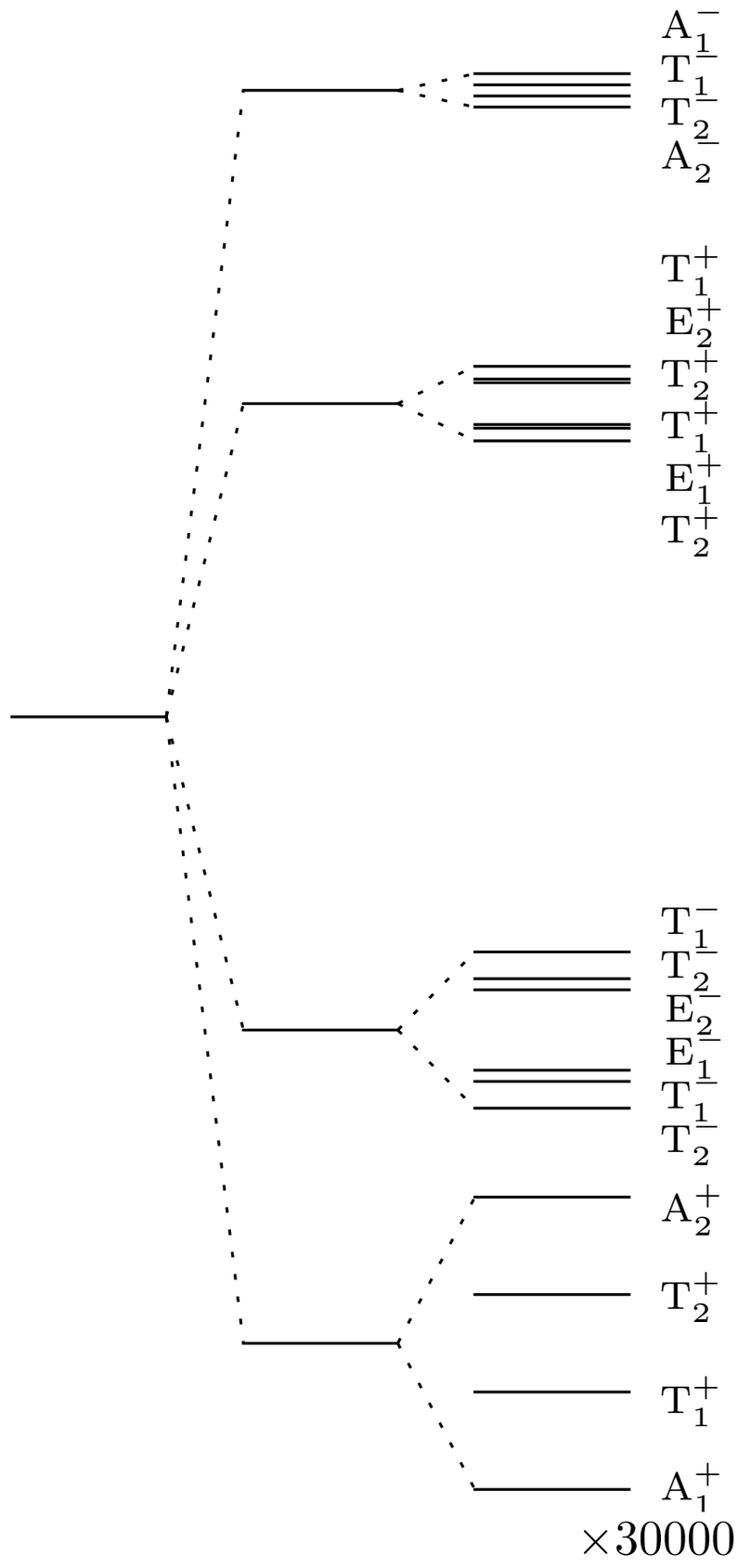
J.O. Richardson, SCA & David Wales → GMIN



