Instanton calculations of tunnelling in water clusters

Michael F. Herbst
michael.herbst@iwr.uni-heidelberg.de

Interdisziplinäres Zentrum für wissenschaftliches Rechnen
Ruprecht-Karls-Universität Heidelberg

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Motivation

- Understanding of tunnelling as QM phenomenon
- Interpretation of high resolution spectra (terahertz)
- Tunnelling splittings very sensitive to short-range anisotropy of PES
- Bulk properties mostly depend on 2-body and 3-body terms of PES

$\Rightarrow$ Assessment of water potential energy surfaces

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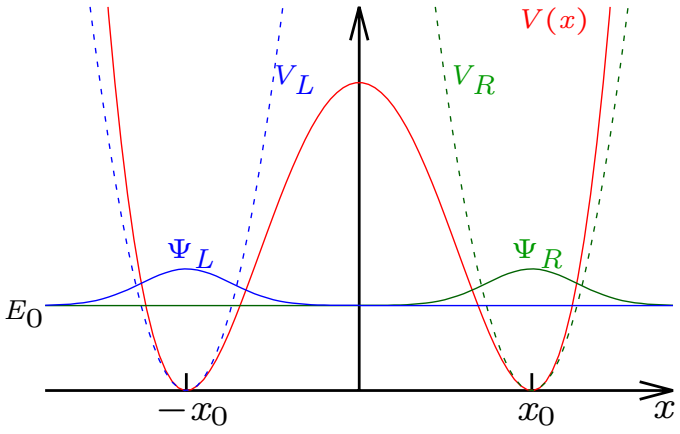
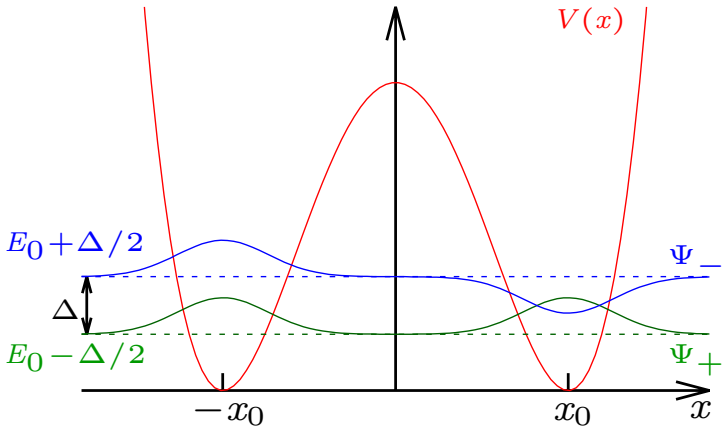
Double well tunnelling model

assume no tunnelling



tunnelling considered



- Variational approach to obtain states in the tunnelling case:

$$\Psi_\pm = \frac{1}{\sqrt{2}}(\Psi_L \pm \Psi_R)$$

- Only consider ground state
- Tunnelling splitting Δ is energy separation

The partition function

Some notation

- As sum over states:

$$Q(\beta) = \sum_i \exp\left(-\beta E_i\right) \qquad \beta = \frac{1}{kT}$$

- As trace over Boltzmann operator:

$$Q(\beta) = \int_{-\infty}^{\infty} \mathrm{d}x \, \left\langle x \middle| \exp\left(-\beta \hat{\mathcal{H}}\right) \middle| x \right\rangle$$

- To show equivalence: Use completeness of bases

$$\int_{-\infty}^{\infty} \mathrm{d}x \, |x\rangle\langle x| = 1 \qquad \sum_i |\Psi_i\rangle\langle\Psi_i| = 1$$

and $\Psi_i(x) \equiv \langle x|\Psi_i\rangle$.

Skip proof

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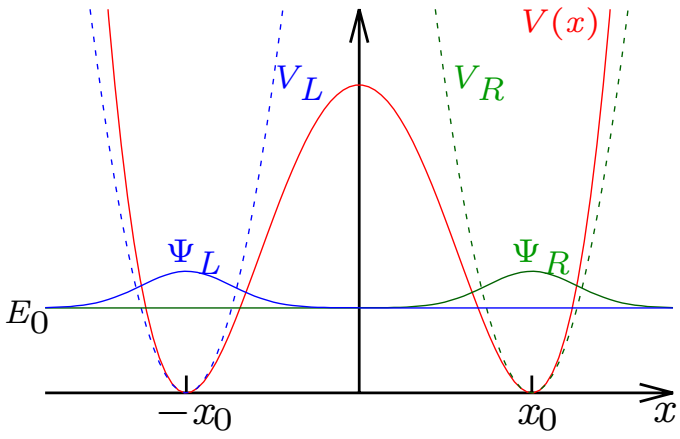
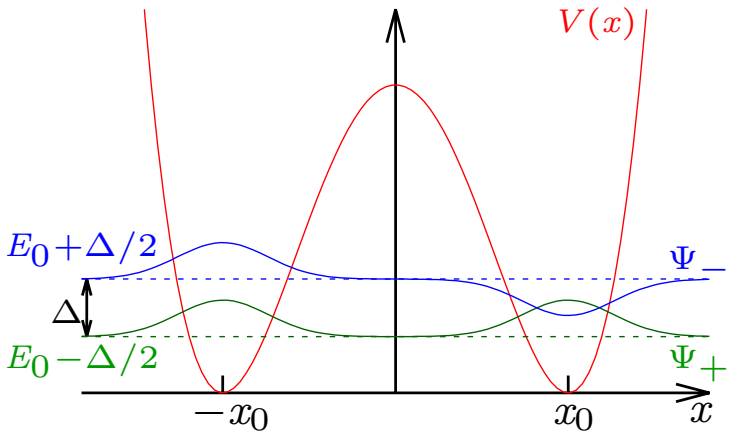
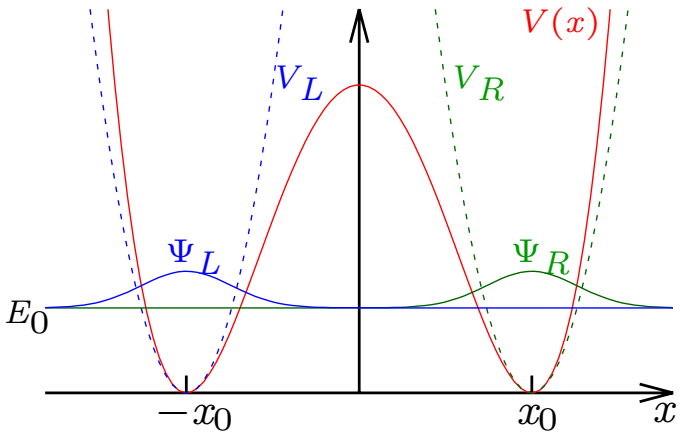


