Quantum Transition-State Theory

Timothy J. H. Hele and Stuart C. Althorpe
Department of Chemistry, University of Cambridge, United Kingdom

tjhh2@cam.ac.uk

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The classical flux-side time-correlation function

$$C_{\rm fs}^{\rm clas}(t)=\frac{1}{2\pi\hbar}\int dp_0\int dq_0\; e^{-\beta H(p_0,q_0)}\delta(q_0-q^\ddagger)\frac{p_0}{m}h(q_t-q^\ddagger) \qquad (1)$$

possesses a non-zero short-time limit, namely classical TST.
The Miller-Schwarz-Tromp (MST) quantum flux-side time-correlation function

$$C_{\rm fs}^{\rm QM}(t)=\mathrm{Tr}\left[e^{-\beta\hat H/2}\hat F e^{-\beta\hat H/2}e^{i\hat Ht/\hbar}\hat h e^{-i\hat Ht/\hbar}\right] \qquad (2)$$

vanishes in the $t\to0_+$ limit.

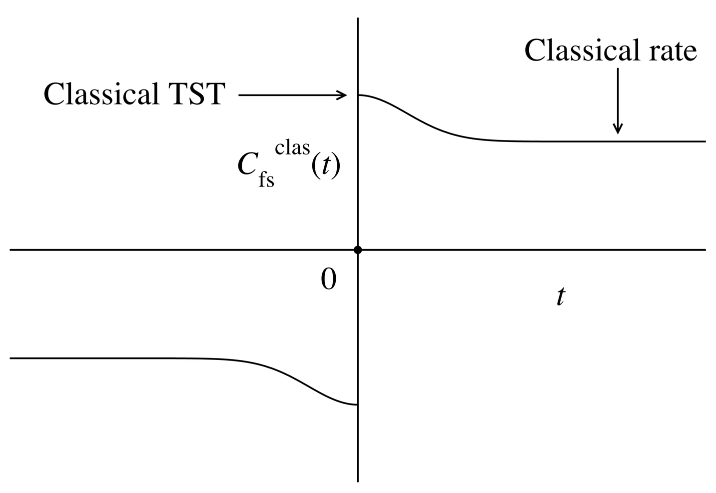

Figure 1: Classical flux-side time-correlation function

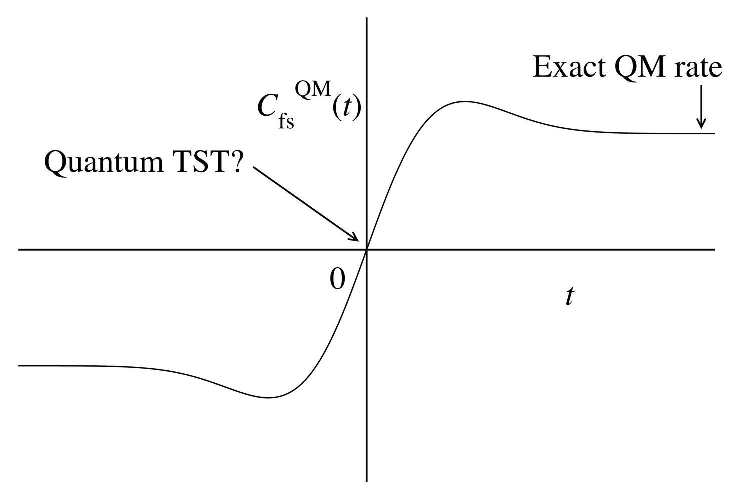

Figure 2: Quantum flux-side time-correlation function

Alignment of dividing surfaces: non-zero QTST

$C_{\rm fs}^{\rm QM}(t\to0_+)$ 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:

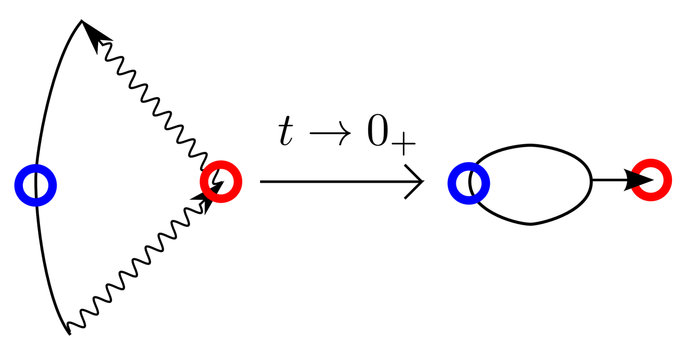

Figure 3: MST form: different dividing surfaces.

