Theories of Molecular Processes and Spectra based on the Quantum-Classical Synergy
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Fighting the Curse of Dimensionality with Semiclassical Approaches in Reaction Rate Theory

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UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI CHIMICA

Exact Rate Constant Calculations

Energy domain

$$k(T) = \frac{1}{hQ(T)} \int_0^{+\infty} dE e^{-\beta E} N(E)$$

$$N(E) = \frac{(2\pi\hbar)^2}{2} Tr\left[\hat{F}\delta\left(E - \hat{H}\right)\hat{F}\delta\left(E - \hat{H}\right)\right]$$

Time domain

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

Semiclassical Transition State Theory[1]

$$k(T) = \frac{1}{hQ(T)} \int_0^{+\infty} dE e^{-\beta E} N(E)$$

Generalized non-separable WKB penetration integral θ.

$$\frac{iS(E)}{\hbar} = -2\theta(E)$$

$$N_{\mathrm{SCI}}(E) = \sum_{k=1}^{\infty} (-1)^{k-1} \mathrm{e}^{\frac{ikS(E)}{\hbar}} \prod_{j=1}^{F-1} \left\{ 2\sinh\left[\frac{ku_j(E)}{2}\right] \right\}^{-1}$$

Generalized non-separable vibrational partition function at TS.

$$N_{\mathrm{SCI}}^{\mathrm{SEP}}(E) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{F-1=0}^{\infty} \left\{1 - \exp\left[2\theta\left(E_n\right)\right]\right\}^{-1}$$

W. H. Miller *J. Chem. Phys* **62**(5), 1899 (1975)

Semiclassical Transition State Theory

For the non-separable case, building the action angle variables for the transition state an analog form holds[1,2]:

$$N_{SCTST}(E) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_{F-1}=0}^{\infty} \left\{1 + \exp\left[2\theta\left(E\right)\right]\right\}^{-1}$$

$$\left(n_F + \frac{1}{2}\right) = \frac{i\theta}{\pi} \longrightarrow E(n_1, \ldots, n_{F-1}, \theta) \longrightarrow \theta\left(E\right)$$

[3]

$$E\left(n_1, ..., n_F\right) = V_0 + \sum_{k=1}^{\mathrm{F}} \omega_k \left(n_k + \frac{1}{2}\right) + \sum_{k \le k'=1}^{F} X_{kk'} \left(n_k + \frac{1}{2}\right)\left(n'_k + \frac{1}{2}\right)$$

$$\omega_F = i\overline{\omega_F} \qquad X_{kF} = -i\overline{X_{kF}}$$

$$\theta\left(n_1, ..., n_{F-1}, E\right) = \frac{2\pi\Delta E}{\hbar\Omega_F\left(1 + \sqrt{1 + 4X_{FF}\Delta E/\hbar^2\Omega_F^2}\right)}$$

[1] W.H. Miller *Faraday Discussion of the Chemical Society* **62**, 40 (1977). [2] W.H. Miller *J. Chem. Phys.* **62**(5), 1899 (1975) [3] R. Hernandez, W. H. Miller, *Chem. Phys. Lett.* **214**(2), 129 (1993).

SCTST Working Formulae

$$k_{SCTST}(T) = \frac{1}{h}\frac{Q^{\dagger}_{\text{tran}}Q^{\dagger}_{\text{rot}}}{Q_{\text{tran}}Q_{\text{rot}}}\frac{\int N(E)e^{-\beta E}dE}{Q_{\text{vib}}(T)}$$

$$N_{\text{SCTST}}(E) = \sum_{n_1,n_2,\ldots,n_{F-1}=0}^{\infty} P_{\mathbf{n}}(E)$$

$$P_{n_1,\ldots,n_{F-1}}(E) = \left\{1 + \exp\left[2\theta(n_1,\ldots,n_{F-1},E)\right]\right\}^{-1}$$

$$\theta(n_1,\ldots,n_{N-1},E) = \frac{2\pi\Delta E}{\hbar\Omega_N\left(1+\sqrt{1+4X_{NN}\Delta E/\hbar^2\Omega_N^2}\right)}$$

$$\Delta E = V_0 - E + \sum_{k=1}^{F-1}\omega_k\left(n_k+\frac{1}{2}\right) + \sum_{k\le k'=1}^{F-1}X_{kk'}\left(n_k+\frac{1}{2}\right)\left(n'_k+\frac{1}{2}\right)$$

$$\hbar\Omega_F = \hbar\overline{\omega_F} - \sum_{k=1}^{F-1}\overline{X_{kF}}\left(n_k+\frac{1}{2}\right)$$

- Hessian
- Cubic + some quartic force constants

R. Hernandez, and W. H. Miller *Chem. Phys. Lett.*, **214**, 129 (1993).

SCTST - The Practical Problem

$$k(T) = \frac{1}{h} \frac{Q^{\dagger}_{\text{tran}} Q^{\dagger}_{\text{rot}}}{Q_{\text{tran}} Q_{\text{rot}}} \frac{\int N(E) e^{-\beta E} dE}{Q_{vib}(T)}$$

$$N_{\text{SCTST}}(E) = \sum_{n_1, n_2, n_{F-1}=0}^{\infty} P_{n_1,\ldots,n_{F-1}}(E)$$

Divide the energy range in bins. ↓ The j-th bin contains $\#_j$ energy levels.

$$\langle P(E_j) \rangle \simeq \frac{\sum_{\boldsymbol{n}} P_{\boldsymbol{n}}(E_j)}{\#_j} \qquad N_{\text{SCTST}}(E) \simeq \sum_{j=1}^{E/\delta E} \delta E \rho^{\dagger}(E_j) \langle P(E_j) \rangle$$

