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Semiclassical limit of path integrals

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Path-integral approach to Quantum Statistics

Quantum partition function can be defined as

$$Z = \mathrm{Tr}[\mathrm{e}^{-\beta\hat{H}}] = \Lambda^N \int \mathrm{e}^{-S_\circ(\mathbf{x})/\hbar}\,\mathrm{d}\mathbf{x},$$

where (using cyclic boundary conditions: $x_0 \equiv x_N$)

$$S_\circ(\mathbf{x}) = \sum_{i=1}^{N} \frac{m}{2\tau_N}|x_i - x_{i-1}|^2 + \tau_N V(x_i).$$

This is equivalent to what you saw in first lectures:

- $S_\circ/\hbar = \beta_N U_N$
- imaginary time: $\tau = \beta\hbar$ and $\tau_N = \tau/N$
- $S_\circ$ is *classical* action (does not explicitly contain $\hbar$)
- $\Lambda = \sqrt{\frac{m}{2\pi\tau_N\hbar}}$. Change to Λ^f for mass-weighted f-dimensional system

Path-integral approach to Quantum Statistics

Quantum density matrix can be defined as

$$\rho(x', x'') = \langle x'|\mathrm{e}^{-\beta\hat{H}}|x''\rangle$$

or equivalently the imaginary-time propagator is

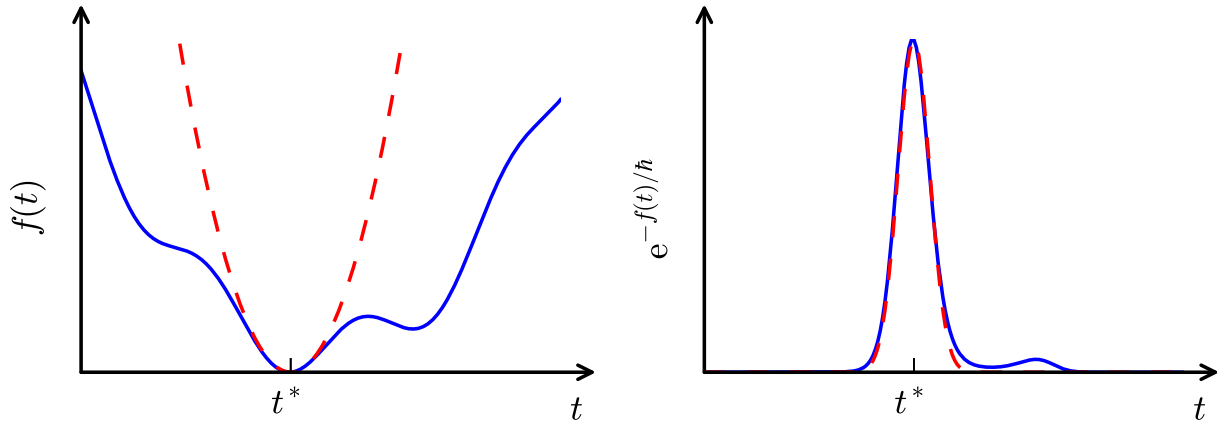
$$K(x', x'', \tau) = \langle x'|\mathrm{e}^{-\hat{H}\tau/\hbar}|x''\rangle = \Lambda^N \int \mathrm{e}^{-S(\mathbf{x})/\hbar}\,\mathrm{d}\mathbf{x},$$

where (no cyclic boundary conditions)

$$S(\mathbf{x}) = \sum_{i=1}^{N} \frac{m}{2\tau_N}|x_i - x_{i-1}|^2 + \tau_N \left[\tfrac{1}{2}V(x_0) + \sum_{i=1}^{N} V(x_i) + \tfrac{1}{2}V(x_N)\right].$$

Here, $x_0 \equiv x'$ and $x_N \equiv x''$ are fixed; there are $N-1$ free beads, $\mathbf{x} = \{x_1, \ldots, x_{N-1}\}$, and N intervals.

Steepest-descent Approximation



An integral of this form has the asymptotic approximation*

$$\int \mathrm{e}^{-f(t)/\hbar}\,\mathrm{d}t \sim \int \mathrm{e}^{-f(t^*)/\hbar-(t-t^*)^2 f''(t^*)/2\hbar}\,\mathrm{d}t, \qquad \hbar \to 0$$

$$= \sqrt{\frac{2\pi\hbar}{f''(t^*)}}\,\mathrm{e}^{-f(t^*)/\hbar},$$

where t^* is chosen at a minimum such that $f'(t^*) = 0$.

