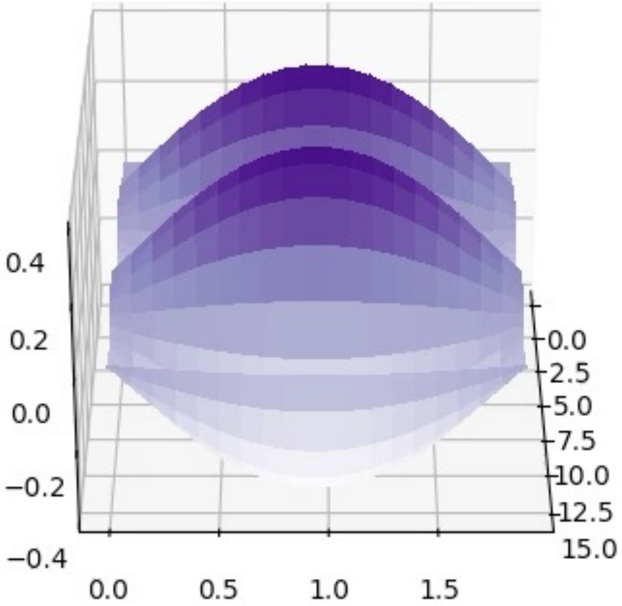
Thinking Outside the Box:
A Quantum Transition-State Theory



Mohan Shankar

Egorov Group

April 19th, 2024

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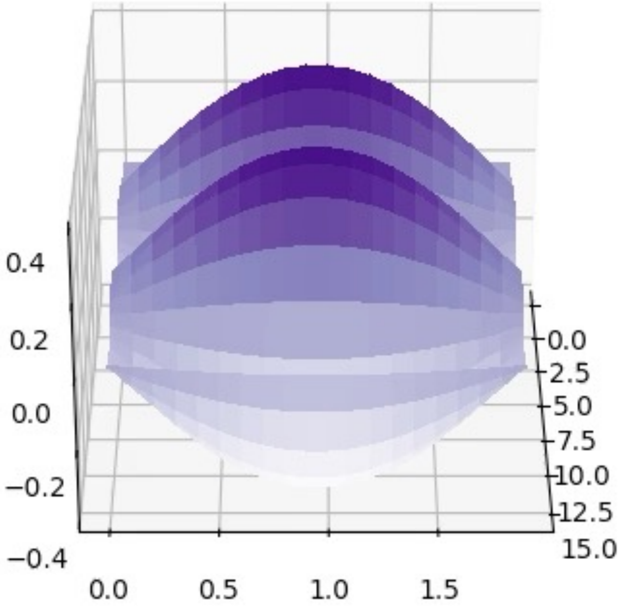


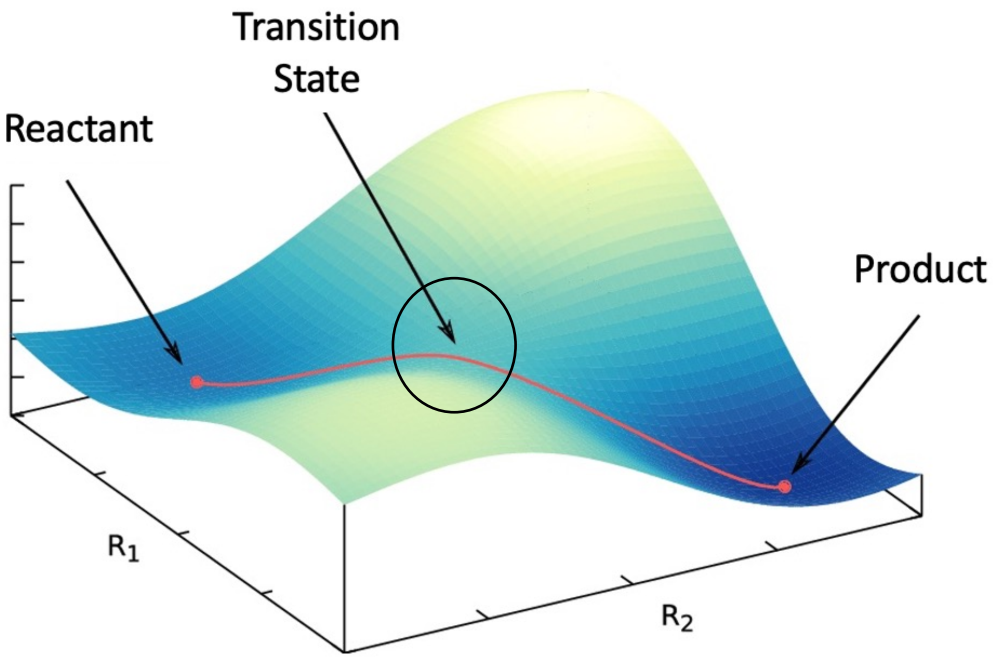
Transition State Theory

Background:

- Developed to find chemical reaction rates
- Based on classical mechanics

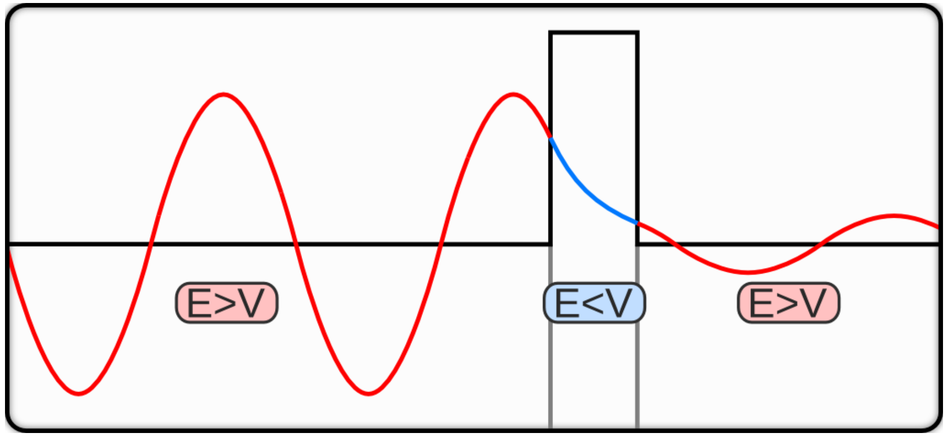
Drawbacks:

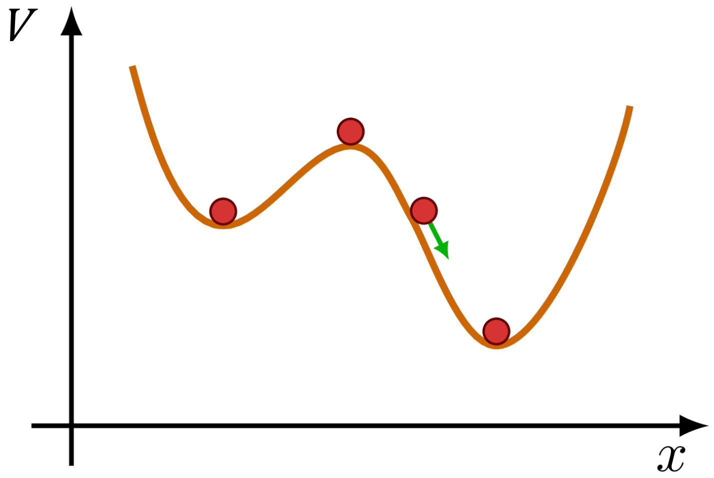
- Not good for light elements and low temps



Quantum Effects

Tunneling:





Zero Point Energy:

$$E_n = \frac{\hbar^2\pi^2}{2ml^2}n^2 \rightarrow \Delta x \Delta p \approx \hbar \text{ where } \Delta x \approx l \text{ and } \Delta p \approx \frac{\hbar}{l} \rightarrow \boxed{E_{min} \approx \frac{\Delta p^2}{2m} \approx \frac{\hbar^2}{2ml^2} \neq 0}$$