SCTST - The Practical Problem

$$k(T) = \frac{1}{h} \frac{Q^{\dagger}_{\text{tran}} Q^{\dagger}_{\text{rot}}}{Q_{\text{tran}} Q_{\text{rot}}} \frac{\int N(E) e^{-\beta E} dE}{Q_{vib}(T)}$$

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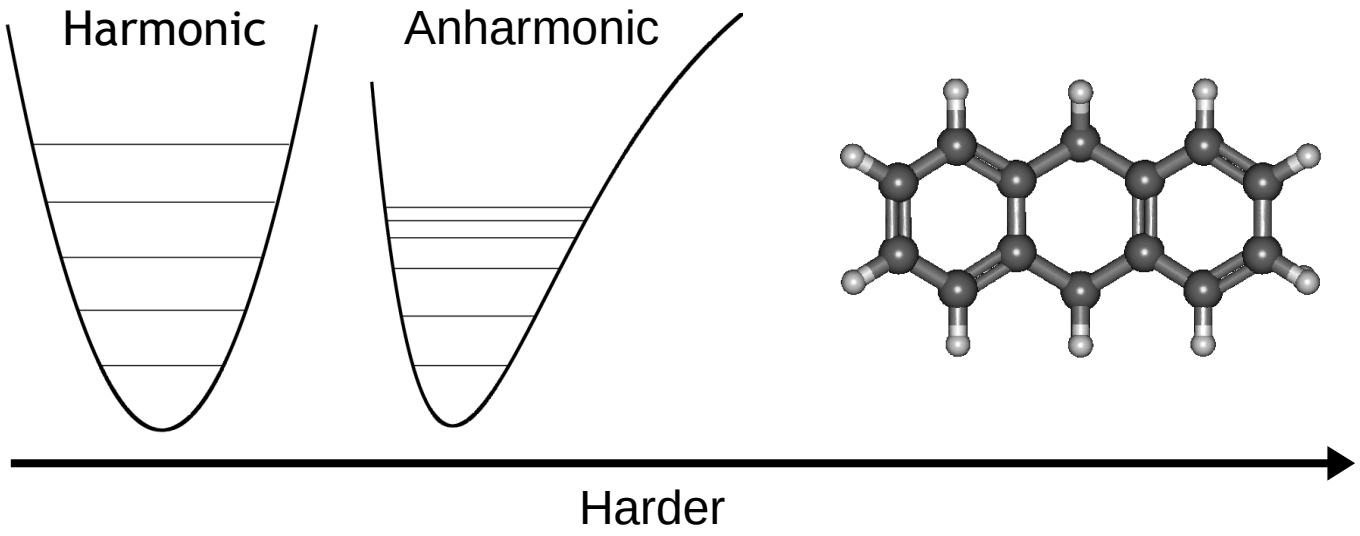
$$Q_{vib}(T) = \int \rho_{vib}(E) e^{-\beta E} dE$$

The Vibrational Density of States

The vibrational density of states $\rho_{\mathrm{vib}}(E)$ is the number of vibrational energy levels per unit energy.



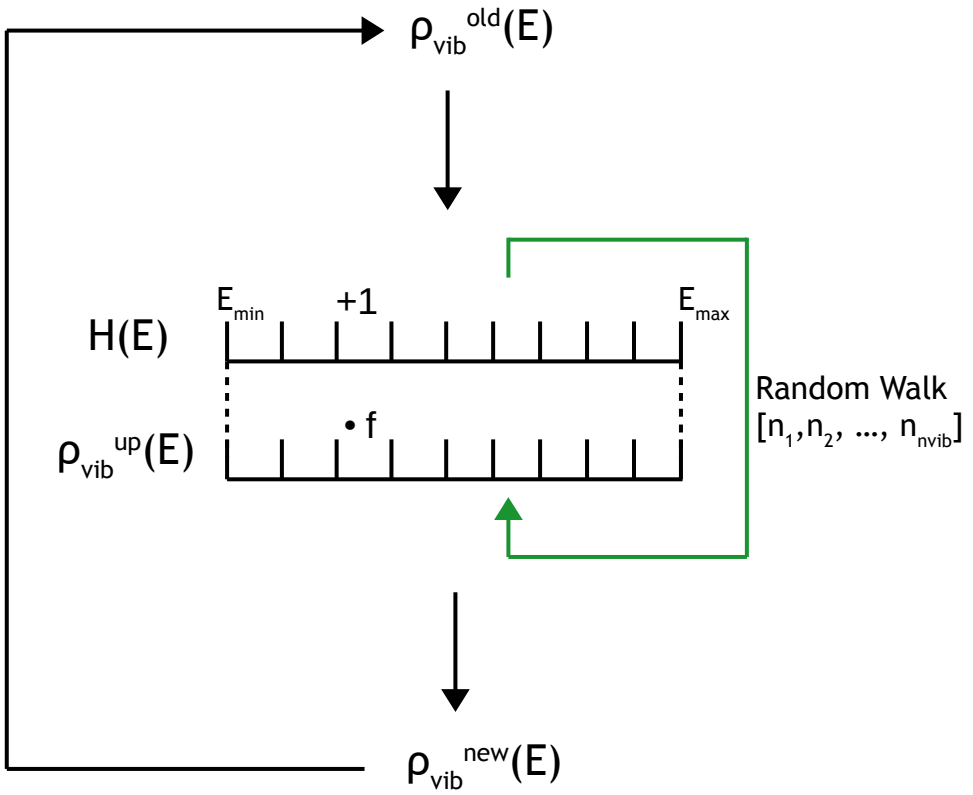
Wang Landau Monte Carlo[1] in ADenSum[2]