*Recommended reading: chapter 6 from Bender & Orzag

Steepest-descent approximation to path integral

- path, $\tilde{\mathbf{x}}$, with minimum action, $S(\tilde{\mathbf{x}})$, will dominate

$$K(x', x'', \tau) = \Lambda^N \int \mathrm{e}^{-S(\mathbf{x})/\hbar}\, \mathrm{d}\mathbf{x}$$

$$\sim \Lambda^N \int \mathrm{e}^{-S(\tilde{\mathbf{x}})/\hbar - (\mathbf{x}-\tilde{\mathbf{x}})^T \boldsymbol{\nabla}^2 S(\tilde{\mathbf{x}})(\mathbf{x}-\tilde{\mathbf{x}})/2\hbar}\, \mathrm{d}\mathbf{x}$$

Find matrix, $\mathbf{U}$, with columns as eigenvectors of the Hessian, $\boldsymbol{\nabla}^2 S(\tilde{\mathbf{x}})$ such that $\mathbf{U}^T \boldsymbol{\nabla}^2 S(\tilde{\mathbf{x}}) \mathbf{U} = \mathbf{D}$ is a diagonal matrix with the (positive) eigenvalues, $m\eta_k^2$, along the diagonal. N.B. it is an orthogonal matrix such that $\mathbf{U}\mathbf{U}^T = \mathbf{1}$. Then define normal mode transform, $\mathbf{q} = \mathbf{U}^T(\mathbf{x} - \tilde{\mathbf{x}})$ and hence $\mathbf{q}^T = (\mathbf{x} - \tilde{\mathbf{x}})^T \mathbf{U}$.

Steepest-descent approximation to path integral

$$
\begin{aligned}
K(x', x'', \tau) &\sim \Lambda^N \int \mathrm{e}^{-S(\tilde{\mathbf{x}})/\hbar - (\mathbf{x}-\tilde{\mathbf{x}})^T \mathbf{U}\mathbf{U}^T \boldsymbol{\nabla}^2 S(\tilde{\mathbf{x}}) \mathbf{U}\mathbf{U}^T (\mathbf{x}-\tilde{\mathbf{x}})/2\hbar} \, \mathrm{d}\mathbf{x} \\
&\sim \Lambda^N \mathrm{e}^{-S(\tilde{\mathbf{x}})/\hbar} \int \mathrm{e}^{-\mathbf{q}^T \mathbf{D}\mathbf{q}/2\hbar} \, \mathrm{d}\mathbf{q} \\
&\sim \Lambda \mathrm{e}^{-S(\tilde{\mathbf{x}})/\hbar} \prod_{k=1}^{N-1} \Lambda \int \mathrm{e}^{-m\eta_k^2 q_k^2/2\hbar} \, \mathrm{d}q_k \\
&\sim \Lambda \mathrm{e}^{-S(\tilde{\mathbf{x}})/\hbar} \prod_{k=1}^{N-1} \sqrt{\frac{m}{2\pi\tau_N \hbar}} \sqrt{\frac{2\pi\hbar}{m\eta_k^2}} \\
&\sim \sqrt{\frac{C}{2\pi\hbar}} \, \mathrm{e}^{-S(\tilde{\mathbf{x}})/\hbar}
\end{aligned}
$$

Steepest-descent approximation to path integral

We have defined:

$$
\begin{aligned}
C &= 2\pi\hbar \frac{m}{2\pi\tau_N\hbar} \prod_{k=1}^{N-1} \frac{1}{\tau_N \eta_k^2} \\
&= \frac{m^N}{\tau_N^N} \prod_{k=1}^{N-1} \frac{1}{m\eta_k^2} \\
&= \frac{m^N}{\tau_N^N} \left|\boldsymbol{\nabla}^2 S(\tilde{\mathbf{x}})\right|^{-1}
\end{aligned}
$$

because the determinant of a matrix is equal to the product of its eigenvalues.*

*For numerically stable ways to compute this efficiently see Winter & J.O.R. "Divide-and-conquer method for instanton rate theory." *submitted to JCTC* (2019).

Steepest-descent approximation to path integral

More generally in f-dimensions, and allowing for more than one minimum-action pathway, it becomes

$$K(x', x'', \tau) \sim \sum_{\text{min-S paths}} \sqrt{\frac{C}{(2\pi\hbar)^f}}\, \mathrm{e}^{-S(\tilde{\mathbf{x}})/\hbar}$$

where

$$C = \left(\frac{m}{\tau_N}\right)^f (\det \mathbf{J})^{-1}$$

and the scaled Hessian matrix is

$$\mathbf{J} = \frac{\tau_N}{m} \boldsymbol{\nabla}^2 S(\tilde{\mathbf{x}}).$$

Compute Z for anharmonic well

Here we use cyclic path integral:

$$Z = \Lambda^N \int \mathrm{e}^{-S_\circ(\mathbf{x})/\hbar}\,\mathrm{d}\mathbf{x}$$
$$\sim \Lambda^N (2\pi\hbar)^{N/2} \left|\boldsymbol{\nabla}^2 S_\circ(\tilde{\mathbf{x}})\right|^{-1/2} \mathrm{e}^{-S_\circ(\tilde{\mathbf{x}})/\hbar}$$