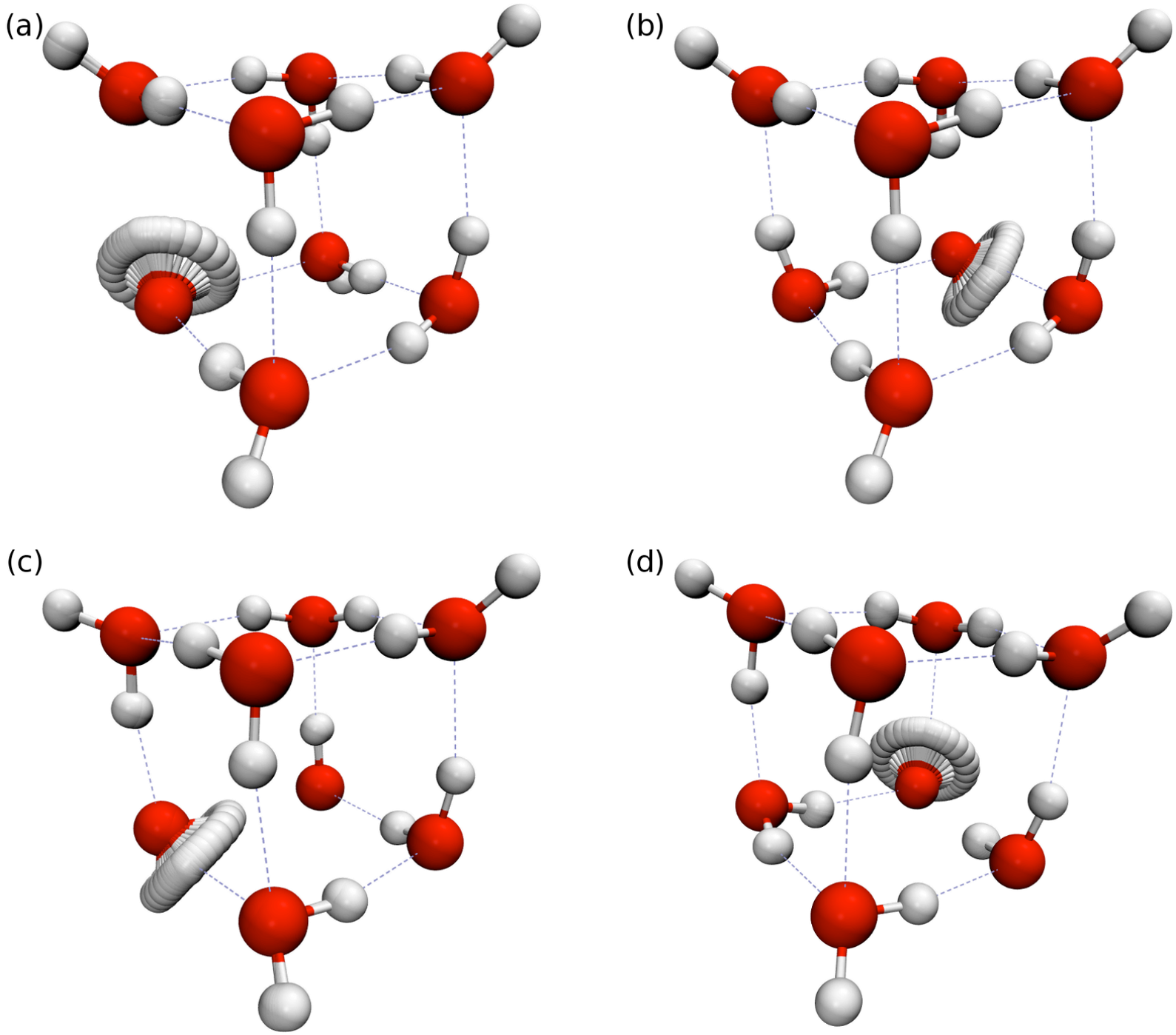


Richardson, SCA, Wales, JCP 2011