Prof. J. R. Barker

MultiWell Program Suite

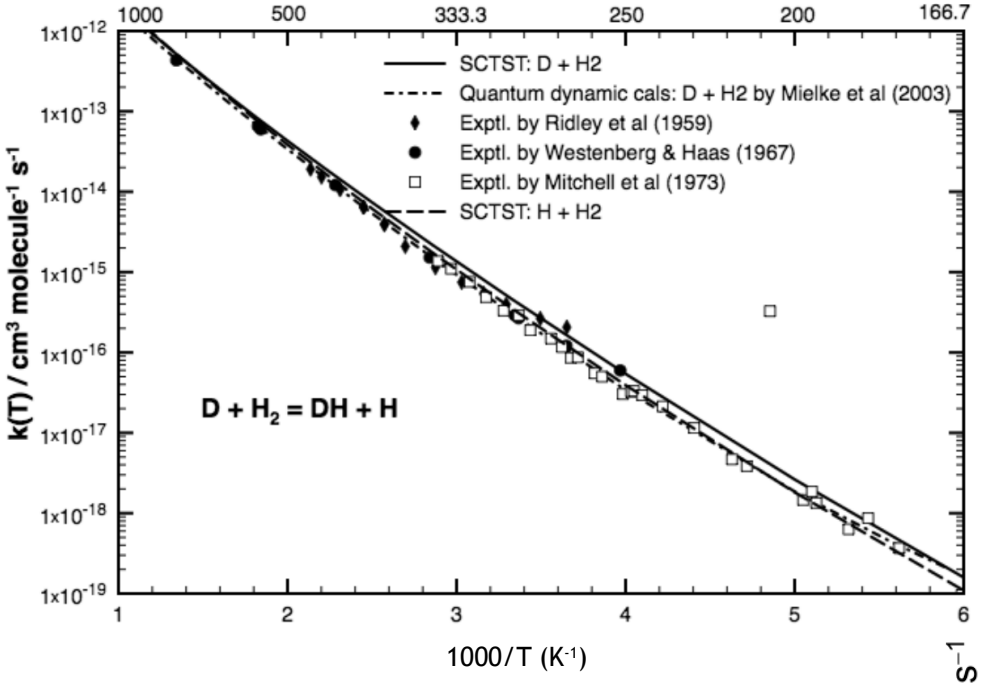
- $$E = \sum_{i=1}^{\mathrm{nvib}} \omega_i \left(n_i + \frac{1}{2} \right) + \sum_{\mathrm{i,j}=1}^{\mathrm{nvib}} X_{ij} \left(n_i + \frac{1}{2} \right) \left(n_j + \frac{1}{2} \right)$$

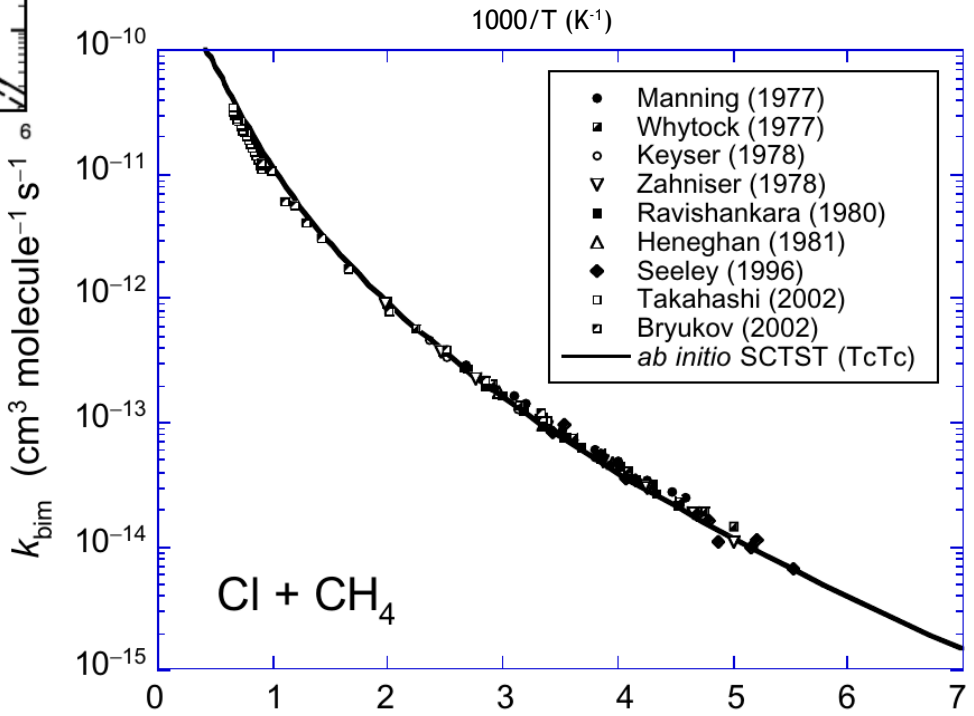
- The histogram of visits H(E) will be flat when the probability of visiting each energy bin is proportional to $1/\rho_{vib}(E)$.



[1] F. Wang, D.P. Landau *Phys. Rev. Lett.* **86**, 2050 (2001). [2] M. Basire, P. Parneix, and F. Calvo *J. Chem. Phys.* **129**, 081101 (2008).; T.L. Nguyen, and J.R. Barker *J. Phys. Chem. A.* **114**, 3718–3730 (2010).