The minimum-action pathway is clearly collapsed at the bottom of the well, $\tilde{x}_i = 0$, where $S_\circ = 0$.

$$Z \sim \left(\frac{m}{\tau_N}\right)^{N/2} \left|\boldsymbol{\nabla}^2 S_\circ(\tilde{\mathbf{x}})\right|^{-1/2}$$

Obtain eigenvalues of $\boldsymbol{\nabla}^2 S_\circ(\tilde{\mathbf{x}})$ by comparing with corresponding cyclic Hückel problem. They are (assuming N is even)

$$m\eta_k^2 = \frac{4}{\tau_N^2} \sin^2 \frac{|k|\pi}{N} + \omega_\mathrm{e}^2 \qquad \text{for } k \in \{-N/2, \ldots, N/2-1\},$$

where $\omega_\mathrm{e} = \sqrt{\nabla^2 V(0)/m}$ is the harmonic frequency of the well.

Compute Z for anharmonic well

It can be shown that the product of these eigenvalues gives*

$$Z \sim \left(\frac{m}{\tau_N}\right)^{N/2} \prod_k \sqrt{\frac{1}{m\eta_k^2}} = [2\sinh(\tau\omega_{\mathrm{e}}^{(N)}/2)]^{-1}$$

where $\sinh(\tau_N\omega_{\mathrm{e}}^{(N)}/2) = \tau_N\omega_{\mathrm{e}}/2$.
Therefore in the limit $N \to \infty$, Z tends to $[2\sinh(\beta\hbar\omega_{\mathrm{e}}/2)]^{-1}$, which is of course the result for the partition function of a quantum harmonic oscillator. In other words, the steepest-descent approximation is here equivalent to a harmonic approximation of the well.

*The proof can be found in Kleinert's book on Path Integrals, but the easiest way to check it for yourself is to compare numerical results for a range of parameters.

Connection to Classical Mechanics

What are the properties of a minimum-action path, $\tilde{\mathbf{x}}$? They obey:

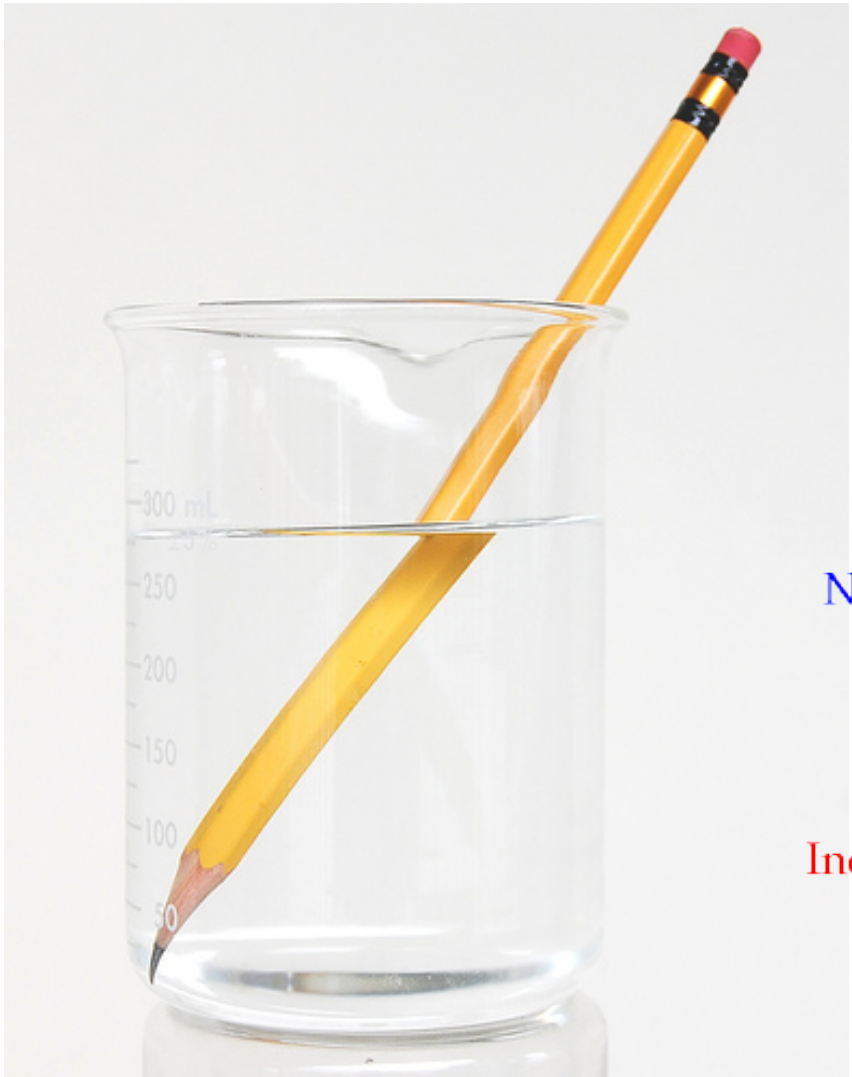
$$\begin{aligned} 0 &= \frac{\partial}{\partial x_i} S(\tilde{\mathbf{x}}) \qquad \text{for } i \in \{1, \ldots, N-1\} \\ &= \frac{m}{\tau_N}(-\tilde{x}_{i+1} + 2\tilde{x}_i - \tilde{x}_{i-1}) + \tau_N \nabla V(\tilde{x}_i) \end{aligned}$$