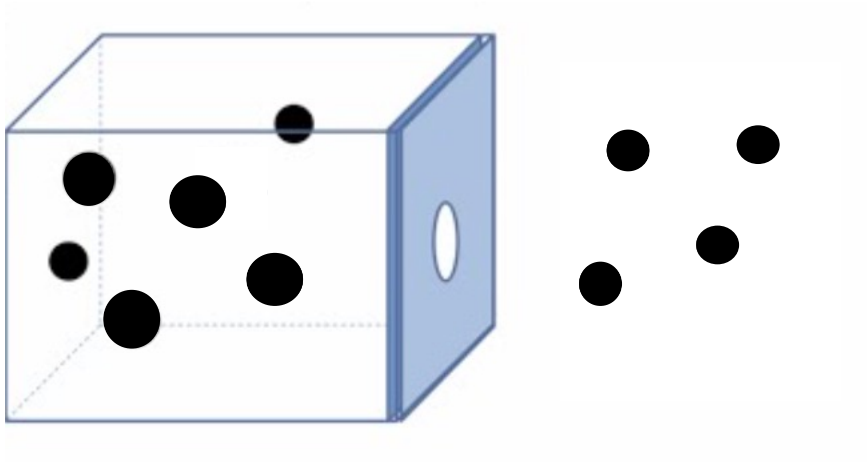
Comparison of Formalisms

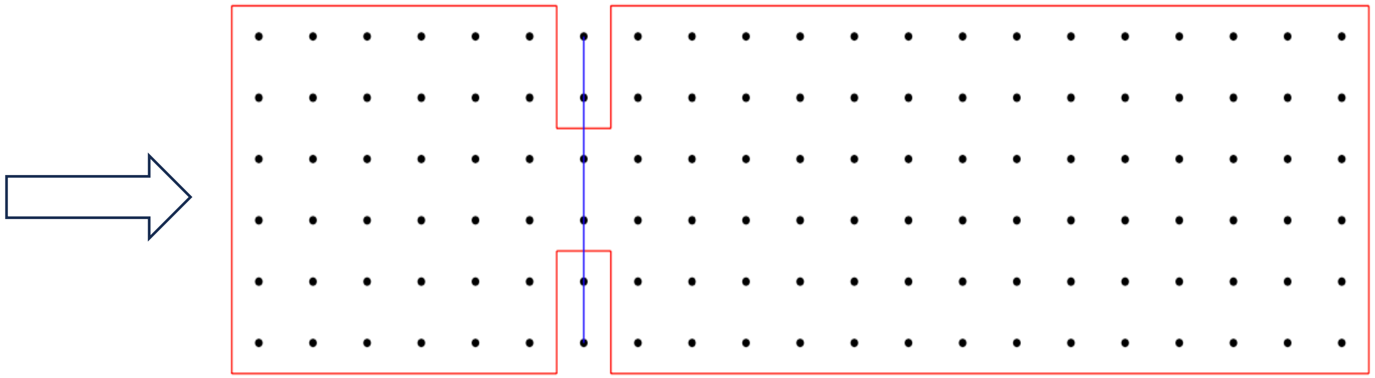
Classical Mechanics:

- Deterministic, described by *x(t)* and *p(t)* of all particles present
- Rates of effusion are known

Quantum Mechanics:

- Probabilistic, described by the *wavefunction* $\psi(x)$
- Modify particle-in-a-box (P.I.B.) system to find **quantum rates**





Methodology

Solver Validation → Add Slit → Find Rates

Solver Validation

Compare known and numeric PIB Results

$$\psi(x,y) = \frac{2}{\mathrm{L}} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi y}{L}\right)$$

$$E_{n,y} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2)$$

Add Slit

Add slit and find Ψ by solving Schrödinger's Eqn.

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left\{\left(\frac{\partial^2}{\partial x^2}\right) + \left(\frac{\partial^2}{\partial y^2}\right)\right\}$$

for effusion system

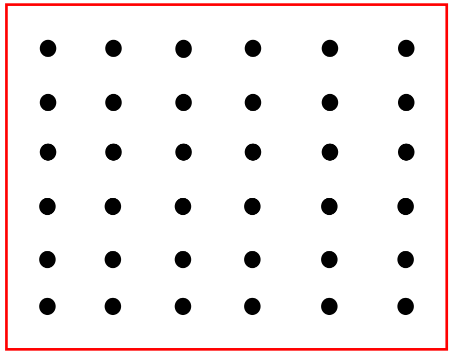
Find Rates

Find rate constants, *k(T)*

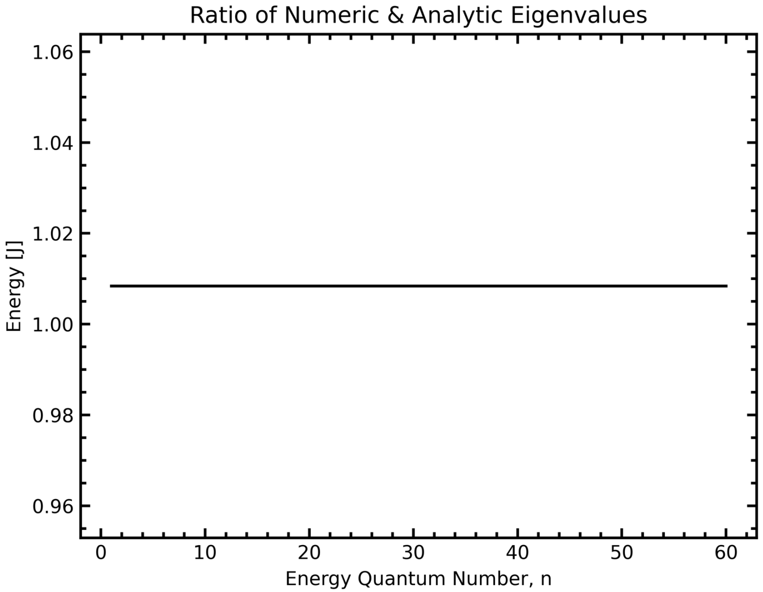
$$k_r(T) = \frac{1}{Q_r(T)} \lim_{t\to\infty} C_{fs}(t)$$

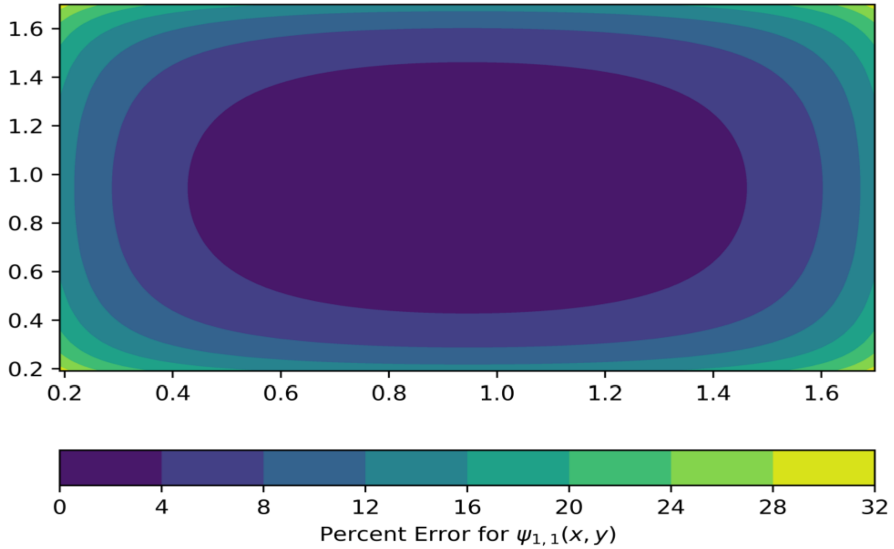
$$k_r(T) = \frac{1}{Q_r(T)} \int_0^\infty dt\, C_{ff}(t)$$

Solver Validation



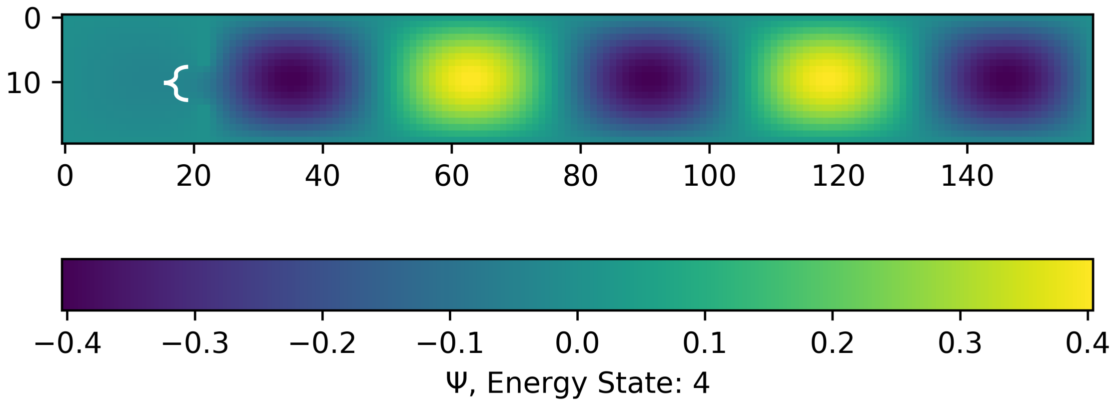
P.I.B.