SCTST Yelds Highly Accurate Rates





T.L. Nguyen, J.R. Barker, and J.F. Stanton. "*Atmospheric reaction rate constants and kinetic isotope effects computed using the HEAT Protocol and semi-classical transition state theory.*" Advances in Atmospheric Chemistry. 403-492 (2017).

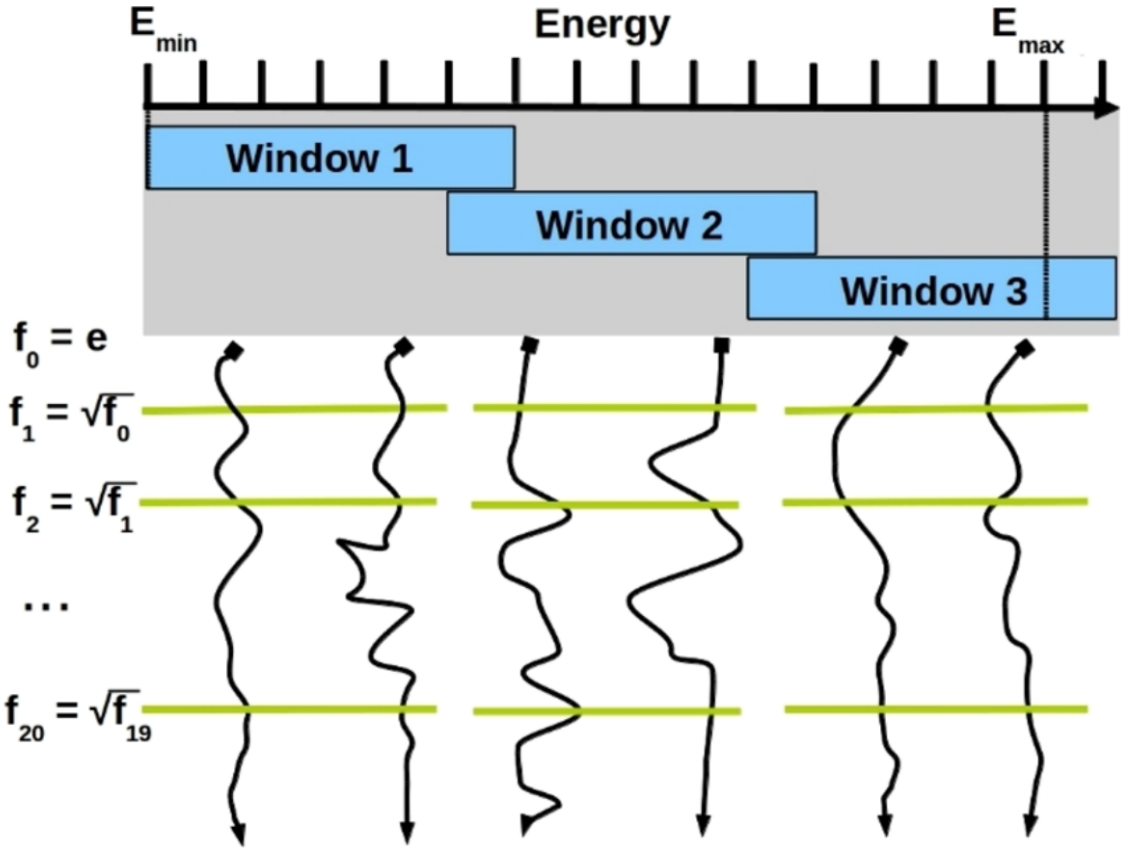
ParADenSum Parallelization Strategy

ADenSum drawbacks

- Serial code.
- Not fully optimized.
- Limited in dimensionality.

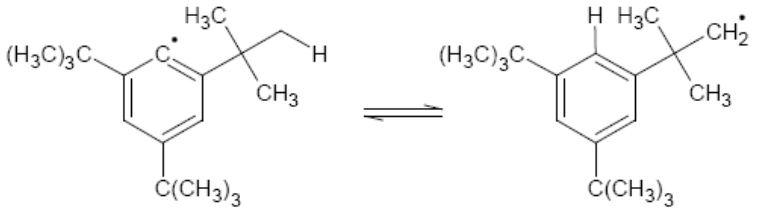
Parallelization Strategy for the new ParADenSum code

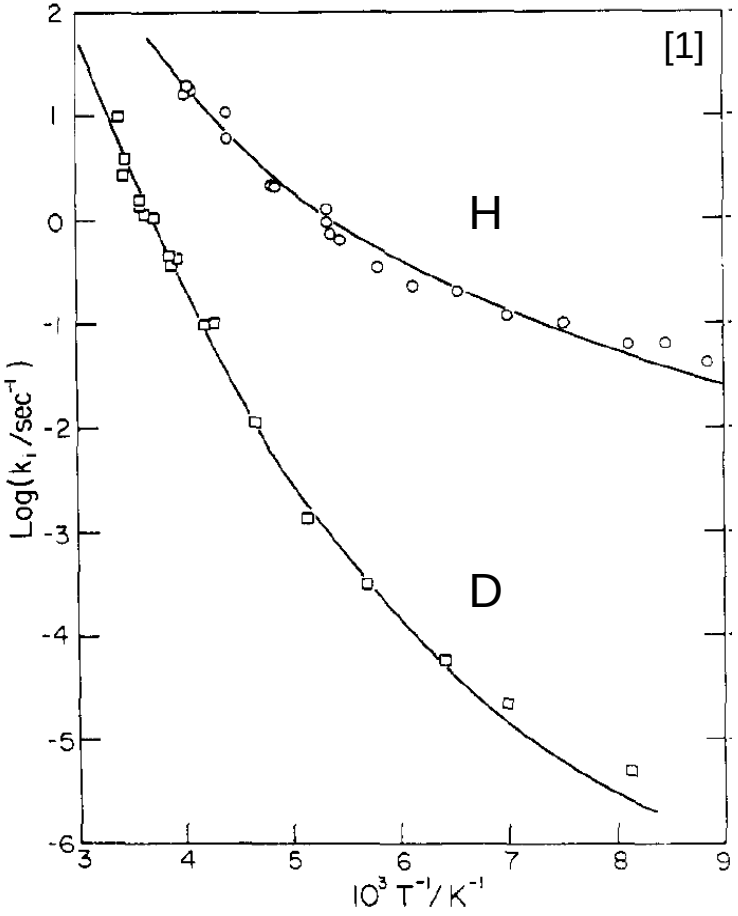
Having to search in smaller energy space the algorithm converges faster!