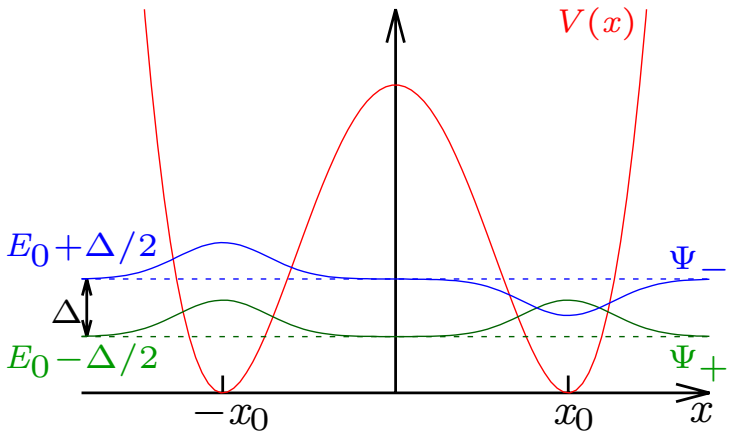


$$\frac{Q(\beta)}{Q_0(\beta)} = \frac{\text{tunnelling case}}{\text{non-tunnelling case}}$$

The partition function

Using sum over states





$$\frac{Q(\beta)}{Q_0(\beta)} = \frac{\sum_i \exp\left(-\beta \tilde{E}_i\right)}{\sum_i \exp\left(-\beta E_i\right)}$$

$$\simeq \frac{\exp\big(-\beta(E_0 - \Delta/2)\big) + \exp\big(-\beta(E_0 + \Delta/2)\big)}{2\exp\left(-\beta E_0\right)}$$

$$= \cosh\left(\frac{\beta\Delta}{2}\right)$$

The partition function

Using operator trace

- Can use Trotter theorem and show

$$Q(\beta) = \int_{-\infty}^{\infty} \mathrm{d}x \, \left\langle x \middle| \exp\left(-\beta \hat{\mathcal{H}}\right) \middle| x \right\rangle$$

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$$Q(\beta) = \lim_{N\to\infty} \int_{-\infty}^{\infty} \mathrm{d}x_1 \int_{-\infty}^{\infty} \mathrm{d}x_2 \cdots \int_{-\infty}^{\infty} \mathrm{d}x_N \prod_{i=1}^{N} \left\langle x_i \middle| \hat{\Omega} \middle| x_{i+1} \right\rangle$$

where $x = x_1 = x_{N+1}$ and

$$\hat{\Omega} = \exp\left(-\frac{\beta}{2N}\hat{\mathcal{V}}\right) \exp\left(-\frac{\beta}{N}\hat{\mathcal{T}}\right) \exp\left(-\frac{\beta}{2N}\hat{\mathcal{V}}\right).$$

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- Insert our system $\hat{\mathcal{V}} = V(x)$, $\hat{\mathcal{T}} = -\frac{\hbar^2}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$ and $\beta_N = \beta/N$ to get

$$Q(\beta) = \lim_{N\to\infty} \left(\frac{1}{2\pi\beta_N\hbar^2}\right)^{\frac{N}{2}} \int_{-\infty}^{\infty} \mathrm{d}\underline{\boldsymbol{x}} \, \exp\left[-\beta_N U_N(\beta, \underline{\boldsymbol{x}})\right]$$

$$U_N(\beta, \underline{\boldsymbol{x}}) = \left[\sum_{i=1}^{N} V(x_i) + \frac{(x_{i+1} - x_i)^2}{2\,(\beta_N\hbar)^2}\right]_{x_{N+1}=x_1}$$

Imaginary time formalism

- Compare

$$\exp\left(-\mathbf{i}\,\frac{\hat{\mathcal{H}}t}{\hbar}\right) \qquad \text{propagator}$$

$$\exp\left(-\beta\hat{\mathcal{H}}\right) \qquad \text{Boltzmann operator}$$

- If $t = -\mathbf{i}\,\beta\hbar$ both identical
- $\tau = \beta\hbar$ has units of time: "imaginary time"
- Propagation of system in τ (somewhat) resembles partition function