$(H_2O)_8$



JCPA 2013 with R.J. Saykally

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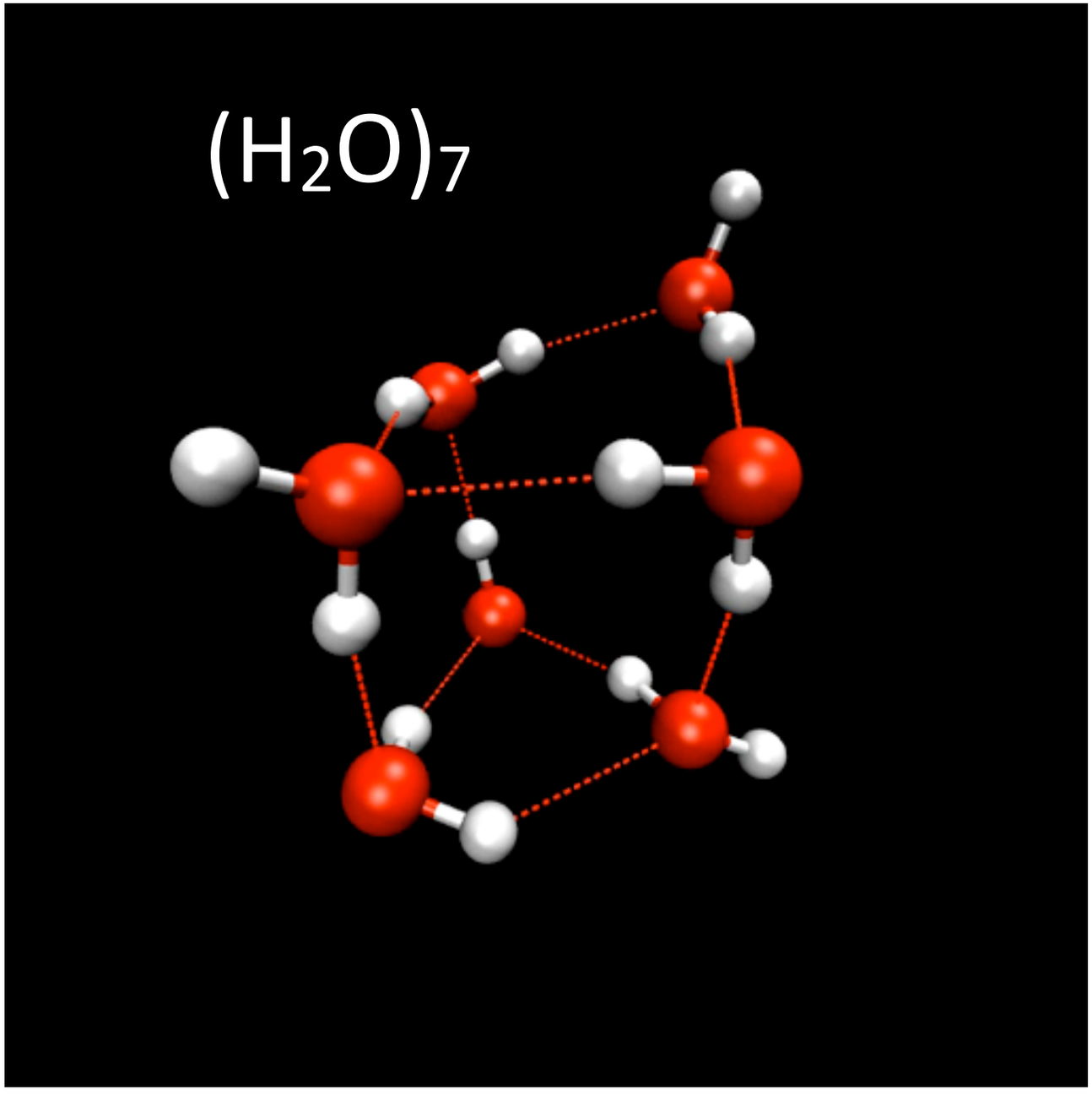
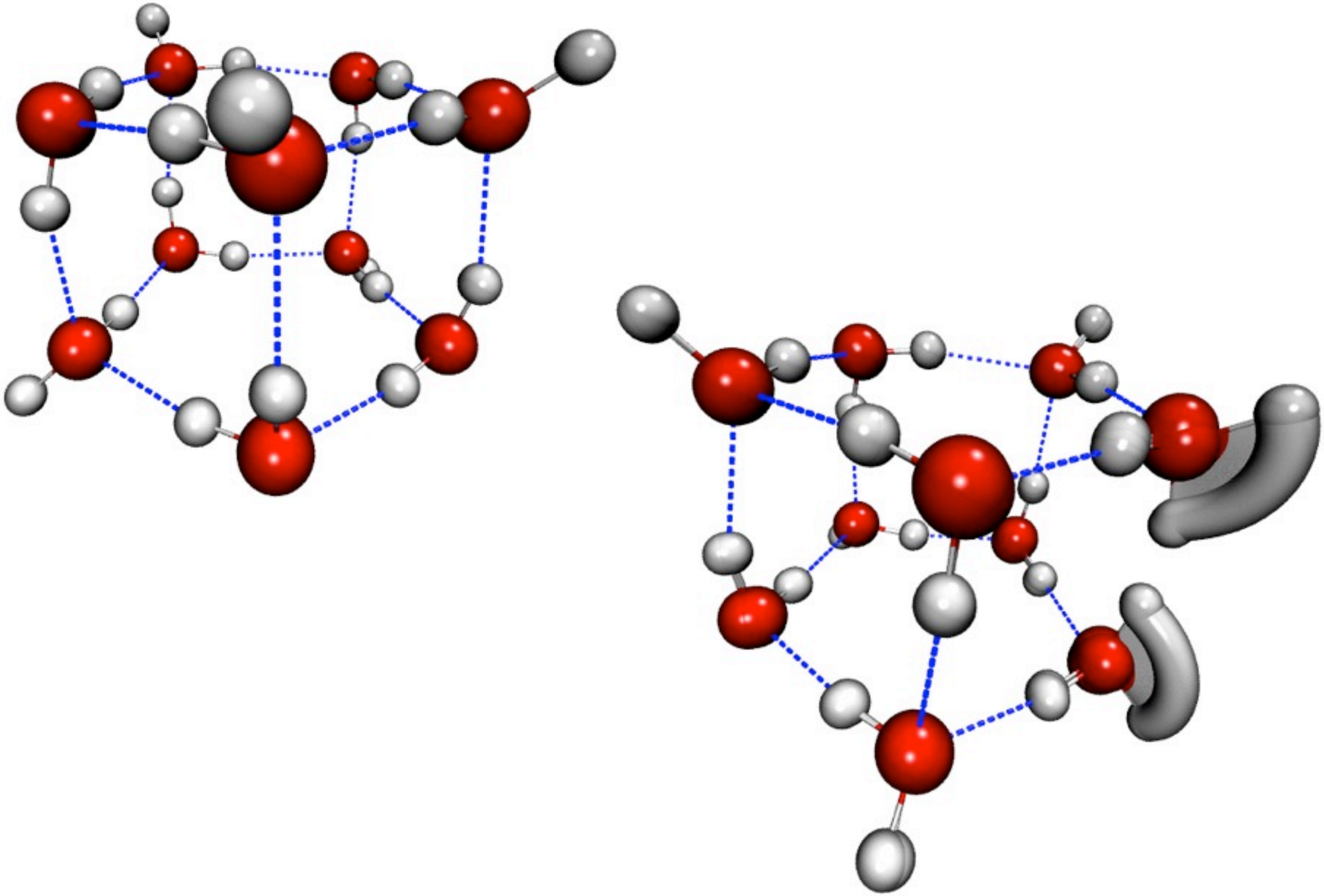