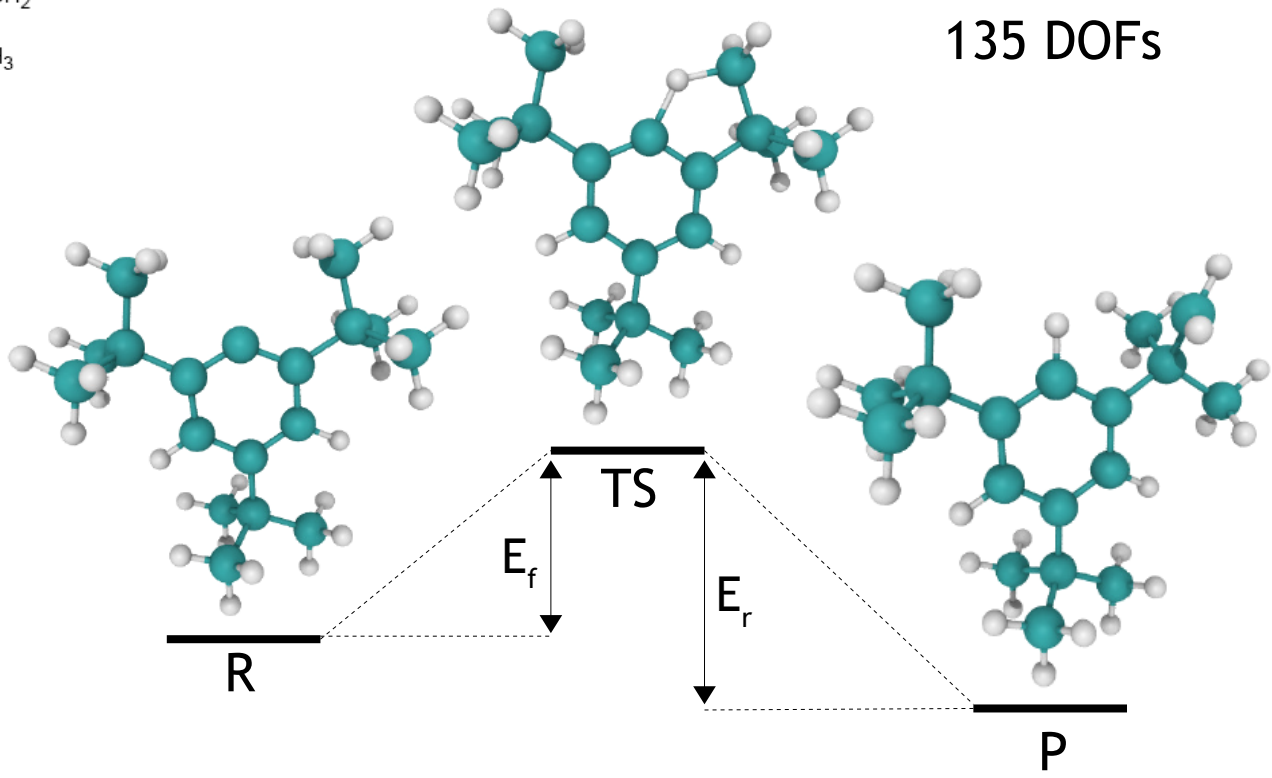


C. Aieta, F. Gabas, and M. Ceotto J. Phys. Chem. A, **120**, 4853, (2016).

SCTST Rates with ParSCTST[3]