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Interpreting U_N in imaginary time formalism

- Recall $U_N(\beta, \underline{\boldsymbol{x}}) = \left[\sum_{j=1}^{N} V(x_j) + \frac{(x_{j+1}-x_j)^2}{2(\beta_N\hbar)^2}\right]_{x_{N+1}=x_1}$
- So using $\tau = \beta\hbar$ and $\tau_N = \tau/N$:

$$\beta_N \hbar U_N = \sum_{j=1}^{N} \tau_N \left(V(x_j) + \frac{(x_{j+1} - x_j)^2}{2\tau_N^2} \right)$$

- This is a discretised version of

$$\int_0^\tau \mathrm{d}\tau' \left(V\Big(x(\tau')\Big) + \frac{1}{2}\left(\frac{\mathrm{d}x(\tau')}{\mathrm{d}\tau'}\right)^2 \right)$$

- which is the action integral

$$S = \int_0^\tau \mathrm{d}\tau' \;\; T - \tilde{V}$$

for a (periodic) motion with $x(0) = x(\tau)$ in $\tilde{V}(x) = -V(x)$.

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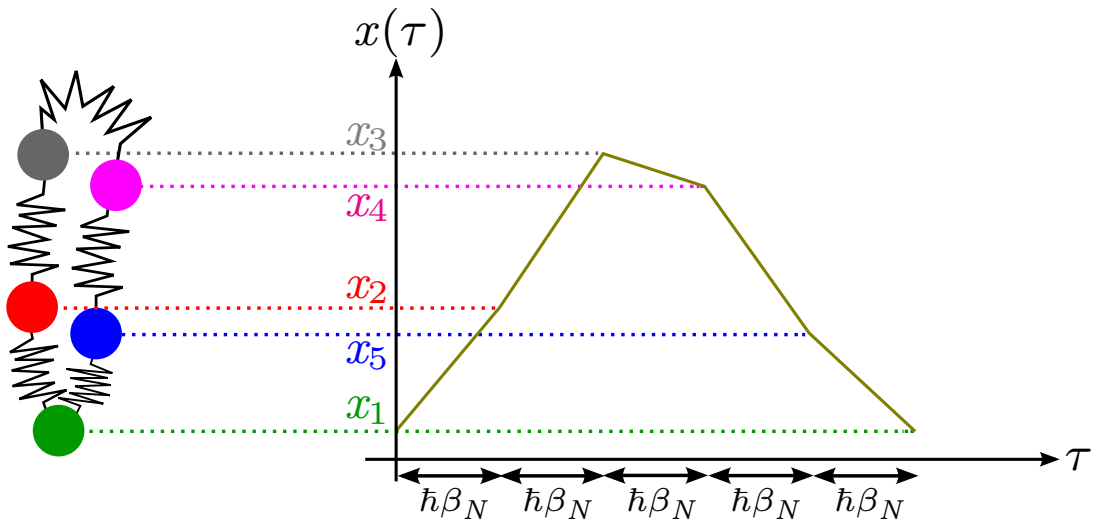
The ring-polymer potential U_N

- Recall $U_N(\beta, \underline{\boldsymbol{x}}) = \left[\sum_{i=1}^{N} V(x_i) + \frac{(x_{i+1}-x_i)^2}{2(\beta_N\hbar)^2}\right]_{x_{N+1}=x_1}$
- Beads connected by harmonic springs of frequency $\frac{1}{\hbar\beta_N}$
- Beads are replica of system propagated in imaginary time



Steepest descent approximation to evaluate Q:

- Recall $Q(\beta) = \lim_{N\to\infty} \left(\frac{1}{2\pi\beta_N\hbar^2}\right)^{\frac{N}{2}} \int_{-\infty}^{\infty} \mathrm{d}\underline{\boldsymbol{x}}\ \exp\left[-\beta_N U_N(\beta, \underline{\boldsymbol{x}})\right]$ and $U_N(\beta, \underline{\boldsymbol{x}}) = \left[\sum_{j=1}^{N} V(x_j) + \frac{(x_{j+1}-x_j)^2}{2(\beta_N\hbar)^2}\right]_{x_{N+1}=x_1}$
- Taylor series about minimum $\underline{\tilde{\boldsymbol{x}}}^M$:

$$U_N(\beta, \underline{\boldsymbol{x}}) \simeq U_N(\beta, \underline{\tilde{\boldsymbol{x}}}^M) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}(x_i - \tilde{x}_i^M)\, G_{ij}^M\, (x_j - \tilde{x}_j^M)$$

- Write Q as sum over minima:

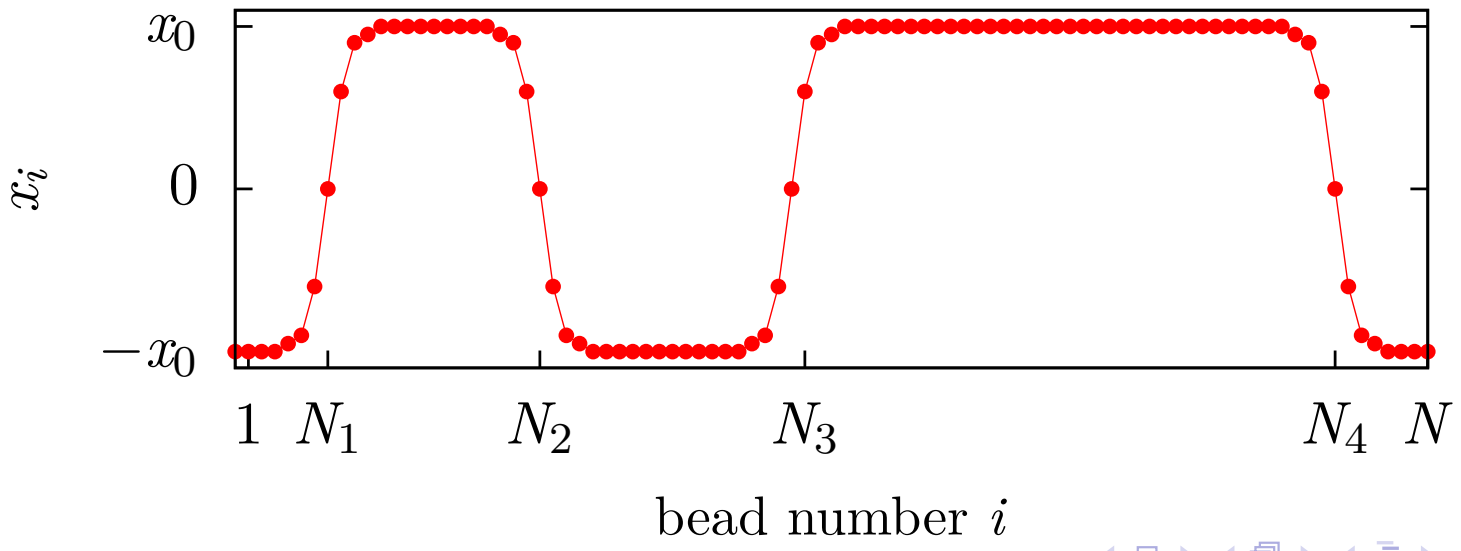
$$Q(\beta) \simeq \tilde{Q}(\beta) = \left(\frac{1}{\beta_N\hbar}\right)^N \sum_{\text{minima } M} \frac{1}{\sqrt{\det \mathbf{G}^M}} \exp\left(-\beta_N U_N(\beta, \underline{\tilde{\boldsymbol{x}}}^M)\right)$$

Kinks and kink action

- Minima of $U_N(\beta, \underline{\boldsymbol{x}})$ are periodic orbits
- Most beads stationary at $x = \pm x_0$ (Minima of V)
- "*Kinks*": Rapid motion in between
- Kink motions virtually independent since well-separated

$\Rightarrow$ All kinks and all n-kink orbits equivalent

- S_{kink}: Action of a single kink



Linear polymers and instantons

$$U_L(\beta, \underline{\boldsymbol{x}}) = \sum_{i=1}^{L} V(x_i) + \frac{1}{2(\hbar\beta_N)^2}\Big((x_1 + x_0)^2 + \sum_{i=1}^{L-1}(x_{i+1} - x_i)^2 + (x_0 - x_L)^2\Big)$$

- Linear string of system replicas between minima at $x = \pm x_0$
- Beads connected by harmonic springs
- Representation of a single kink
- "*Instantons*": Minima $\underline{\tilde{\boldsymbol{x}}}^{n=1}$ of $U_L(\beta, \underline{\boldsymbol{x}})$
- In the limit of large N and L:

$$U_L(\beta, \underline{\tilde{\boldsymbol{x}}}^{n=1}) = \frac{S_{\text{kink}}}{\hbar\beta_N}$$

Ring polymers with n kinks

- Recall $\tilde{Q}(\beta) = \left(\frac{1}{\beta_N \hbar}\right)^N \sum_M \frac{1}{\sqrt{\det \mathbf{G}^M}} \exp\left(-\beta_N U_N(\beta, \underline{\tilde{\boldsymbol{x}}}^M)\right)$
- If $\tilde{Q}_n(\beta)$ is partition function of ring-polymer restricted to have exactly n kinks:

$$\frac{\tilde{Q}_n(\beta)}{\tilde{Q}_0(\beta)} \simeq \frac{1}{2} \left(\theta(\beta)\right)^n$$

where

$$\theta(\beta) = \frac{\hbar \beta_N}{\Phi} \sqrt{\frac{S_{\text{kink}}}{2\pi\hbar}} \exp\left(-\frac{S_{\text{kink}}}{\hbar}\right)$$

- Φ contains the eigenfrequencies of $U_L(\beta, \underline{\tilde{\boldsymbol{x}}}^{n=1})$

$\Rightarrow$ Minimising $U_L(\beta, \underline{\boldsymbol{x}})$ gives both S_{kink} and Φ

- There are $\frac{2N^n}{n!}$ such n-kink polymers

Putting it all together

- Separate $\tilde{Q}(\beta)$ into contributions of n-kink polymers

$$\begin{aligned}\frac{\tilde{Q}(\beta)}{\tilde{Q}_0(\beta)} &= \frac{\tilde{Q}_0(\beta) + \frac{2N^2}{2!}\tilde{Q}_2(\beta) + \cdots + \frac{2N^n}{n!}\tilde{Q}_n(\beta)}{\tilde{Q}_0(\beta)} \\ &= \sum_{\substack{n=0,\\ n \text{ even}}}^{\infty} \frac{2N^n}{n!} \cdot \frac{1}{2}\left(\theta(\beta)\right)^n \\ &= \cosh\left(N\theta(\beta)\right)\end{aligned}$$

