Quantum Transition-State Theory?

The classical flux-side time-correlation function
\[ C_{fs}^{cl}(t) = \int dp \int q e^{-i\mathcal{H}(p,q)t}\delta(q_0 - q)\mathcal{P}(q_1 - q^2) \]
possesses a non-zero short-time limit, namely classical TST.

The Miller-Schwarz-Tromp (MST) quantum flux-side time-correlation function
\[ C_{fs}^{QM}(t) = \text{Tr} e^{-i\mathcal{H}/2} e^{-i\mathcal{H}(p,q)t} e^{-i\mathcal{H}/2} \]
vanishes in the \( t \to 0^+ \) limit.

Alignment of dividing surfaces: non-zero QTST

\[ C_{fs}^{QM}(t \to 0^+) \] vanishes because its dividing surfaces are in different places in path-integral space (Figure 3), but by moving the flux dividing surface they can be aligned:

Positive-definite Boltzmann Statistics: RPMD-TST

Positive-definite statistics are obtained upon polymerizing Eq. (3);
\[ C_{fs}^{QM}(t) = \int dq \int d\mathcal{A} \int dz \hat{f}[q]h[\hat{f}(z)] \times \prod_{i=1}^{N} \langle q_{i-1} - \hat{\mathcal{A}}_{i-1} q_i + \hat{\mathcal{A}}_{i-1} q_{i} + \hat{\mathcal{A}}_{i} q_i \rangle e^{i\mathcal{H}(q)/\hbar} \]
where \( f(q) \) is a dividing surface in path-integral space, and \( \hat{f}[q] \) is the ‘ring polymer flux operator’,
\[ \hat{f}[q] = \frac{1}{2m} \sum_{i=1}^{N} \left( \frac{\partial f(q)}{\partial q} \right) \langle \mathcal{P}(q) \rangle + \hat{\mathcal{A}} \frac{\partial f(q)}{\partial q} \]
which measures the flux normal to the dividing surface \( f(q) \).

Numerical results for the symmetric Eckart barrier

Wigner TST produces poor results at low temperatures, as demonstrated by the negative result in Figure 6!

Summary

- A true \( t \to 0^+ \) Quantum Transition-State Theory (QTST) was thought not to exist, i.e. there was no quantum flux-side time-correlation function with a non-zero short-time limit.
- Such correlation functions do exist, and can be formed when the flux and side dividing surfaces are in the same location in path-integral space [1].
- Only one known QTST produces positive-definite quantum statistics and this is identical to RPMD-TST [3].
- QTST (≡ RPMD-TST) gives the exact quantum rate in the absence of recrossing [2].