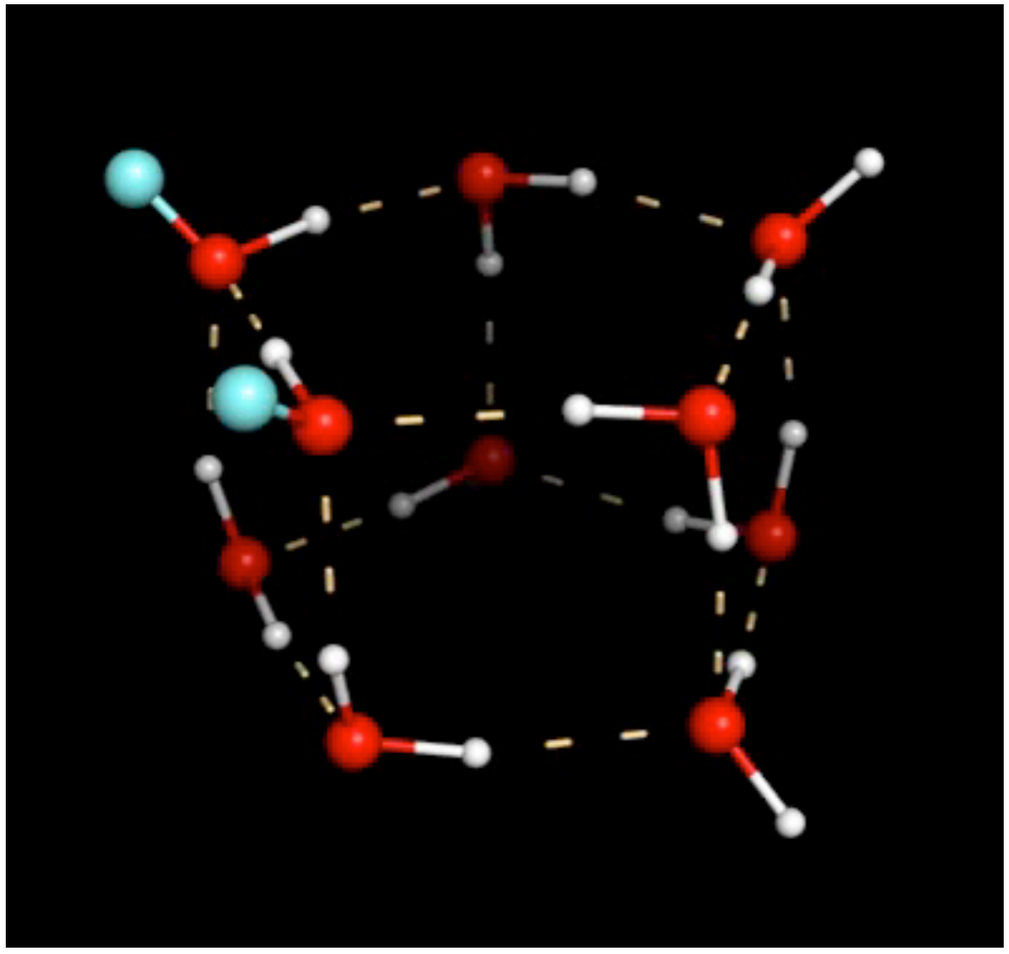
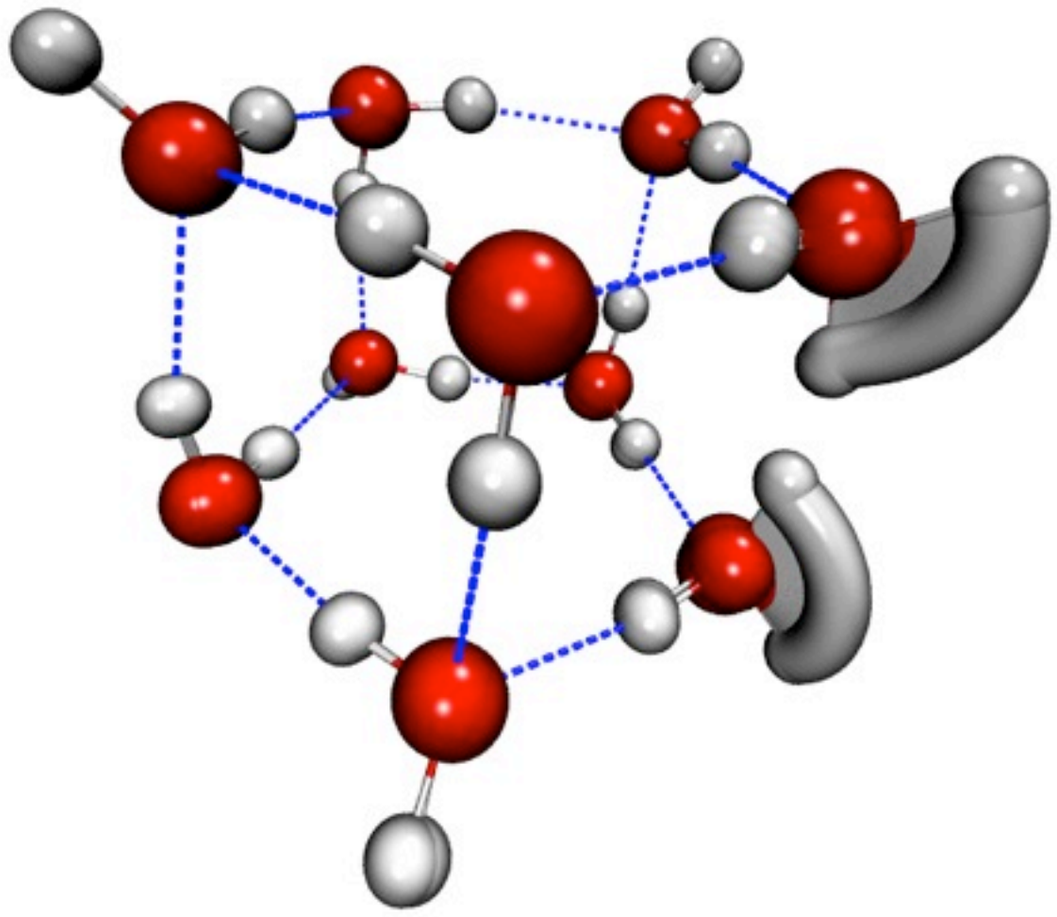