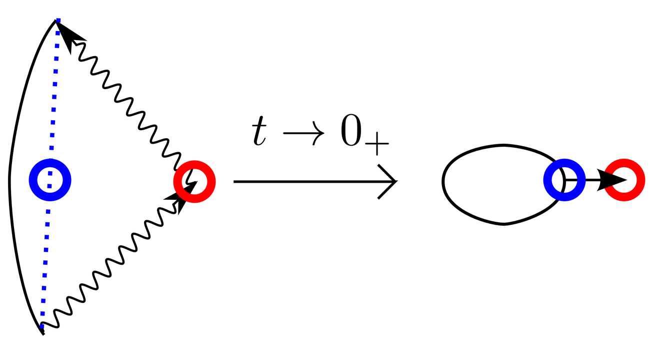

Figure 4: New Form: same dividing surface.

The equation for the new form (Fig. 4) is

$$C_{\rm fs}^{[1]}(t)=\int dq\int dz\int d\Delta\; h(z)\hat F(q)\langle q-\Delta/2|e^{-\beta\hat H}|q+\Delta/2\rangle \times\langle q+\Delta/2|e^{i\hat Ht/\hbar}|z\rangle\langle z|e^{-i\hat Ht/\hbar}|q-\Delta/2\rangle, \qquad (3)$$

and in the short-time limit this reduces to Wigner TST:

$$\lim_{t\to0_+}C_{\rm fs}^{[1]}(t)=\frac{1}{2\pi\hbar}\int dq\int dp\;\frac{p}{m}h(p)\delta(q)\times\int d\Delta\langle q-\Delta/2|e^{-\beta\hat H}|q+\Delta/2\rangle e^{ip\Delta/\hbar} \qquad (4)$$

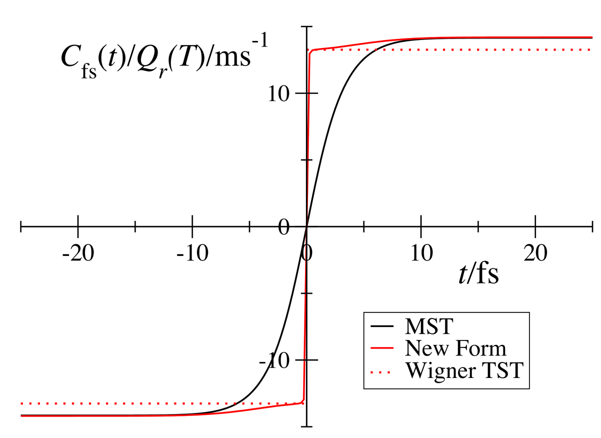

Figure 5: 1000K, good quantum TST

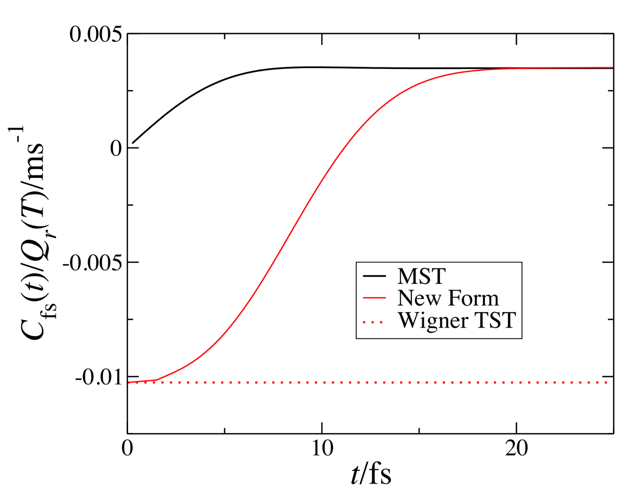

Figure 6: 333K, spurious half-instantons cause a negative quantum TST!

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

References

[1] T. J. H. Hele and S. C. Althorpe, *J. Chem. Phys.* **138**, 084108 (2013).
[2] S. C. Althorpe and T. J. H. Hele, *J. Chem. Phys.* **139**, 084115 (2013).
[3] T. J. H. Hele and S. C. Althorpe, *J. Chem. Phys.* **139**, 084116 (2013).
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Positive-definite Boltzmann Statistics: RPMD-TST