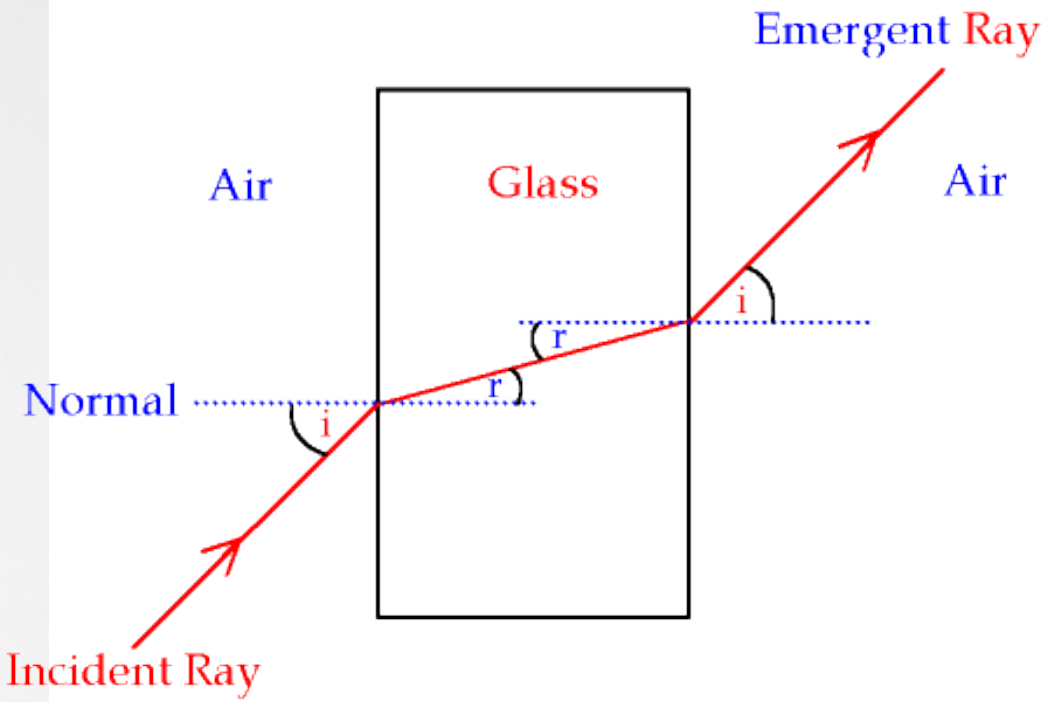
This rearranges to give

$$\nabla V(\tilde{x}_i) = m \frac{-\tilde{x}_{i+1} + 2\tilde{x}_i - \tilde{x}_{i-1}}{\tau_N^2}$$

which is the finite-difference version of Newton's second law, $F = ma$, in imaginary time $\tau = -it$. Equivalent to usual equation with the modification that $F = \nabla V$ instead of the usual $F = -\nabla V$. Therefore in the limit $N \to \infty$, the minimum-action path is a classical trajectory moving on the upside-down potential-energy surface.

Principle of least action





Numerically finding minimum-action pathways

Easiest method: simply minimize $S(\mathbf{x})$ using quasi-Newton solver e.g. L-BFGS.*

$$\mathbf{G} = \frac{\partial S}{\partial \mathbf{x}} \qquad \mathbf{H} = \frac{\partial^2 S}{\partial \mathbf{x} \partial \mathbf{x}}$$