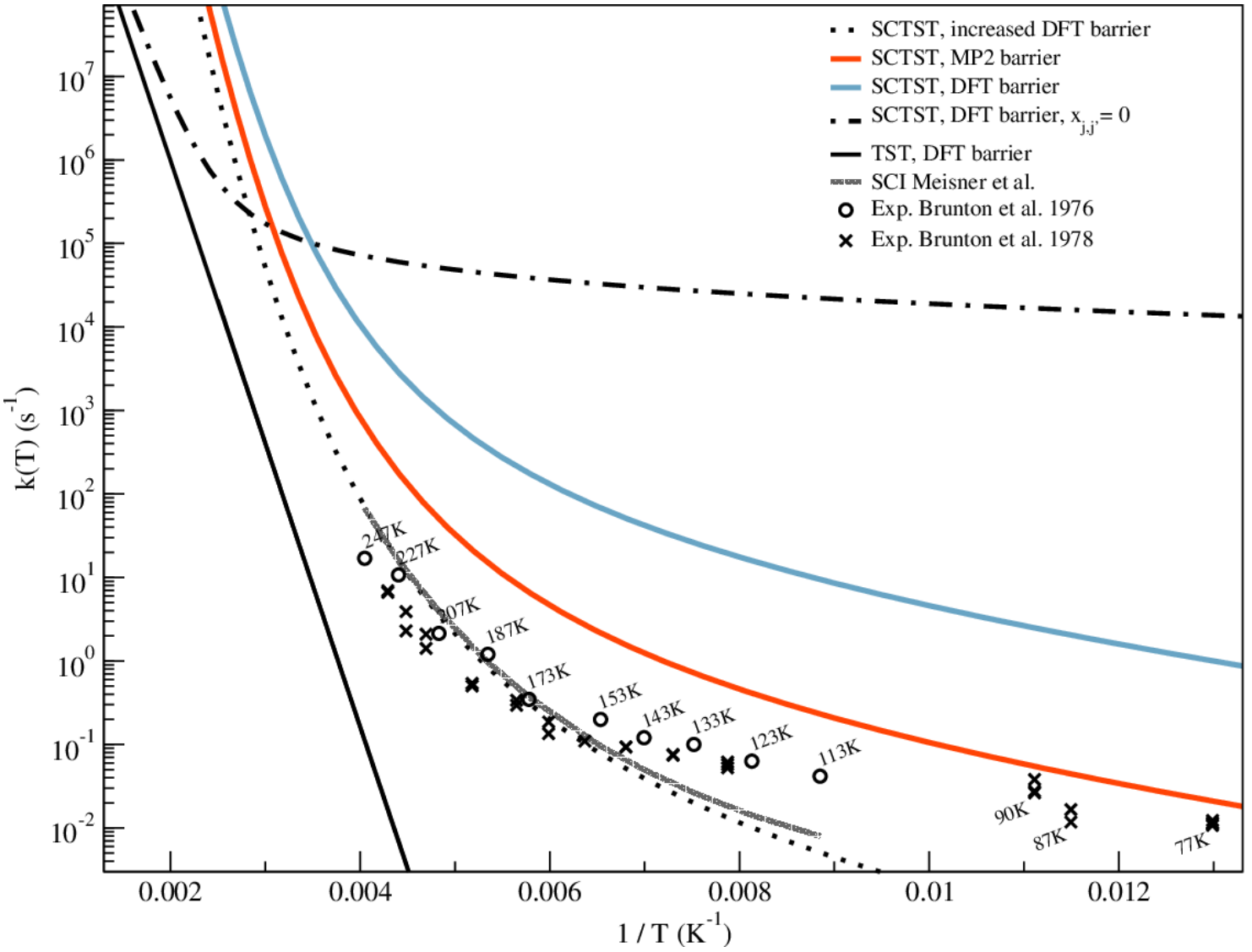




	E_f (kJ/mol)	E_r (kJ/mol)
[2] UB3LYP-D3/def2-TZVP	64.00	99.8
UB3LYP/6-311G** + D3	63.83	97.99
UB3LYP/6-311G** + D3 + PCM	63.87	98.07
UMP2/6-311G**	69.27	130.10

[1] G. Brunton, D. Griller, L. R. C. Barclay, and K. U. Ingold *JACS* **98**, 6803 (1976). [2] J. Meisner, M. N. Markmeyer, M. U. Bohner, J. Kästner *Phys. Chem. Chem. Phys.* **19**, 2308523094 (2017). [3] C. Aieta, F. Gabas, M. Ceotto *J. Chem. Theory Comput.* **15**, 4, 2142-2153 (2019).

SCTST Rates with ParSCTST



- **Barriers and harmonic frequencies:**

- UB3LYP+D3 / 6-311G**

- MP2 / 6-311G**

- UB3LYP+D3 /def2TZVP

- $X_{k,k'}$:

UB3LYP+D3 / 6-311G**

C. Aieta, F. Gabas, M. Ceotto *J. Chem. Theory Comput.* **15**, 4, 2142-2153 (2019); G. Burton, D. Griller, L.R.C. Barclay, and K.U. Igold *J. Am. Chem. Soc.* **98**, 22 (1976); G. Brunton, J. A. Gray, D. Griller, L. Bar lay, K. Ingold *J. Am. Chem. Soc.* **100** , 41974200 (1978); J. Meisner, M. N. Markmeyer, M. U. Bohner, J. Kästner *Phys. Chem. Chem. Phys.* **19**, 2308523094 (2017).

General Parallel Algorithm to compute $X_{k,k'}$

Anharmonic couplings for transition states (GVPT2+K)

$$\chi_{kk} = \frac{\hbar^2}{16\omega_k^2}\left[f_{kkkk} + \frac{f_{kkN}^2}{\tilde{\omega}_N^2}\left(\frac{8\omega_k^2 + 3\tilde{\omega}_N^2}{4\omega_k^2 + \tilde{\omega}_N^2}\right) - \sum_{m=1}^{N-1}\frac{f_{kkm}^2}{\omega_m^2}\left(2 + \frac{\omega_m}{2(2\omega_k + \omega_m)} - \frac{\omega_m}{2(2\omega_k - \omega_m)}\right)\right]$$