Positive-definite statistics are obtained upon polymerizing Eq. (3);

$$C_{\rm fs}^{[N]}(t)=\int d\mathbf{q}\int d\mathbf{\Delta}\int d\mathbf{z}\;\hat{\mathcal F}[f(\mathbf{q})]h[f(\mathbf{z})] \times\prod_{i=1}^{N}\langle q_{i-1}-\tfrac12\Delta_{i-1}|e^{-\beta_N\hat H}|q_i+\tfrac12\Delta_i\rangle\langle q_i+\tfrac12\Delta_i|e^{i\hat Ht/\hbar}|z_i\rangle \times\langle z_i|e^{-i\hat Ht/\hbar}|q_i-\tfrac12\Delta_i\rangle \qquad (5)$$

where $f(\mathbf{q})$ is a dividing surface in path-integral space, and $\hat{\mathcal F}[f(\mathbf{q})]$ is the 'ring polymer flux operator',

$$\hat{\mathcal F}[f(\mathbf{q})]=\frac{1}{2m}\sum_{i=1}^{N}\left\{\frac{\partial f(\mathbf{q})}{\partial q_i}\delta[f(\mathbf{q})]\hat p_i+\hat p_i\delta[f(\mathbf{q})]\frac{\partial f(\mathbf{q})}{\partial q_i}\right\} \qquad (6)$$

which measures the flux normal to the dividing surface $f(\mathbf{q})$.