Taylor expansion around current point, $\mathbf{x}_0$,

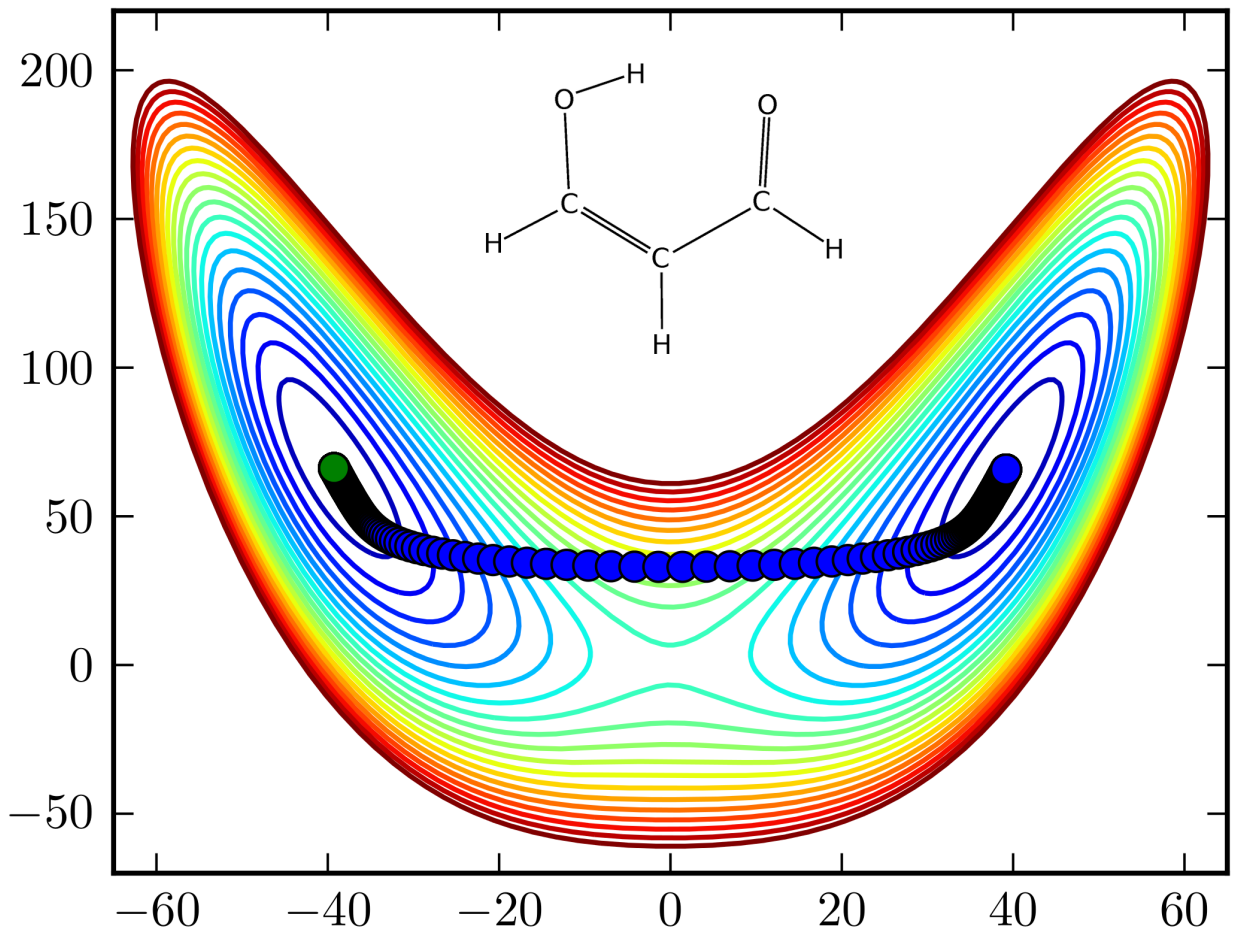
$$\mathbf{G}(\mathbf{x}) \approx \mathbf{G}(\mathbf{x}_0) + \mathbf{H}(\mathbf{x}_0) \cdot (\mathbf{x} - \mathbf{x}_0)$$

so choose Newton-Raphson step to attempt to find $\mathbf{G}(\mathbf{x}) = \mathbf{0}$,

$$\mathbf{x} - \mathbf{x}_0 = -\mathbf{H}(\mathbf{x}_0)^{-1}\mathbf{G}(\mathbf{x}_0)$$

*More efficient and more complicated methods exist using Hamilton-Jacobi formalism, e.g. Cvitaš. "Quadratic string method for locating instantons in tunneling splitting calculations." *J. Chem. Theory Comput.* **14**, 1487 (2018).

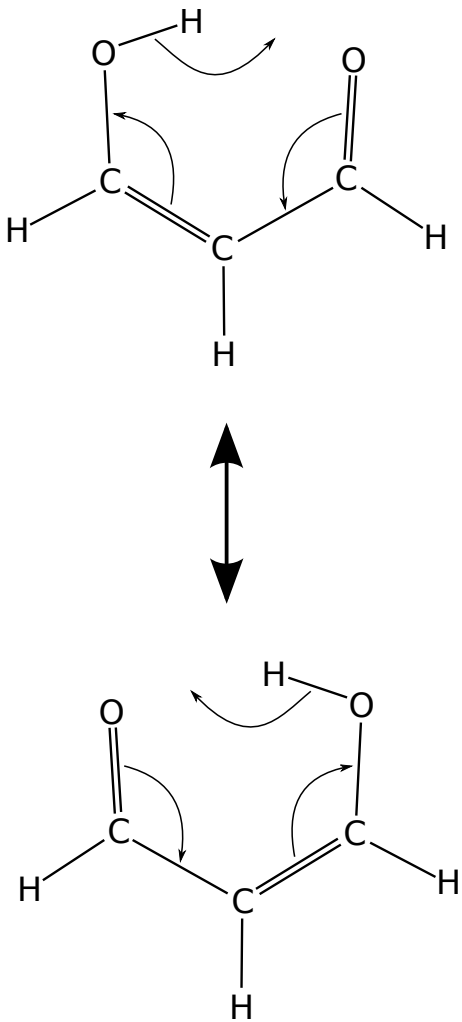
Minimum-action pathway in 2D model of malonaldehyde