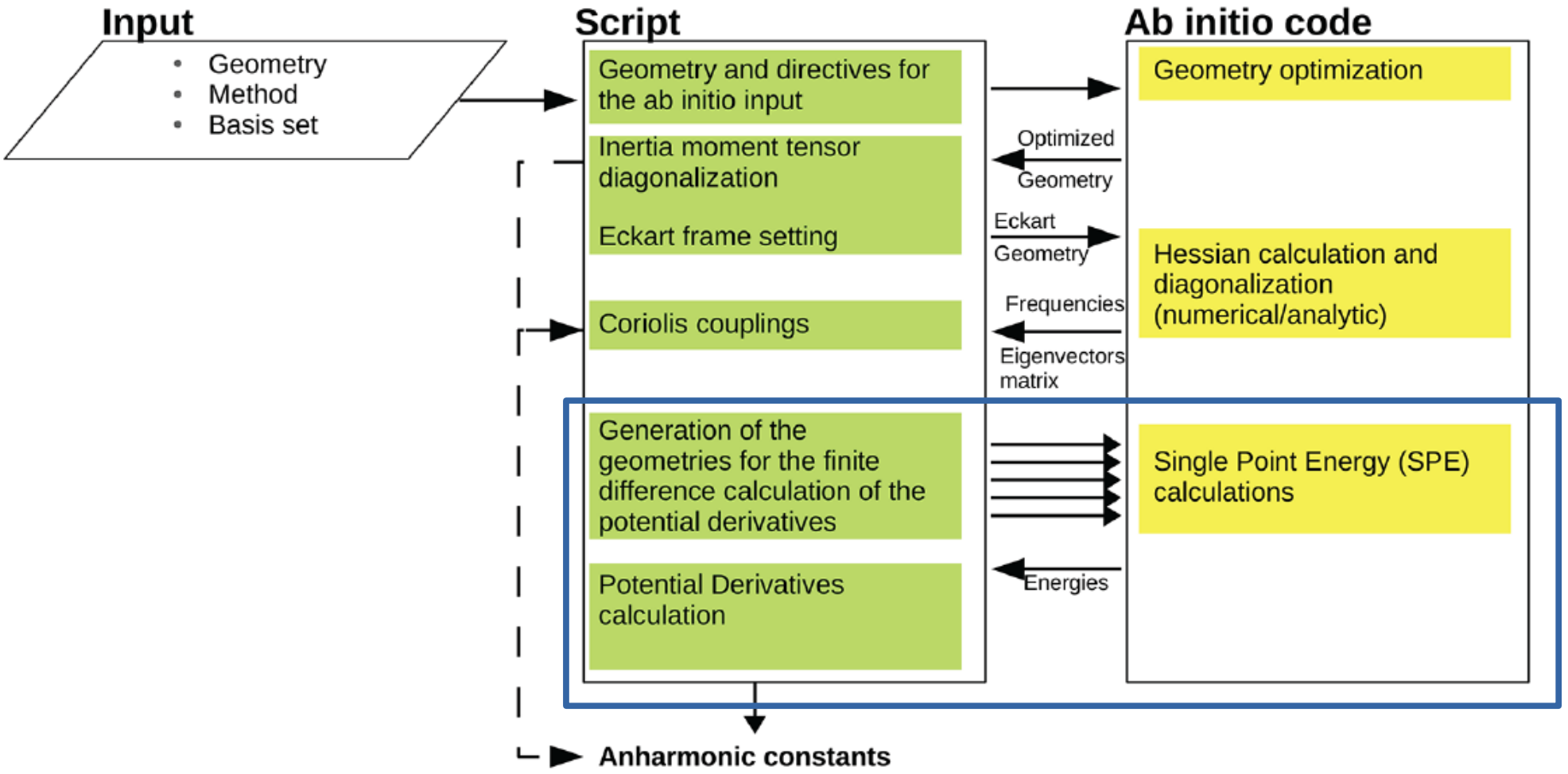
$$\chi_{kk'} = \frac{\hbar^2}{4\omega_k\omega_{k'}}\left[f_{kkk'k'} + \frac{f_{kkN}f_{k'k'N}}{\tilde{\omega}_N^2} + \frac{2f_{kk'N}^2(\omega_k^2 + \omega_{k'}^2 + \tilde{\omega}_N^2)}{[(\omega_k + \omega_{k'})^2 + \tilde{\omega}_N^2][(\omega_k - \omega_{k'})^2 + \tilde{\omega}_N^2]} - \sum_{m=1}^{N-1}\frac{f_{kkm}f_{k'k'm}}{\omega_m^2} - \sum_{m=1}^{N-1}\frac{f_{kk'm}^2}{2\omega_m}\left(\frac{1}{\omega_k + \omega_{k'} + \omega_m} - \frac{1}{\omega_k + \omega_{k'} - \omega_m} + \frac{1}{\omega_k - \omega_{k'} + \omega_m} - \frac{1}{\omega_k - \omega_{k'} - \omega_m}\right)\right] + \left(\frac{\omega_k}{\omega_{k'}} + \frac{\omega_{k'}}{\omega_k}\right)\sum_\alpha B_\alpha(\zeta_{kk'}^\alpha)^2$$

- Harmonic vibrational frequencies
- Cubic force constants
- Some quartic force constants
- Rotational constants
- Coriolis couplings