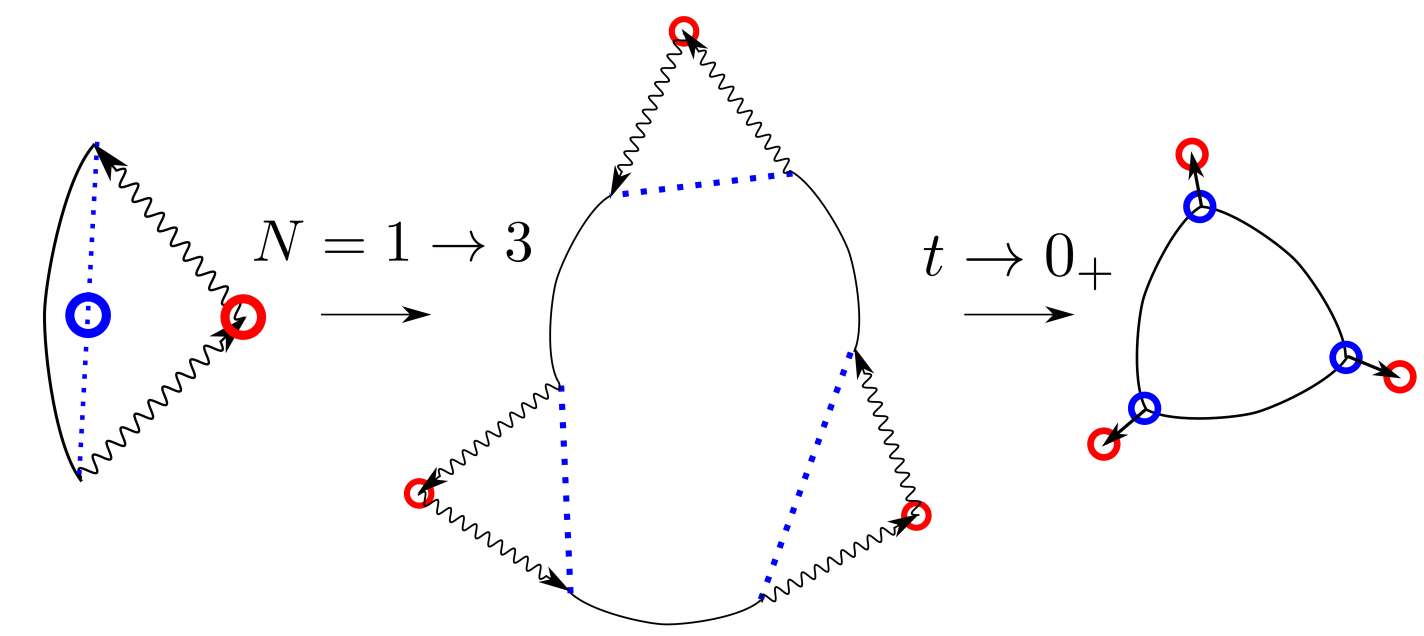


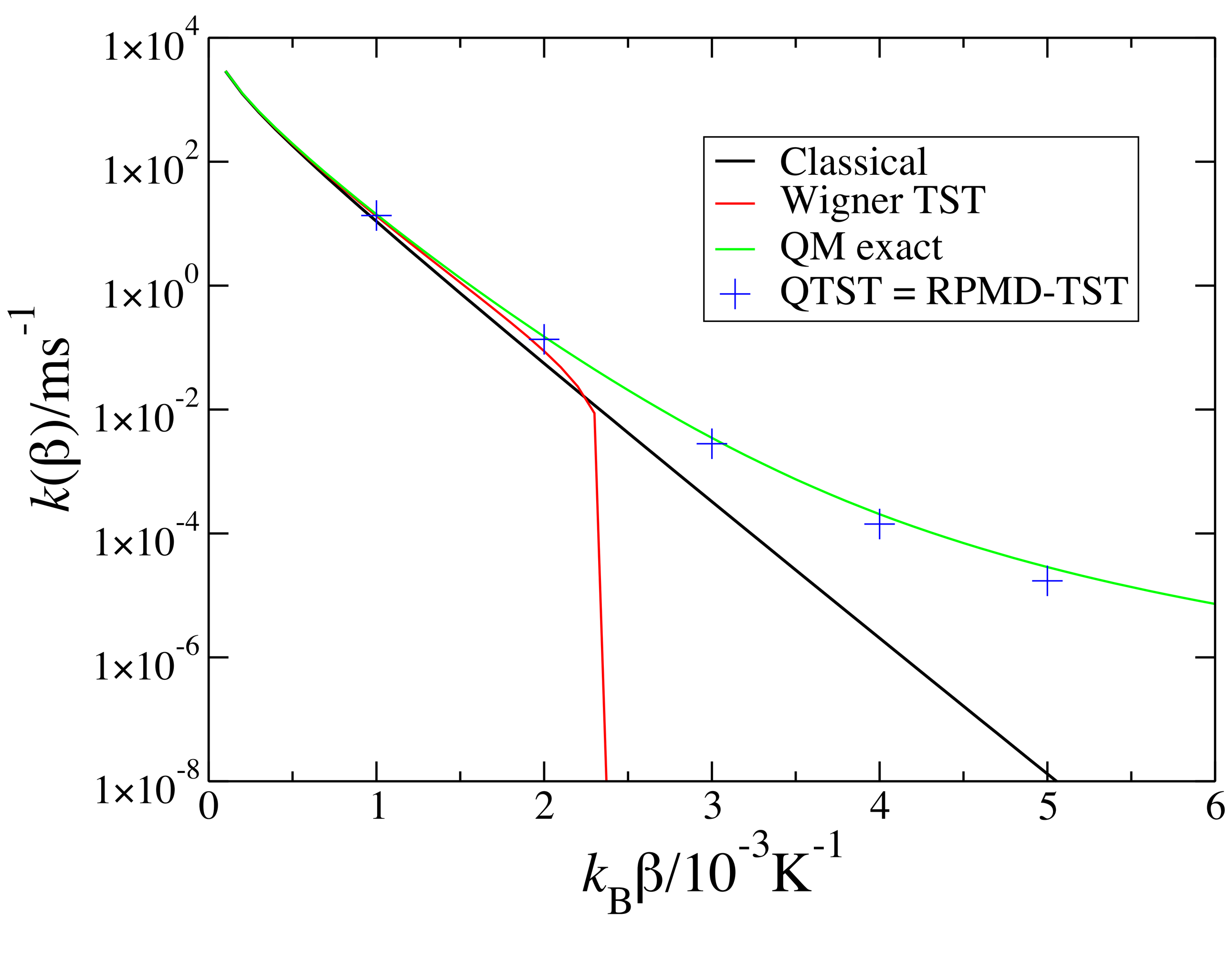
Figure 7: Polymerising Eq. (3) to form Eq. (5), and taking the short-time limit, illustrated for $N=3$.

The large-N, short-time limit of equation (5) is **positive-definite** and **identical to RPMD-TST**:

$$k_\ddagger^{\rm QM}(\beta)Q_r(\beta)=\lim_{t\to0_+}\lim_{N\to\infty}C_{\rm fs}^{[N]}(t) =\frac{1}{(2\pi\hbar)^N}\int d\mathbf{q}\int d\mathbf{p}e^{-\beta_N H_N(\mathbf{q},\mathbf{p})}\;\delta[f(\mathbf{q})]S(\mathbf{q},\mathbf{p})h[S(\mathbf{q},\mathbf{p})] \qquad (7)$$

where $S(\mathbf{q},\mathbf{p})$ represents the ring-polymer flux perpendicular to $f(\mathbf{q})$ and $H_N(\mathbf{q},\mathbf{p})$ is the N-bead ring-polymer Hamiltonian.

Numerical results for the symmetric Eckart barrier



Summary

- A true ($t\to0_+$) 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 ($\equiv$ RPMD-TST) gives the exact quantum rate in the absence of recrossing [2].