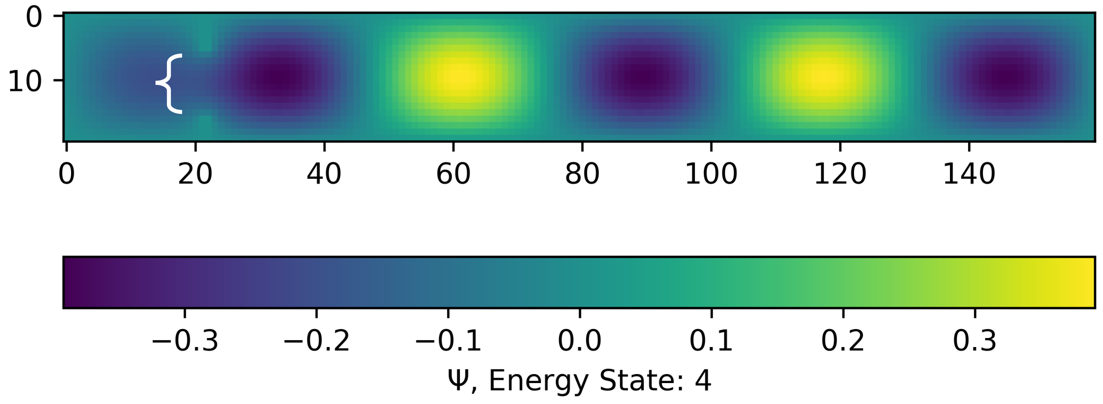


Quantum Effusion

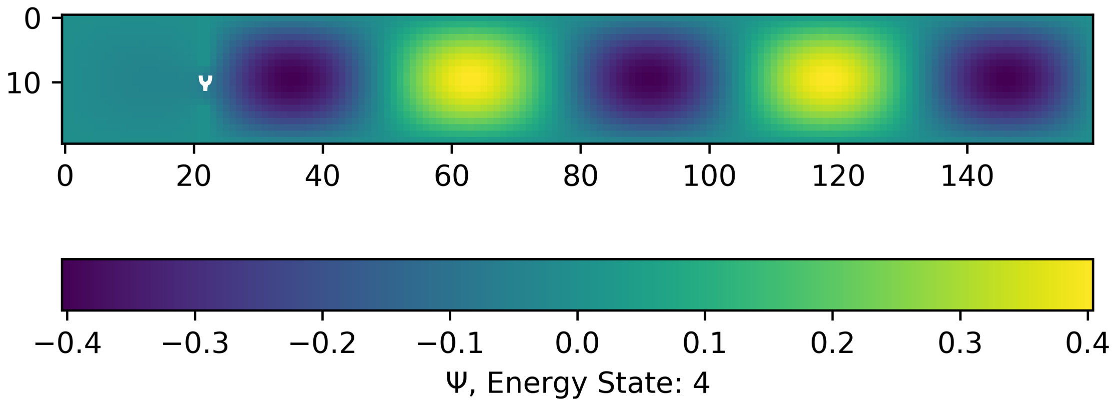
6 PT. Gap, 2 PT. Wall Thickness



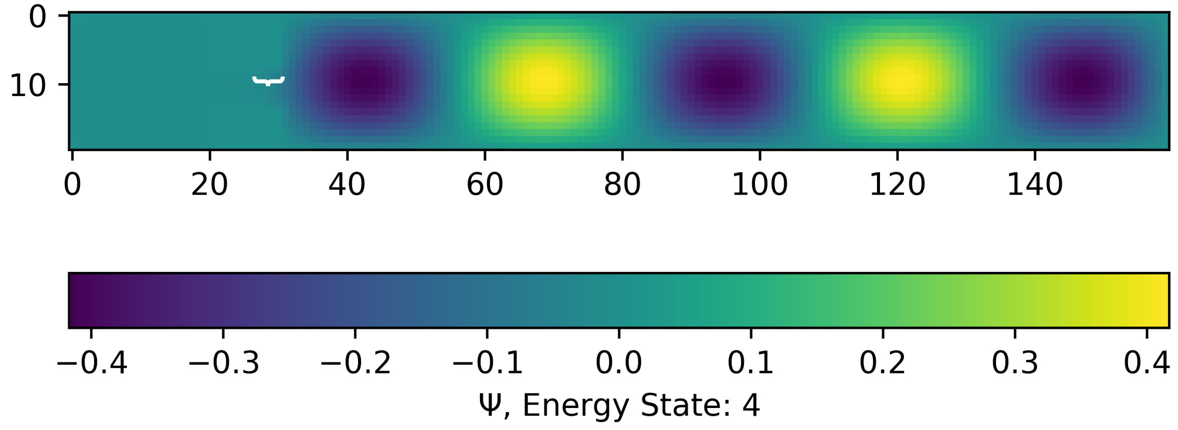
10 PT. Gap, 2 PT. Wall Thickness



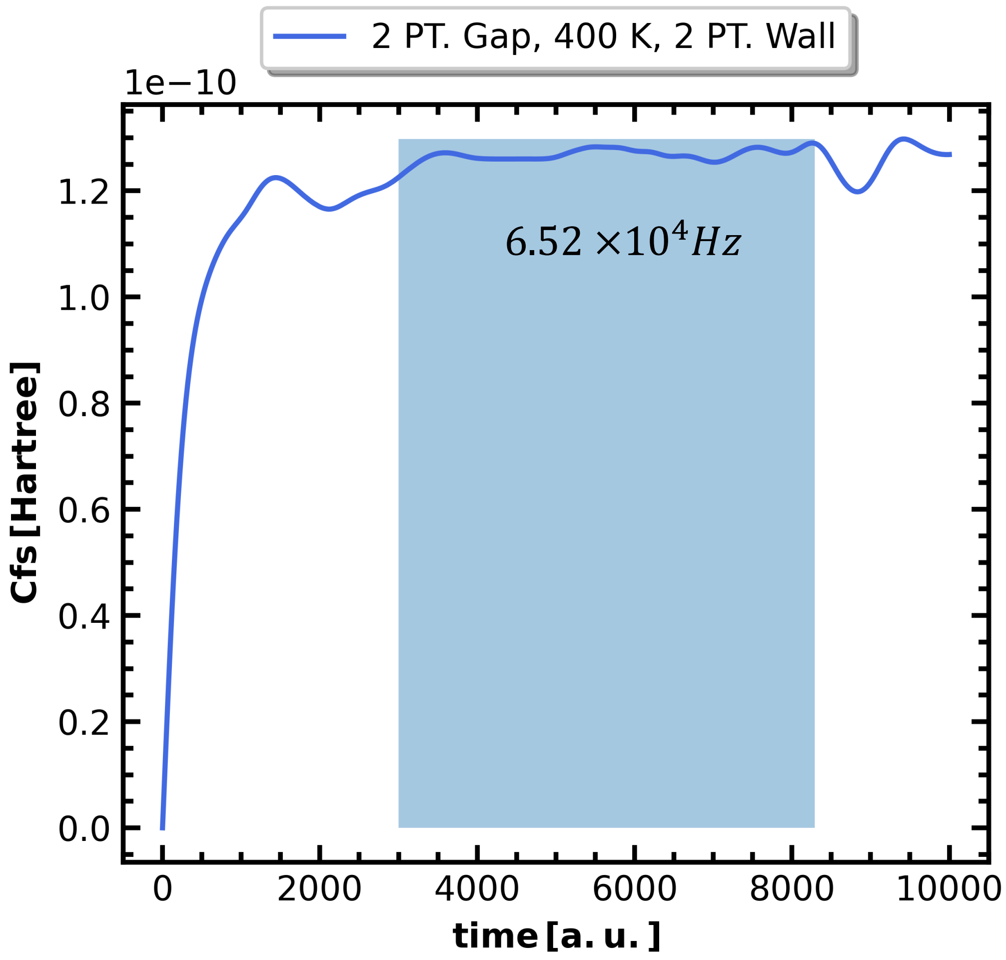