- Compare with previously $\frac{Q(\beta)}{Q_0(\beta)} = \cosh\left(\frac{\beta\Delta}{2}\right)$:

$$\boxed{\Delta \simeq \frac{2}{\beta_N}\theta(\beta) \qquad \text{(large } \beta, L)}$$

General 3D case

Defining the quantities

- System of degenerate wells (labelled $\lambda, \mu, \nu, \ldots$)
- $\theta(\beta)$ generalises to

$$\Theta_{\lambda\mu}(\beta) = \frac{\hbar\beta_N}{\Phi^{(\lambda\mu)}}\sqrt{\frac{S_{\text{kink}}^{(\lambda\mu)}}{2\pi\hbar}}\exp\left(-\frac{S_{\text{kink}}^{(\lambda\mu)}}{\hbar}\right)$$

- Define *kink path weight* matrix $\mathbf{h}$

$$h_{\lambda\mu} = -\lim_{\beta\to\infty}\frac{1}{\beta_N}\Theta_{\lambda\mu}(\beta)$$

- and *tunnelling matrix* $\mathbf{W}$

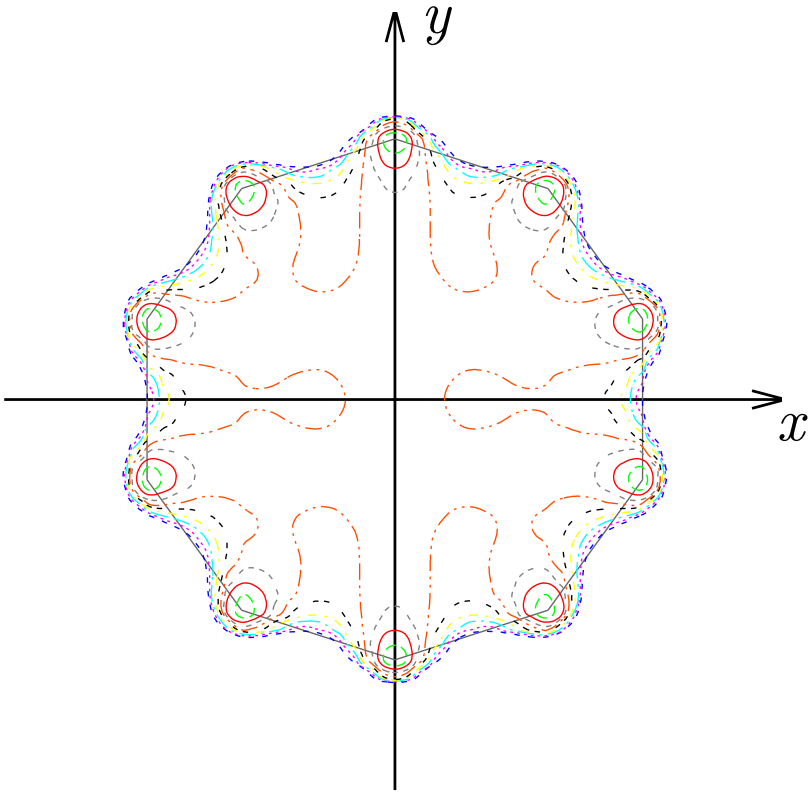
$$W_{\lambda\mu} = A_{\lambda\mu}h_{\lambda\mu}$$

- Eigenvalues of $\mathbf{W}$ give energy splittings $E_\nu - E_0$

Skip ex.