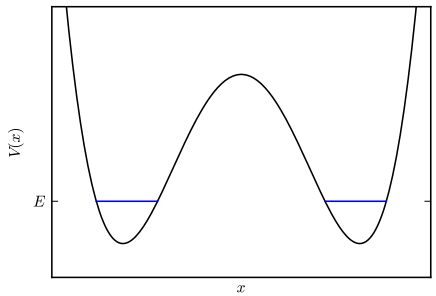


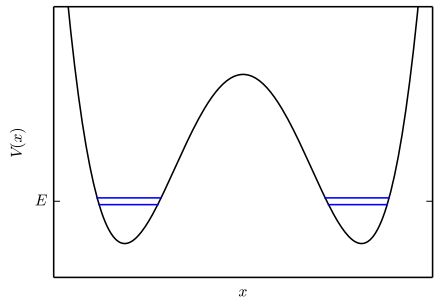
Notes for practical implementation

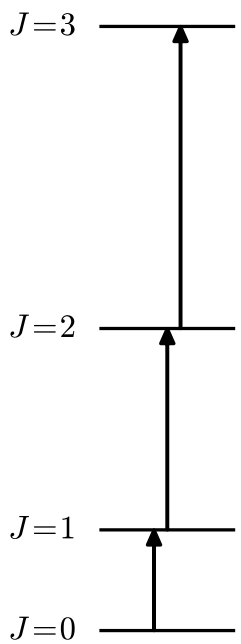
- Fix end points in correct places if known, otherwise you may want to optimize end beads as well.
- Choose good initial guess with a small number of beads, e.g. evenly spaced in straight line. In some cases, an angular coordinate will be better.
- Iteratively optimize and grow the number of beads until convergence. Add new beads in between the old ones (maybe using spline interpolation or normal mode transforms)
- Implementation in i-PI and Molpro, as well as our own group code
- Consider building a machine-learning PES around the pathway

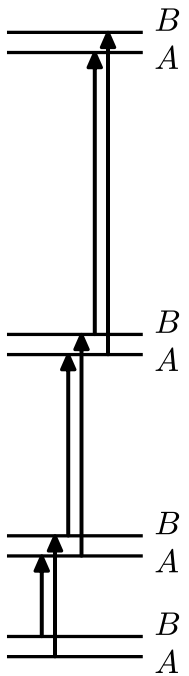
Tunnelling splitting











Tunnelling splitting

Path can be broken into pieces which remain in a well:

$$K_0(\tau) \sim \left(\frac{m}{2\pi\tau_N\hbar}\right)^{f/2} (\det J_0)^{-\frac{1}{2}},$$

or which tunnel from one well to another (at a specified time):

$$K_1'(\tau) \sim \frac{1}{\tau_N}\left(\frac{m}{2\pi\tau_N\hbar}\right)^{f/2} \sqrt{\frac{S_{\text{kink}}}{2\pi\hbar}} (\det{}' J)^{-\frac{1}{2}}\, \mathrm{e}^{-S_{\text{kink}}/\hbar}.$$

$$\begin{aligned}\Omega &= \lim_{\tau\to\infty} \frac{K_1'(\tau)}{K_0(\tau)} \\ &= \frac{1}{\Phi}\sqrt{\frac{S_{\text{kink}}}{2\pi\hbar}}\, \mathrm{e}^{-S_{\text{kink}}/\hbar},\end{aligned}$$

where

$$\Phi = \tau_N \left(\frac{\det{}' J}{\det J_0}\right)^{\frac{1}{2}}.$$

Tunnelling splitting

In low-temperature limit, $\beta \to \infty$, only the ground state tunnelling states contribute to the partition function