2 PT. Wall Thickness, 6 PT. Gap

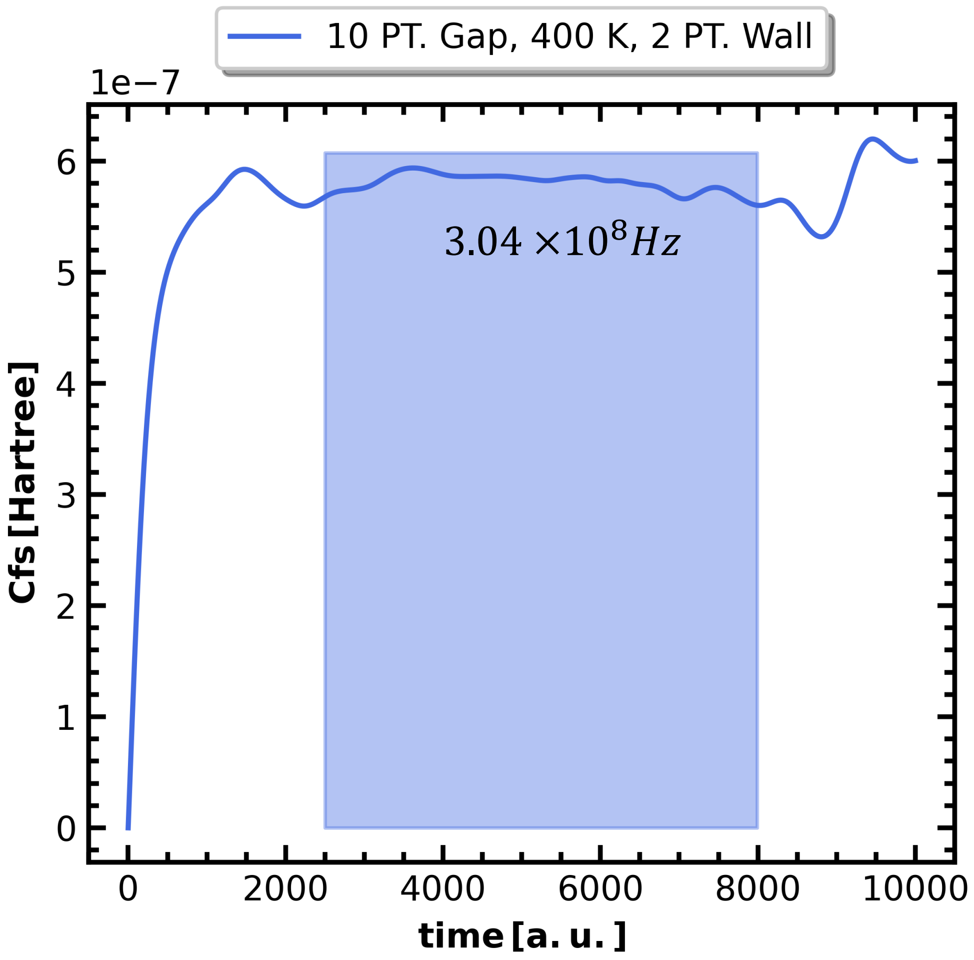


10 PT. Wall Thickness, 6 PT. Gap

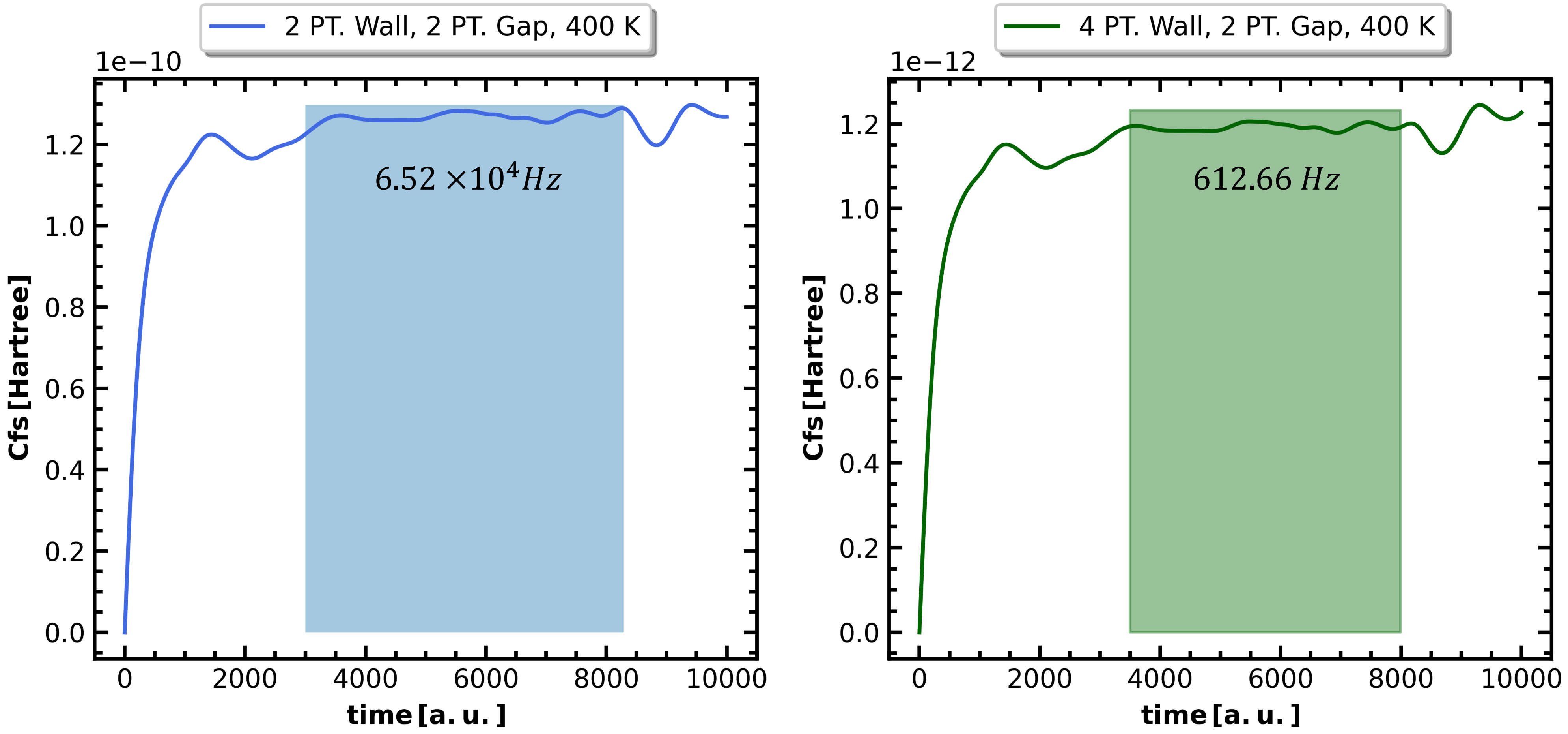


Rates at Different Gap Size

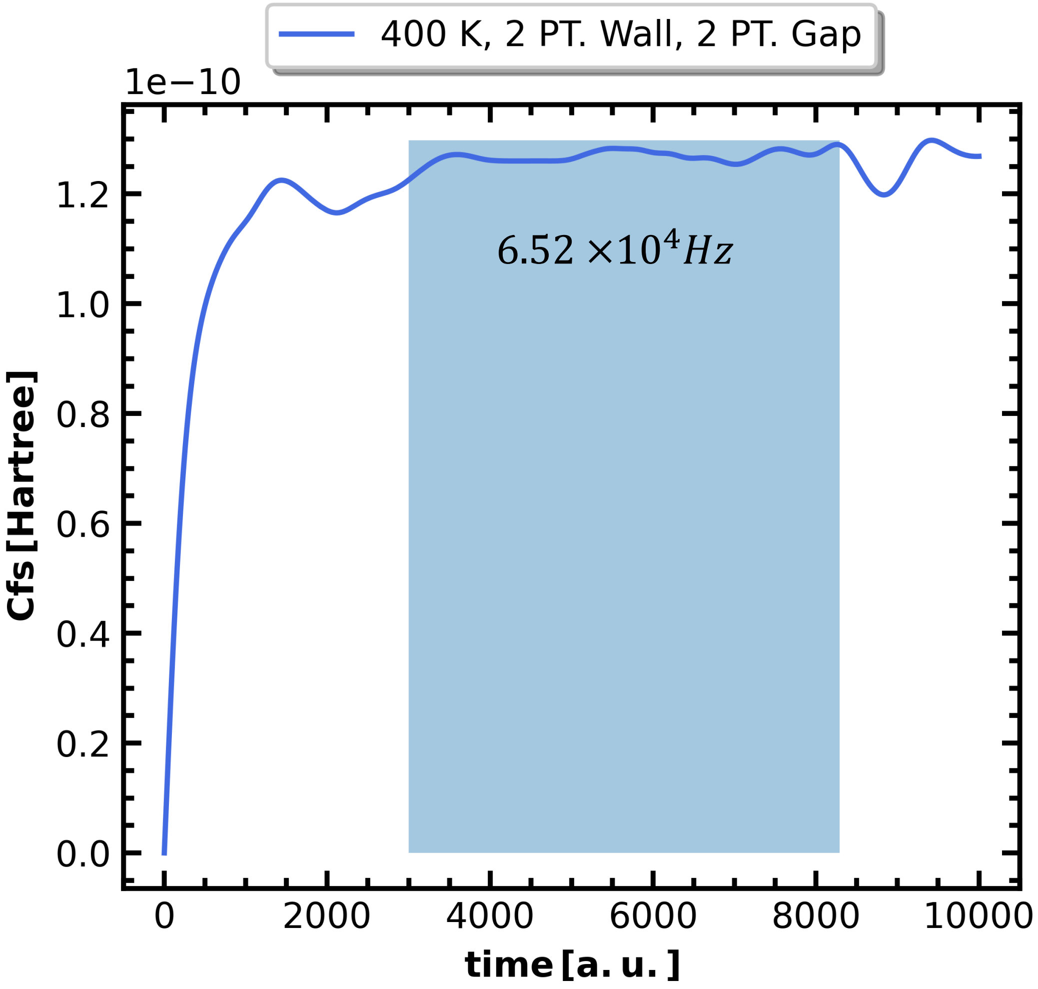


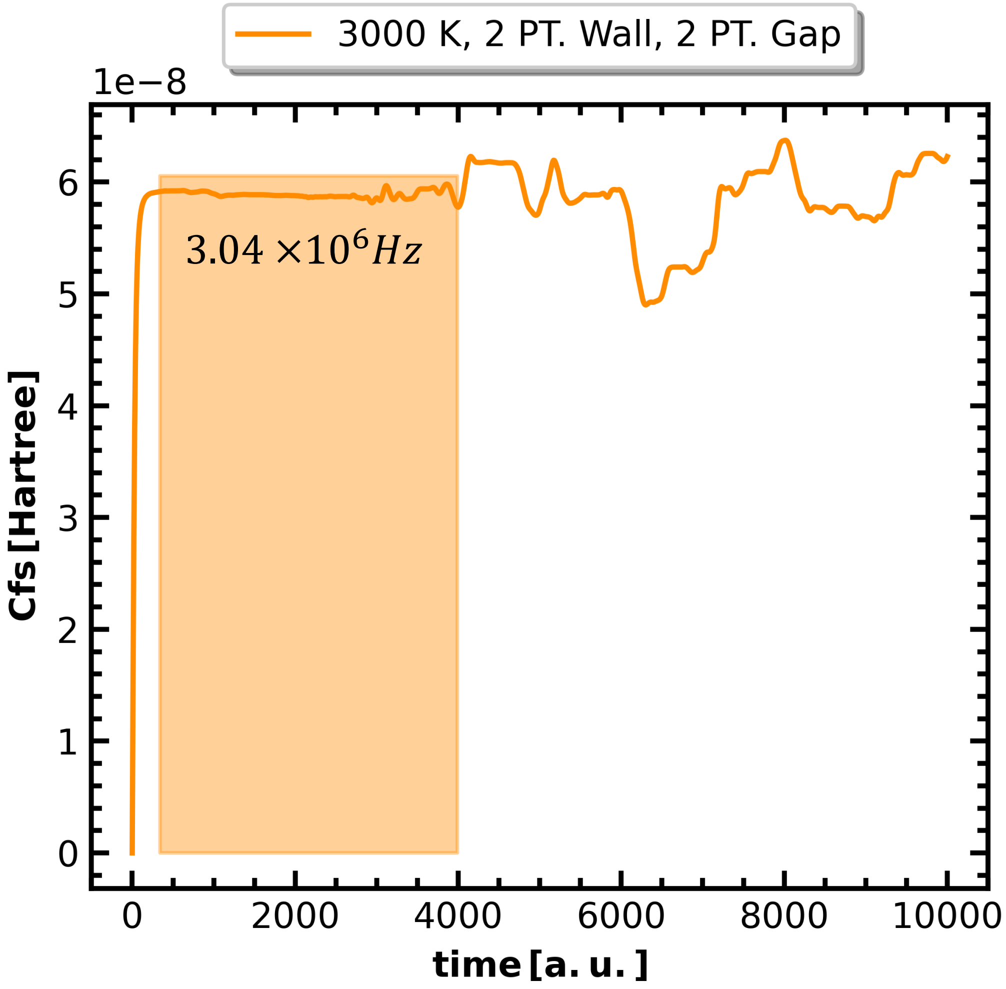