General 3D case

Example for **W**



General 3D case

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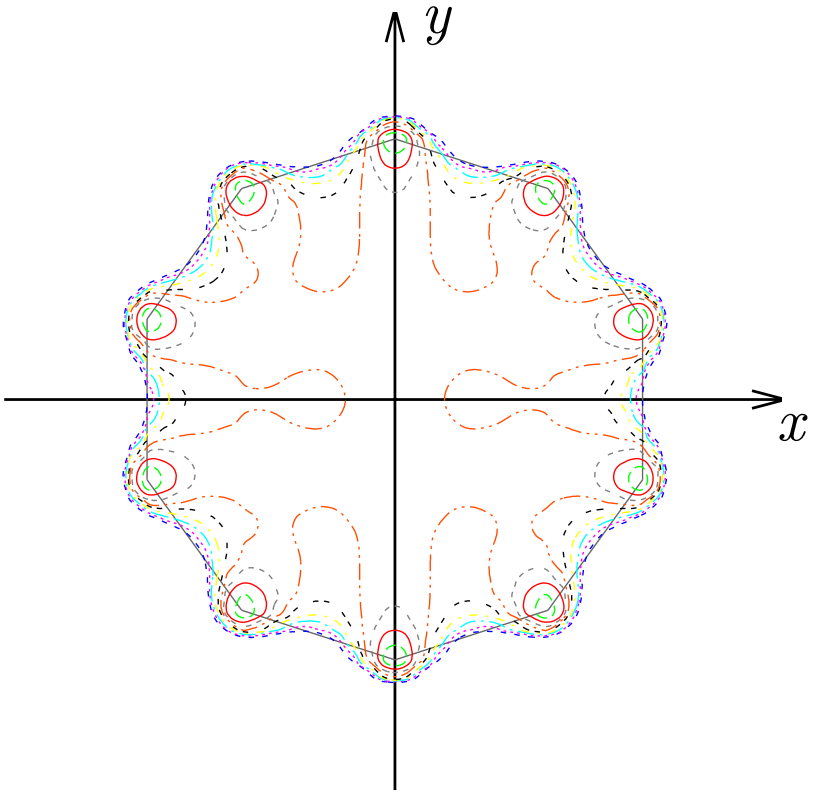
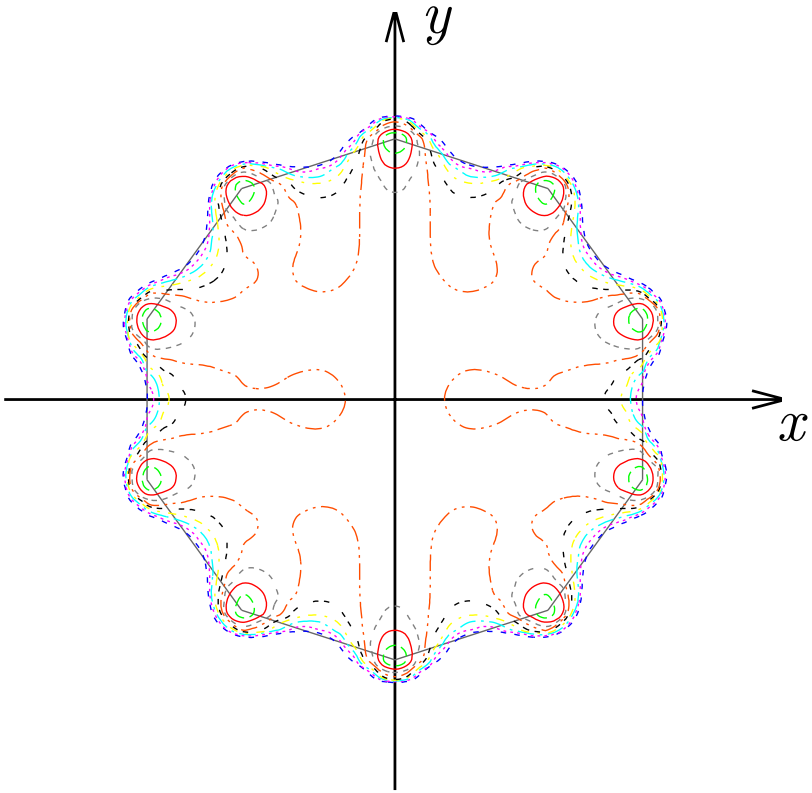


Adjacency matrix:

$$\mathbf{A} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}$$

General 3D case

Example for $\mathbf{W}$



Tunnelling matrix:

$$\mathbf{W} = \begin{pmatrix} 0 & h_{1,2} & 0 & \cdots & 0 & h_{1,10} \\ h_{1,2} & 0 & h_{2,3} & & 0 & 0 \\ 0 & h_{2,3} & 0 & \ddots & 0 & 0 \\ \vdots & & \ddots & \ddots & h_{8,9} & 0 \\ 0 & 0 & 0 & h_{8,9} & 0 & h_{9,10} \\ h_{1,10} & 0 & 0 & 0 & h_{9,10} & 0 \end{pmatrix}$$

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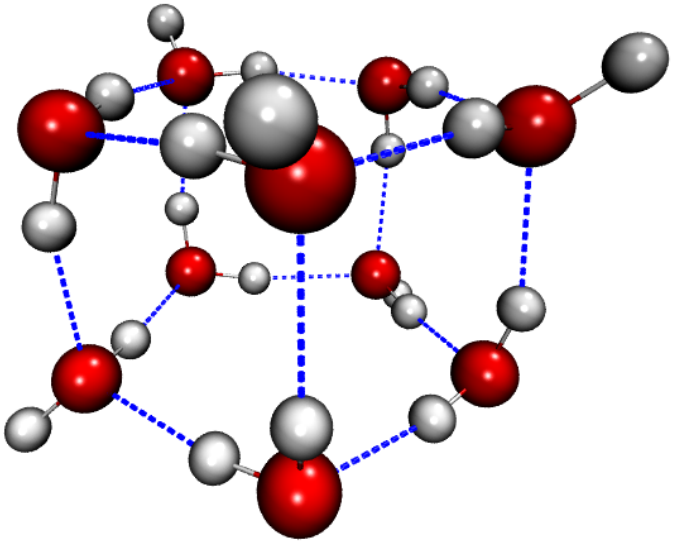
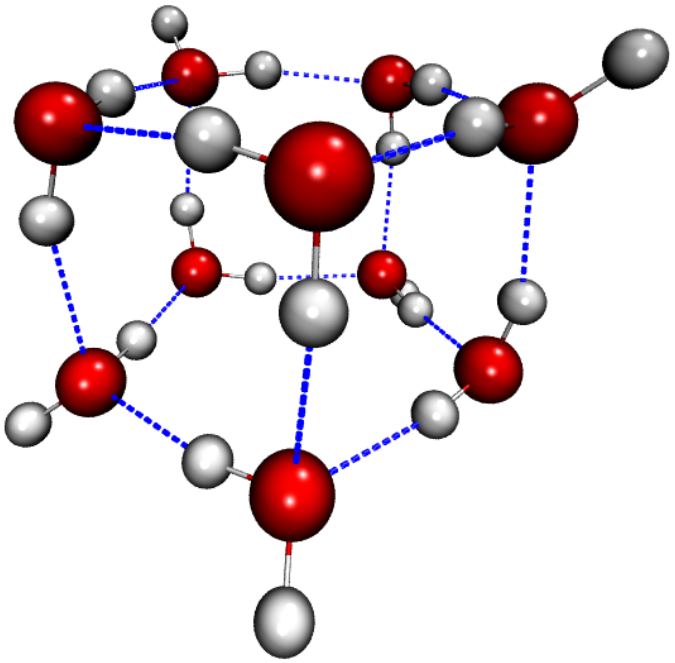
Structure