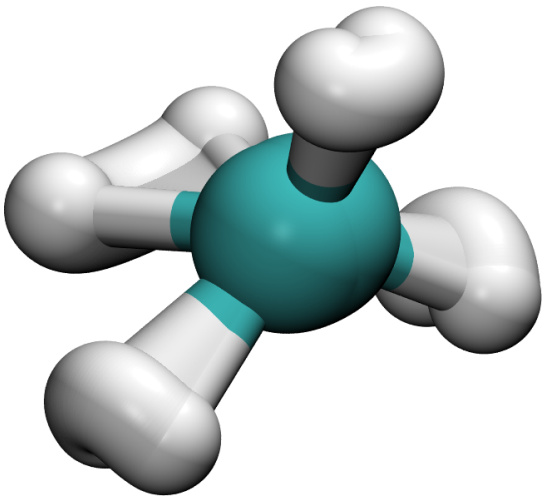
$$\begin{aligned} Z &= \sum_{\nu} \mathrm{e}^{-\beta E_\nu} = \mathrm{e}^{-\beta E_0} \sum_{\nu} \mathrm{e}^{-\beta(E_\nu - E_0)} \\ &= \int K(x, x, \tau) \mathrm{d}x \end{aligned}$$

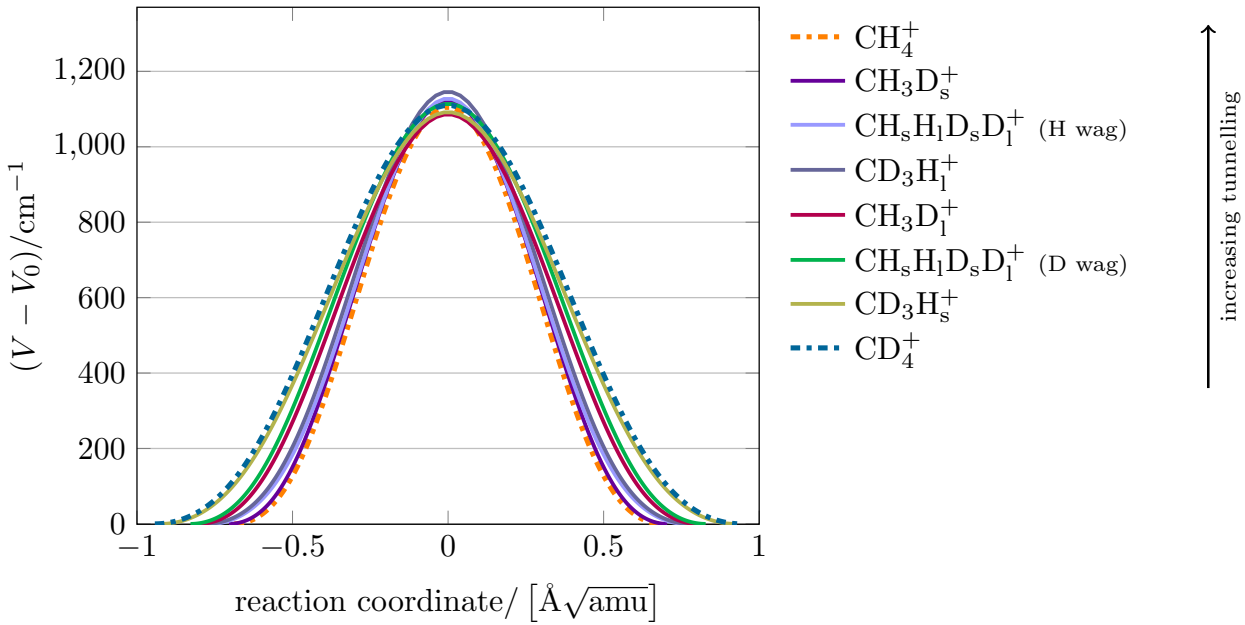
Define tunnelling matrix, $W_{ij} = -\hbar \Omega_{ij} A_{ij}$

$$\begin{aligned} Z &\sim Z_0 \sum_{n=0}^{\infty} \frac{1}{\hbar^n} \int_{\tau_{n-1}}^{\beta\hbar} \mathrm{d}\tau_n \cdots \int_{\tau_1}^{\beta\hbar} \mathrm{d}\tau_2 \int_0^{\beta\hbar} \mathrm{d}\tau_1 \ \mathrm{Tr}[(-\mathbf{W})^n] \\ &= Z_0 \, \mathrm{Tr}[\mathrm{e}^{-\beta \mathbf{W}}], \end{aligned}$$

So splitting pattern, $E_\nu - E_0$ is defined as eigenvalues of $\mathbf{W}$.

Tunnelling splitting in methane cation*





*Gandolfi, Calderini, Laude, Tew & J.O.R. "Quantum tunnelling and the geometric-phase effect in the methane cation." *In preparation* (2019).