Rates at Different Wall Thickness

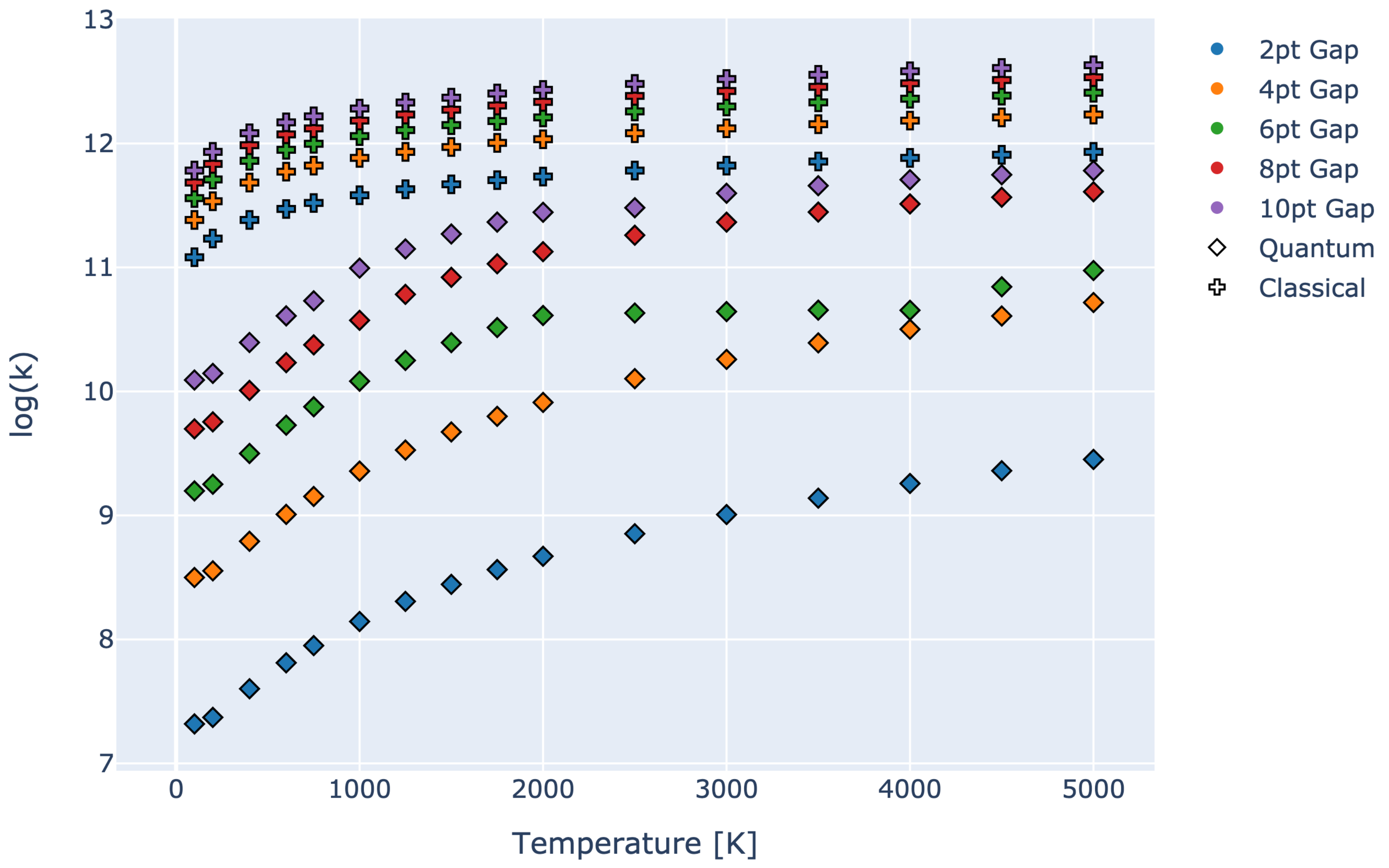


Rates at Different Temperature

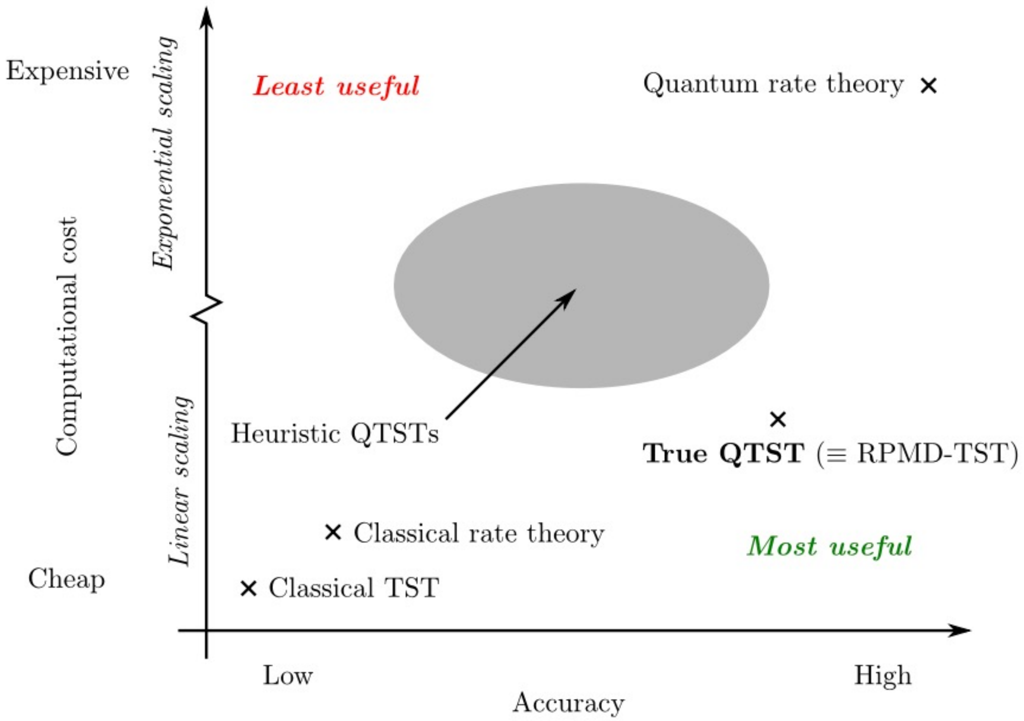




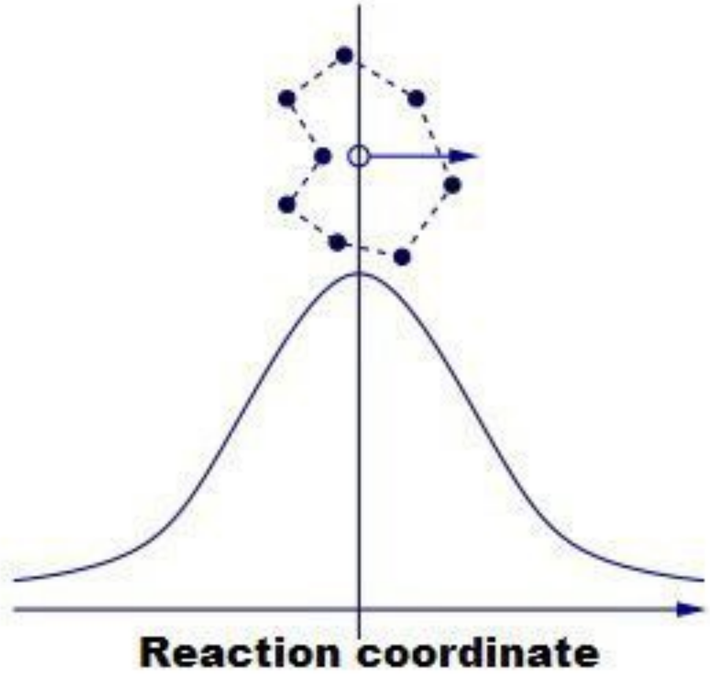
Extrapolated Rates for 0 PT. Wall Thickness