- Cluster of 10 water molecules
- 10 symmetry-related degenerate minima
- Can ignore all tunnelling paths but O−H flips

⇒ Get 10 symmetry-related tunnelling paths





Tunnelling matrix

- All wells only connected to two neighbours
- All contributing paths equal weight h
- Get tunnelling matrix:

$$\mathbf{W} = \begin{pmatrix} 0 & h & 0 & \cdots & 0 & h \\ h & 0 & h & & 0 & 0 \\ 0 & h & 0 & \ddots & 0 & 0 \\ \vdots & & \ddots & \ddots & h & 0 \\ 0 & 0 & 0 & h & 0 & h \\ h & 0 & 0 & 0 & h & 0 \end{pmatrix}$$

$\Rightarrow$ Only need to converge a single instanton

Converging the instanton

- $V(x)$: Use empirical water potential
- Setup table for S_{kink} and Φ in $\hbar\beta$ and L
- Diagonal convergence pattern
- Best estimate is largest ratio $\hbar\beta/L$
- Table shows $S_{\text{kink}}/\hbar$

$\hbar\beta$(a.u.) / L	16	32	64	128	256	512	1024	2048
10000	19.43	20.45	20.60	20.64	20.65	20.65	20.65	20.65
20000	12.96	19.48	20.50	20.66	20.69	20.70	20.70	20.70
40000	7.24	12.97	19.49	20.51	20.66	20.70	20.70	20.71
80000	3.89	7.24	12.97	19.49	20.51	20.66	20.70	20.70

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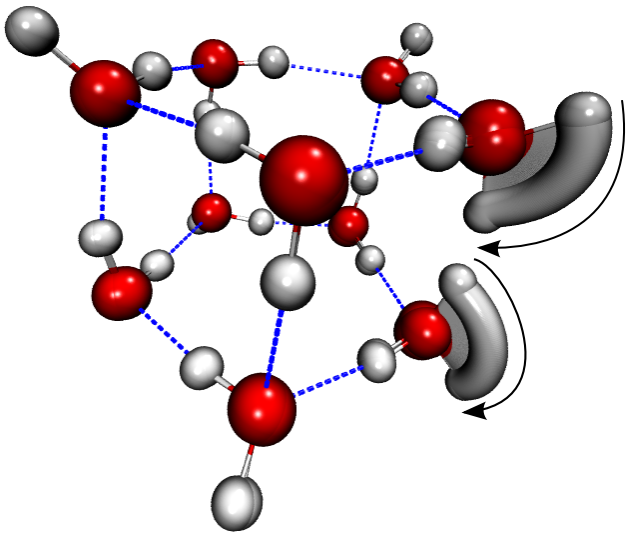
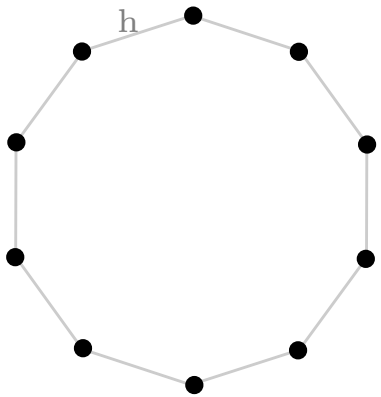
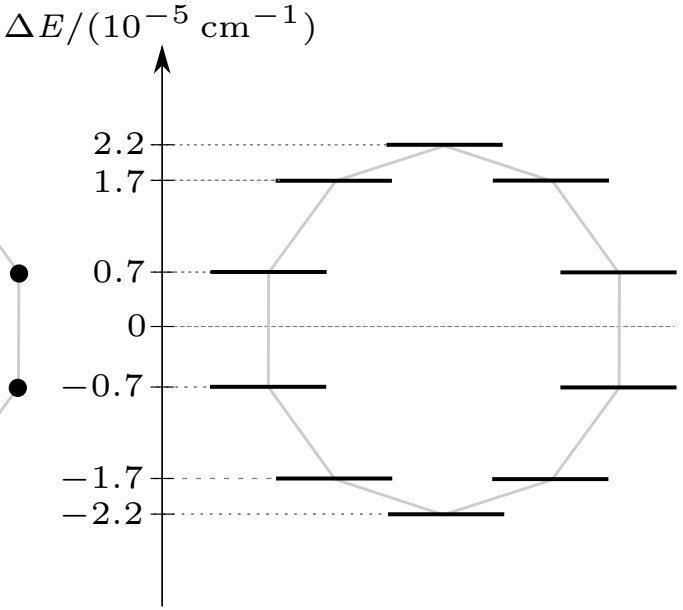
40000	7.24	12.97	19.49	20.51	20.66	20.70	20.70	20.71
80000	3.89	7.24	12.97	19.49	20.51	20.66	20.70	20.70