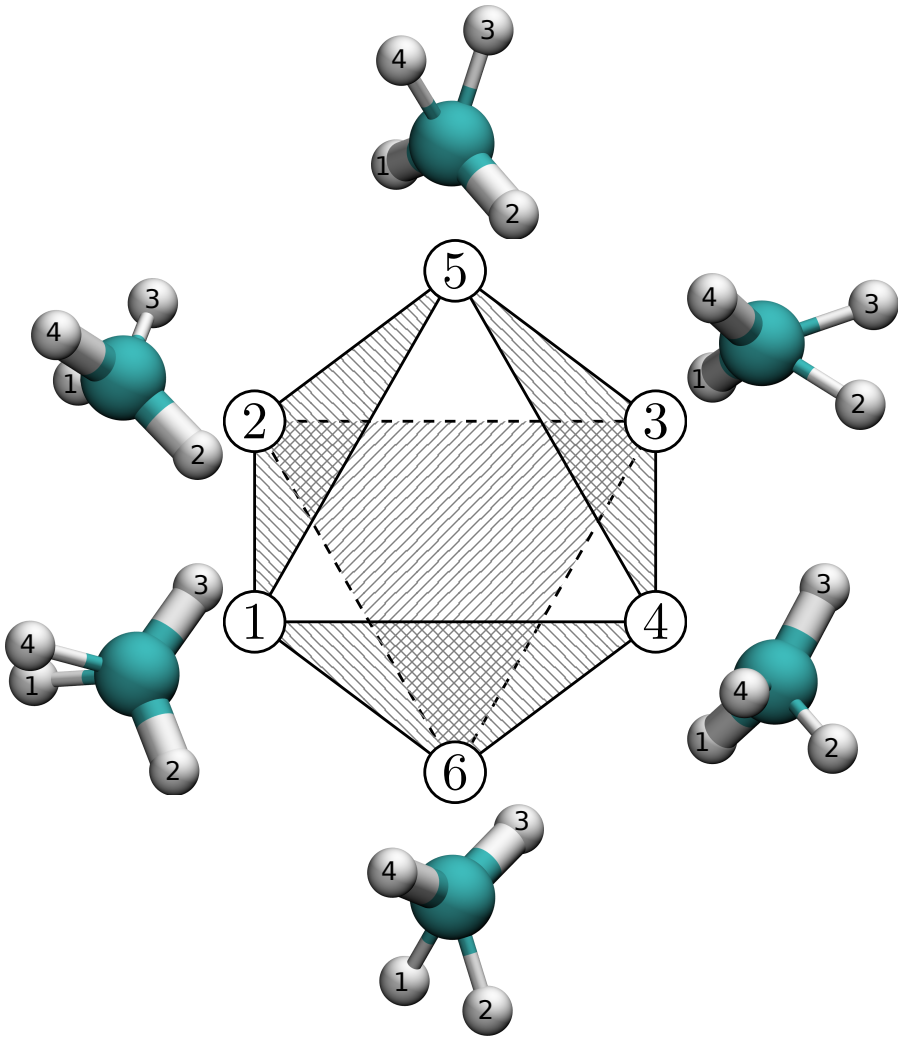
Convergence of tunnelling calculation

Converge of the action with respect to β and N simultaneously*

	$\beta\hbar$				
N	15	30	60	120	240
8	9.309	8.762	5.967	3.242	1.655
16	9.381	9.336	8.762	5.967	3.242
32	9.399	9.406	9.336	8.762	5.967
64	9.403	9.423	9.406	9.336	8.762
128	9.404	9.427	9.423	9.406	9.336
256	9.404	9.428	9.427	9.423	9.406
512	9.405	9.428	9.428	9.427	9.423

*Example from J.O.R. & Althorpe. "Ring-polymer instanton method for calculating tunneling splittings." *J. Chem. Phys.* **134**, 054109 (2011).

Tunnelling matrix for CH_4^+



N.B. Negative signs in adjacency matrix are necessary to take account of geometric phase effect.

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

Eigenvalues of $\mathbf{W} = -\hbar\Omega\mathbf{A}$ are $[-2\hbar\Omega, 2\hbar\Omega]$, both triply degenerate with irrep F_2 and F_1 in $T_\mathrm{d}(\mathrm{M})$ molecular symmetry group.

Summary of most important concepts

- A steepest-descent approximation to the path integral gives a simpler object that can be computed much more efficiently.
- One just needs to find the minimum-energy pathway and the Hessians of each bead.
- It is equivalent to making a harmonic approximation when computing partition-functions, so should not be applied to very anharmonic environments such as liquids.
- Can be used to compute tunnelling splittings of molecules and clusters in the gas phase
- We will show in the next lectures how to use it to compute reaction rates of molecules in the gas phase, or those absorbed on surfaces or trapped in solids.

Reading List

- Bender & Orszag. *Advanced Mathematical Methods for Scientists and Engineers.* (McGraw-Hill: New York, 1978)
- Gutzwiller. *Chaos in Classical and Quantum Mechanics.* (Springer-Verlag: New York, 1990). doi: 10.1007/978-1-4612-0983-6
- J.O.R., Althorpe & Wales. "Instanton calculations of tunneling splittings for water dimer and trimer." *J. Chem. Phys.* **135**, 124109 (2011).
- J.O.R. "Ring-polymer instanton theory." *Int. Rev. Phys. Chem.* **37**, 171 (2018).