Future Work



RPMD



arXiv:1408.0996

Thank you!
Any Questions?

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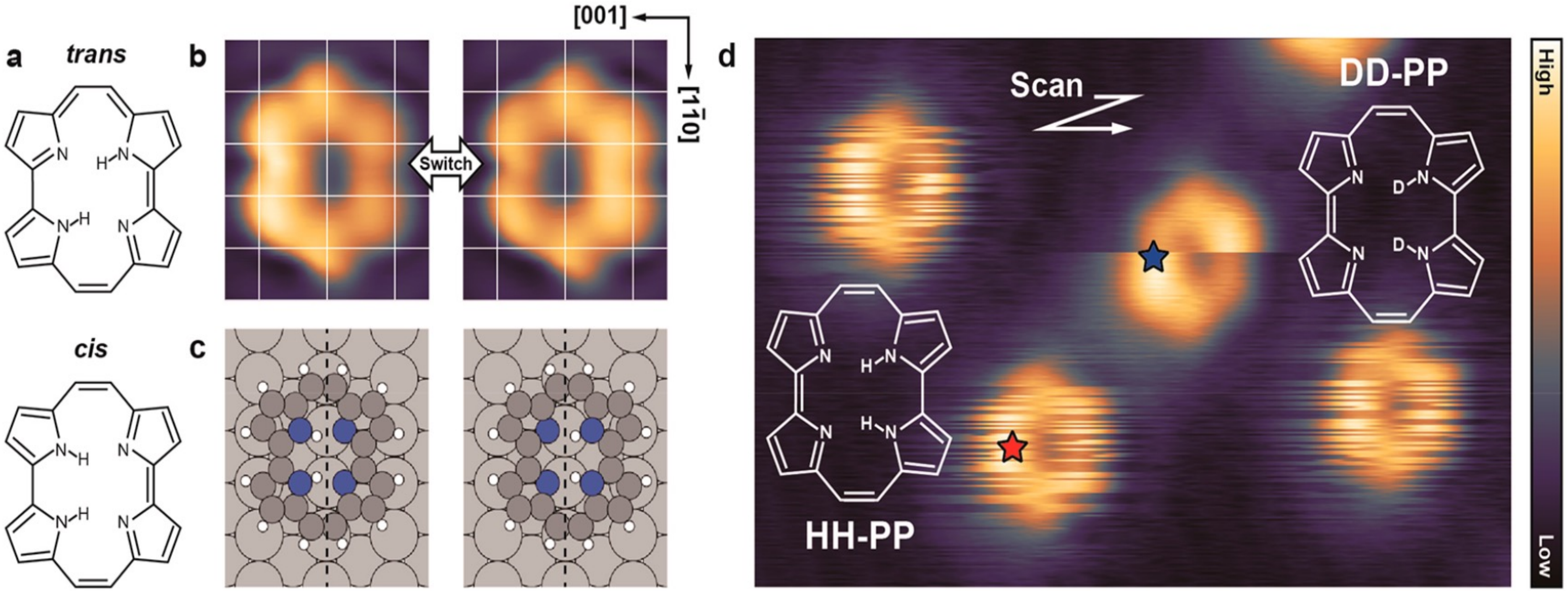
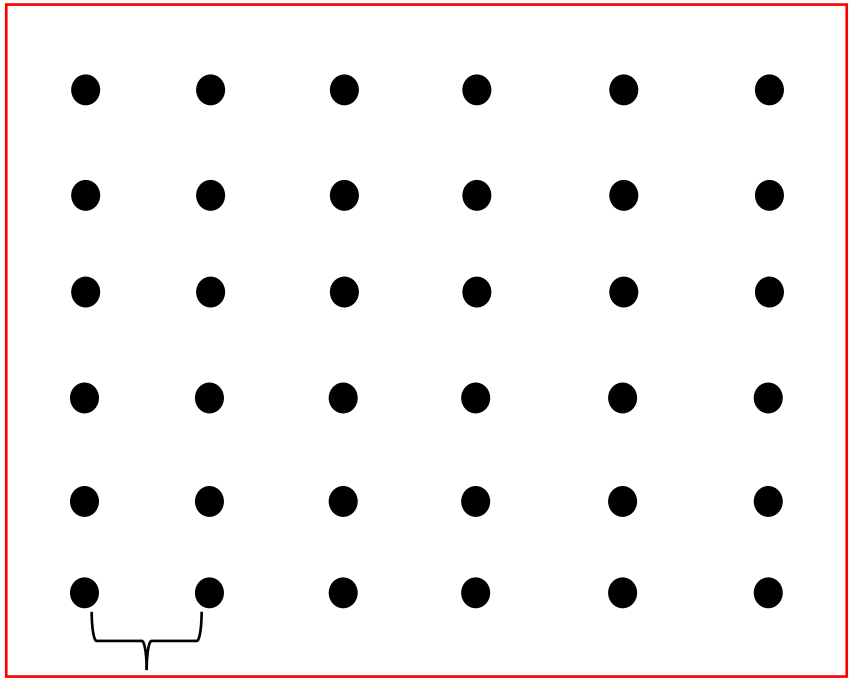
Double Hydrogen Transfer via Tunneling