Results





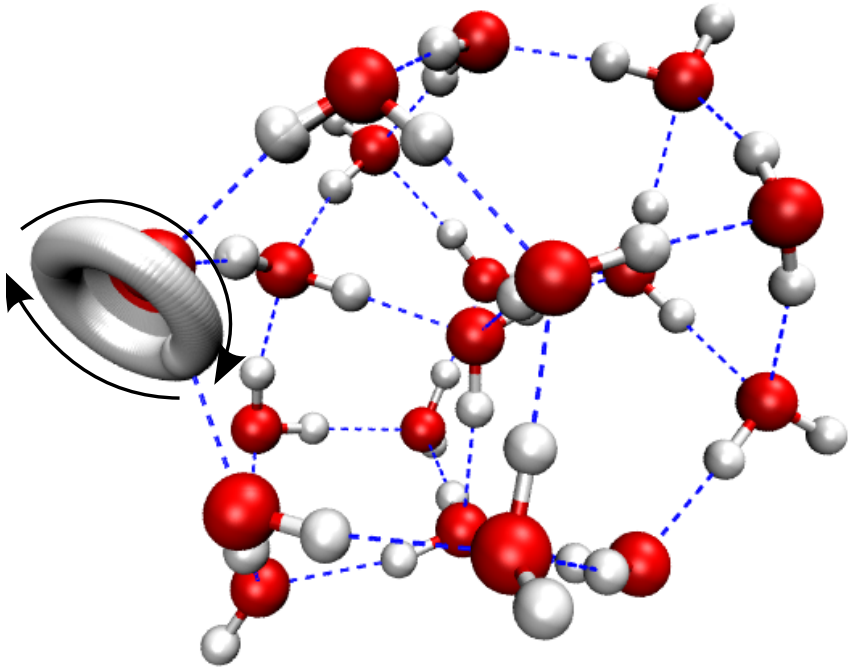
Connectivity graph

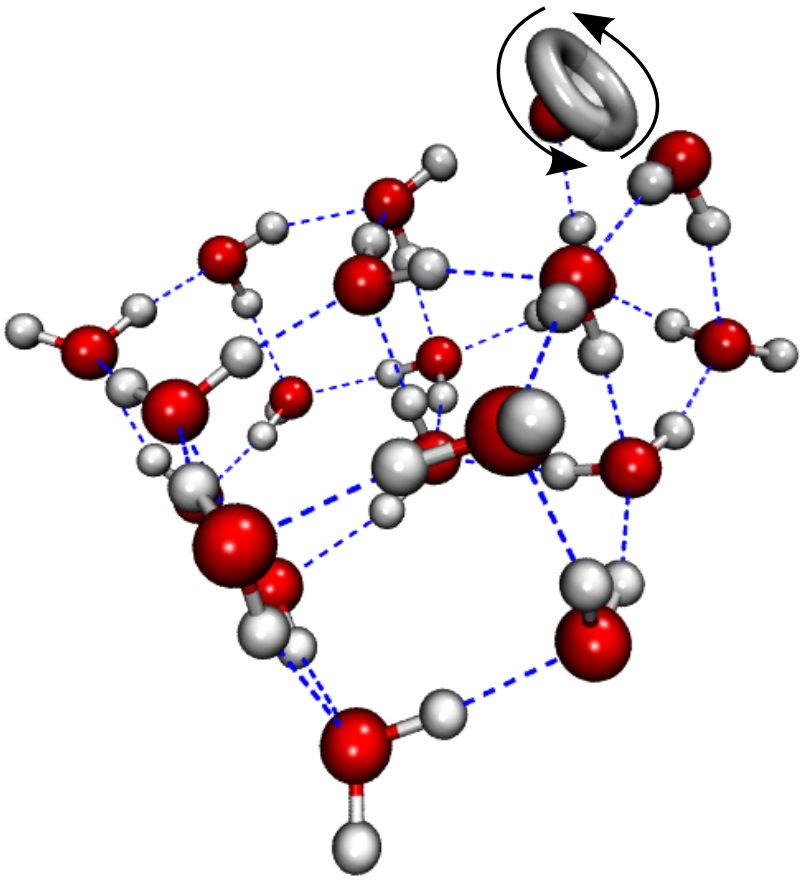


Splitting pattern

Jump to conclusion

19mer and 20mer





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Summary

- Built up tunnelling picture from non-tunnelling reference
- Imaginary-time formalism: More intuitive interpretation of expressions
- Apart from steepest descent: Method is exact for infinite L
- Even for finite L good qualitative predictions possible

Acknowledgements

Many thanks to

Prof. Stuart Althorpe

Adam Reid

- and the whole Althorpe group

Links and further reading

- Ring-polymer instanton theory papers:
  - Richardson, J. O. and Althorpe, S. C., J. Chem. Phys., **2011**, *134*
  - Richardson, J. O. *et al.*, J. Chem. Phys., **2011**, *135*
- My dissertation (extended version is recommended)
  - `http://blog.mfhs.eu/2013/08/10/master-thesis-tunnelling-in-water-clusters/`
  - This document will be available shortly.