$(H_2O)_7$

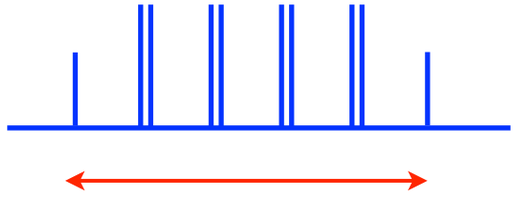
$(H_2O)_{10}$



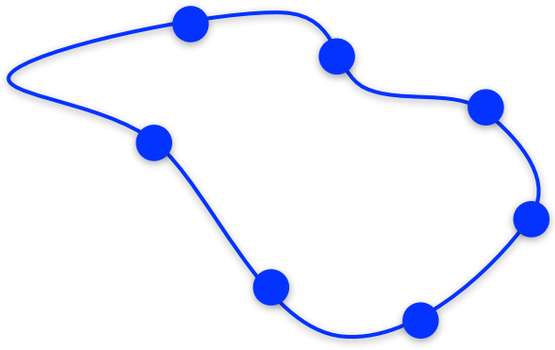
$(H_2O)_{10}$







Conclusions



ring polymer instanton

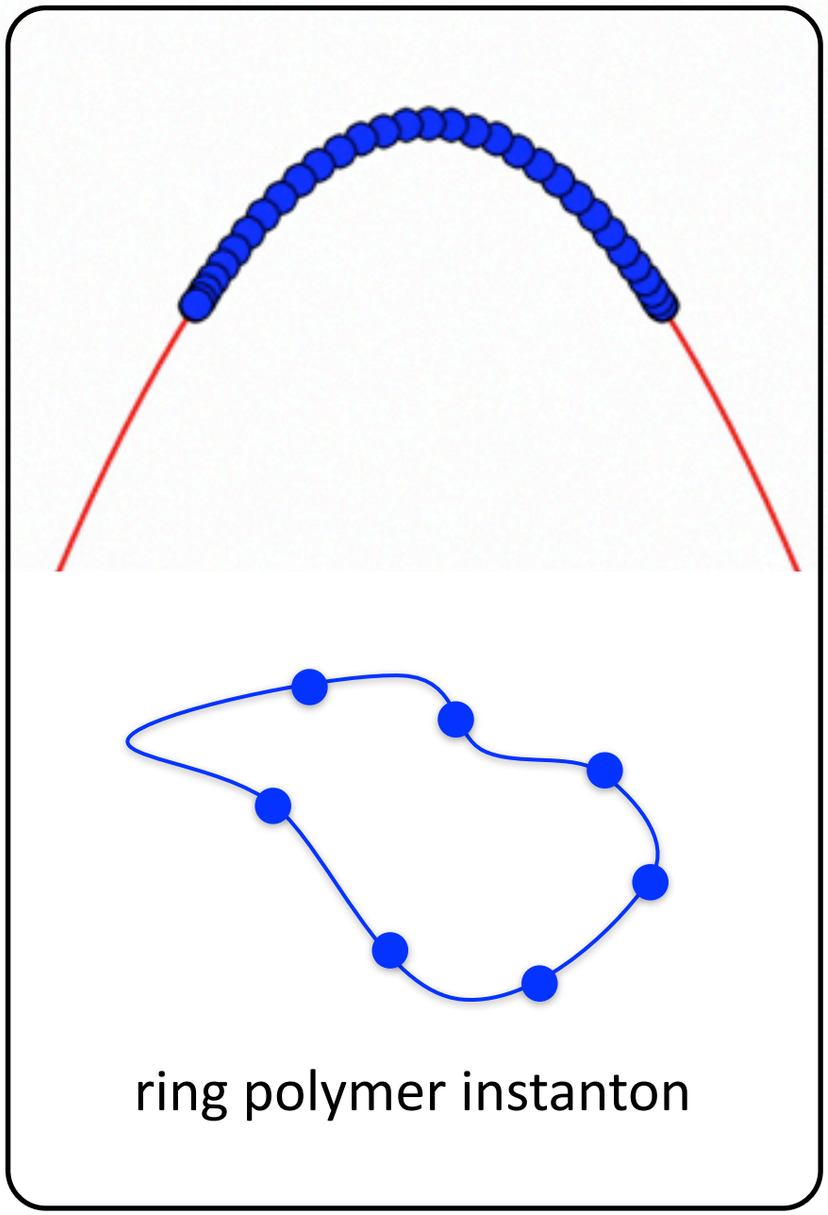
Instanton rates

RPMD rate-theory

Tunnelling splittings

water clusters

Conclusions



ring polymer instanton

Instanton rates

RPMD rate-theory

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water clusters

Acknowledgements

David Wales
(OPTIM)

EPSRC

NSF

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