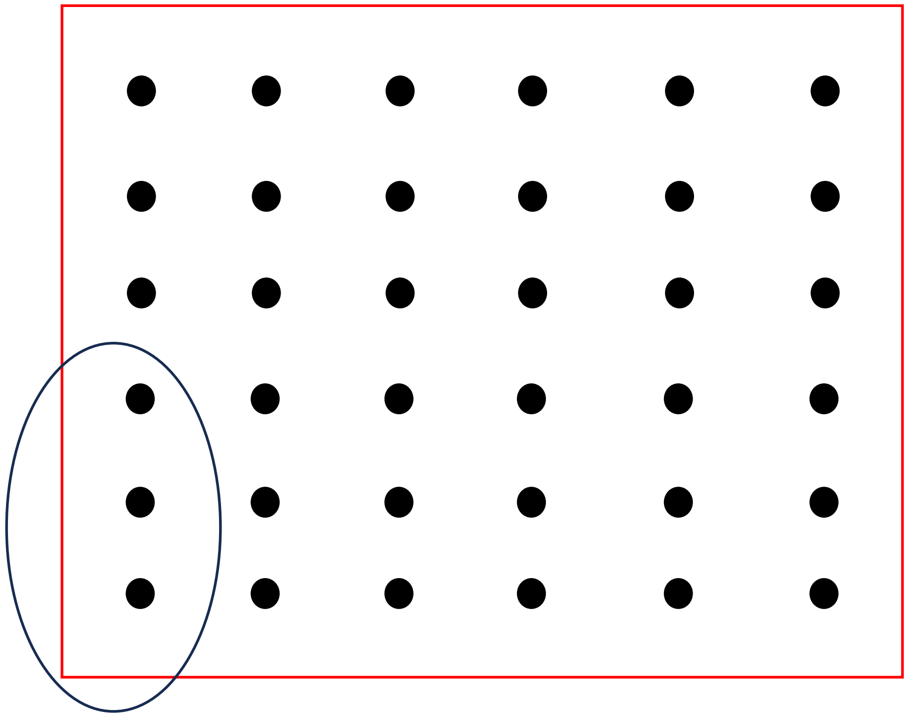
J. Am. Chem. Soc. **2017**, 139, 36, 12681–12687

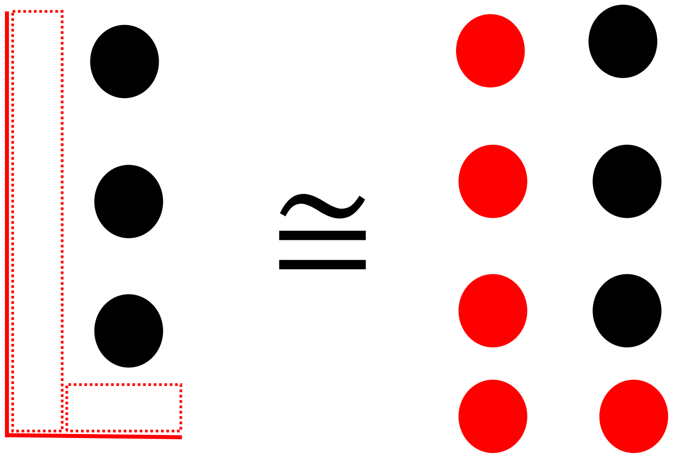
Discretization



$$dx, dy = \frac{(L_{max} - L_{min})}{nx, ny \pm 1}$$

Discretization



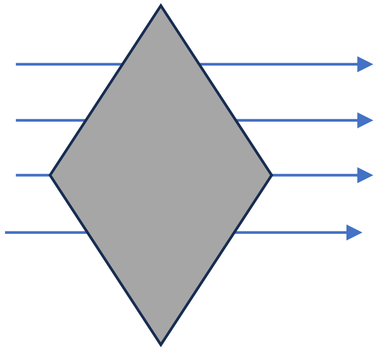


$$dx, dy = \frac{(L_{max} - L_{min})}{nx, ny \pm 1}$$

C_{fs} Functions

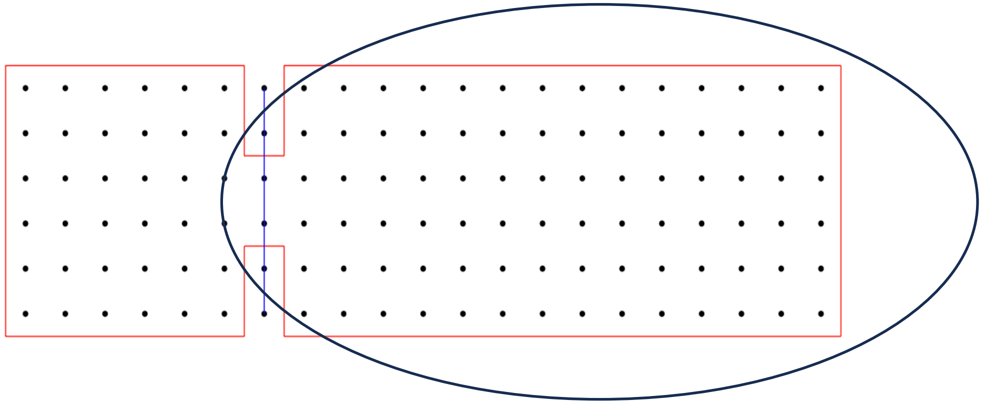
Flux:

Number of particles through an area over time



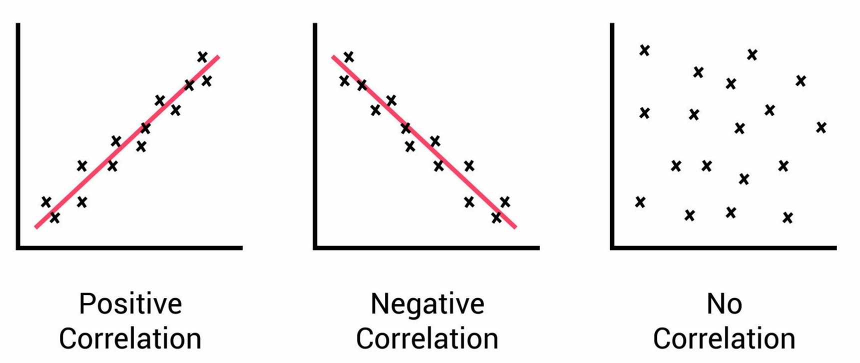
Side:

Product side of system



Correlation Function:

Describes a statistical relationship b/t quantities



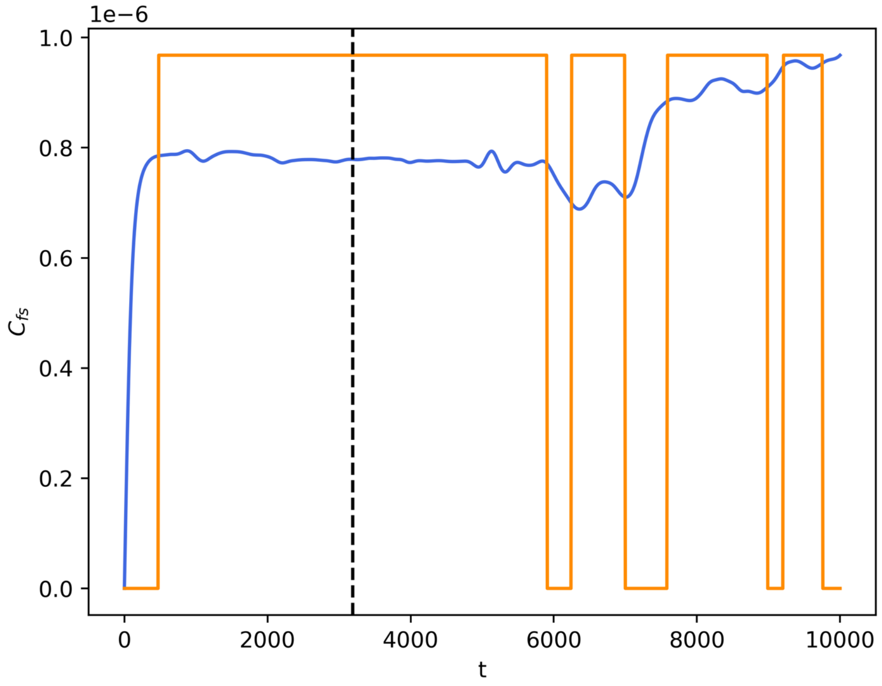
Finding Rates

Classical Approach

$$k(T) = \sqrt{\frac{k_B T}{2\pi m}} \cdot \frac{A}{V}$$

k_B: Boltzmann Constant
A: Size of slit opening
V: Area of box

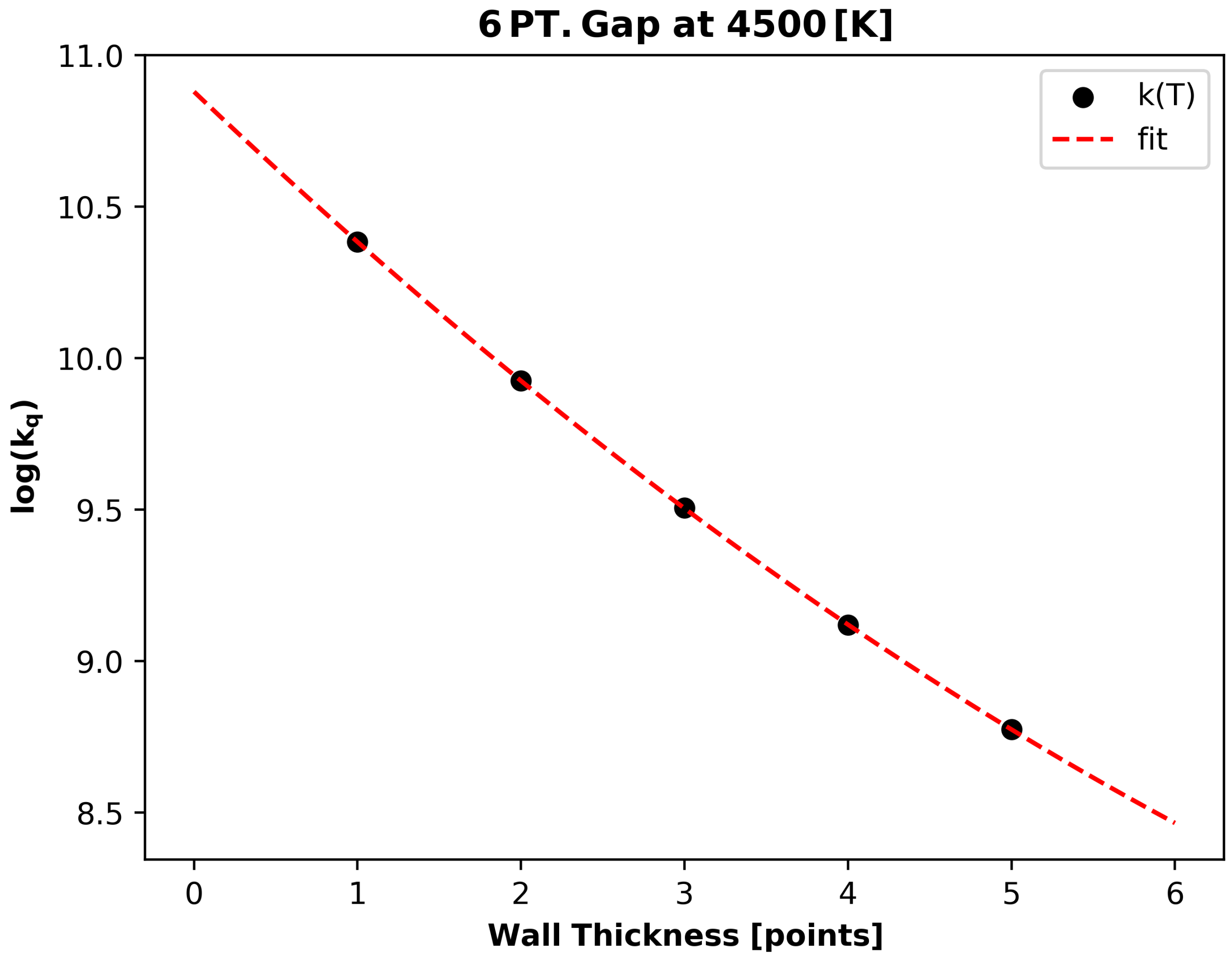
Quantum Approach



$$k(T) = \frac{1}{Q_r(T)} \lim_{t\to\infty} C_{fs}(t)$$

$$Q_r(T) = \sum_{n_x, n_y} \exp\left[-\frac{n_x^2 \pi^2 \hbar^2}{k_B T 2 m l_x^2}\right] \cdot \exp\left[-\frac{n_y^2 \pi^2 \hbar^2}{k_B T 2 m l_y^2}\right]$$

Extrapolating Rates



Kinetics using Correlation Functions

$$\hat{F}(s) = -\frac{i\hbar}{2m}\left\{\delta(x-s)\frac{d}{dx} + \frac{d}{dx}\delta(x-s)\right\}$$

$$j(s,t) \equiv \langle\psi|\,\hat{F}(s)\,|\psi\rangle = -\frac{i\hbar}{2m}\left\{\psi(s,t)^*\frac{\partial\psi(s,t)}{\partial s} - \frac{\partial\psi(s,t)^*}{\partial s}\psi(s,t)\right\}$$

$$C_{fs} = \sum_{i,j} exp\left[-\frac{\beta(E_i+E_j)}{2}\right]\frac{\hbar\sin\left(\frac{t(E_i-E_j)}{\hbar}\right)}{(E_i-E_j)}|\,\langle i|\hat{F}|j\rangle\,|^2$$

“Quantum mechanical rate constants for bimolecular reactions”.

Chem Phys **79** (Nov. 1983), pp. 4889–4898.