+

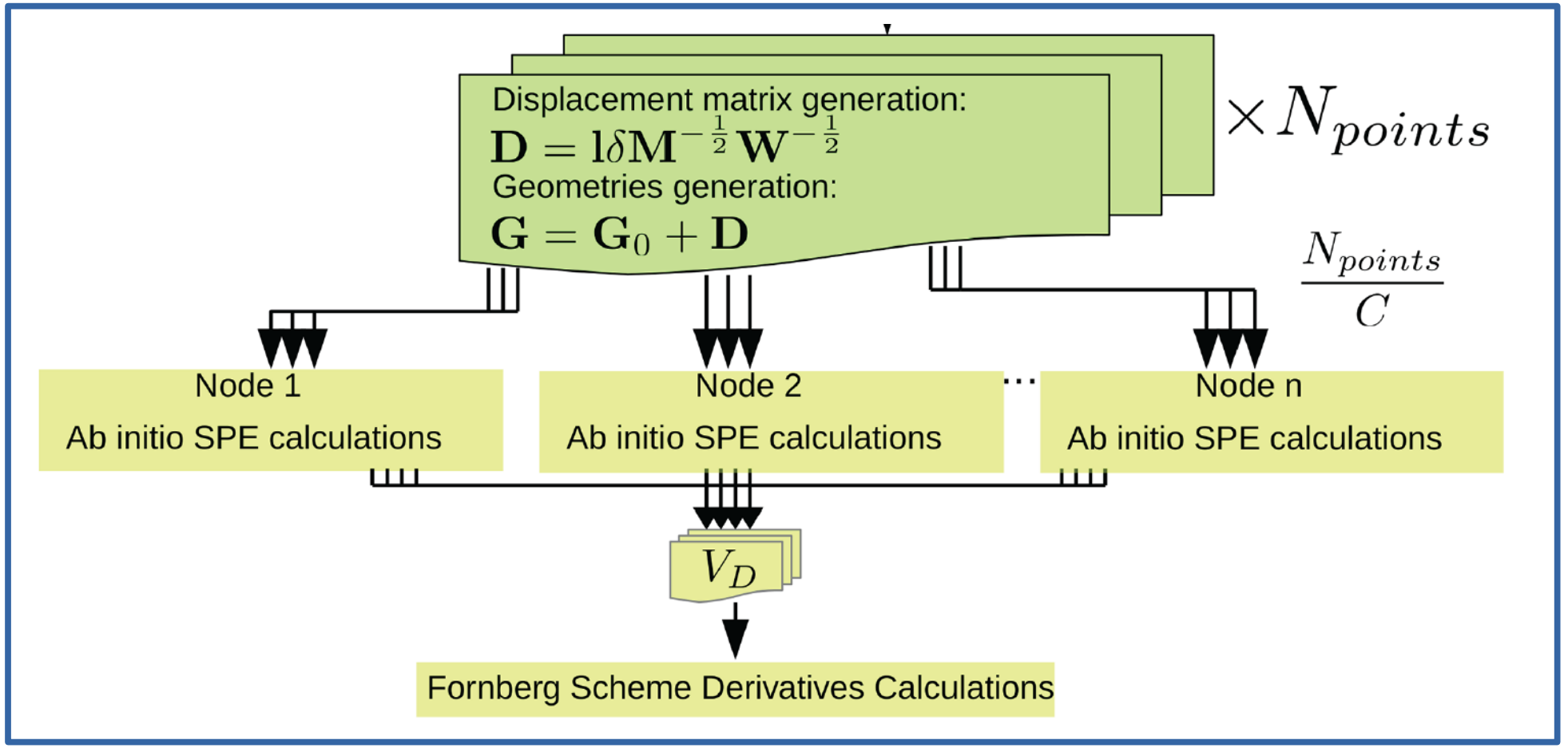
Proper resonance treatment

General Parallel Algorithm to compute $X_{k,k'}$



G. Mandelli, C. Aieta, M. Ceotto *J. Chem. Theory Comput.* **18**, 623 (2022).

General Parallel Algorithm to compute $X_{k,k'}$

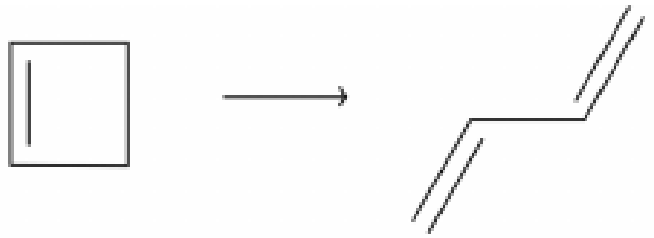


G. Mandelli, C. Aieta, M. Ceotto *J. Chem. Theory Comput.* **18**, 623 (2022).

Study of Heavy Atom Tunneling (HAT) Reactions

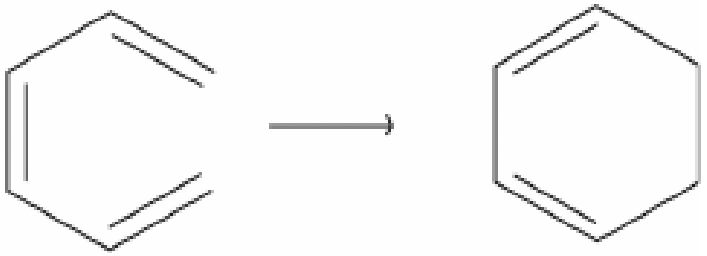
- R1: Cyclobutene ring opening reaction

  10 atoms



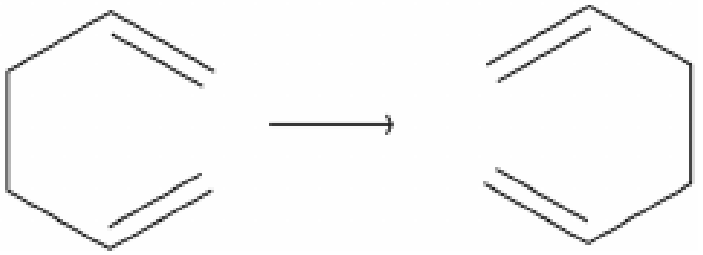
- R2: cis-1,3,5-hexatriene electrocyclic ring closing reaction

  14 atoms



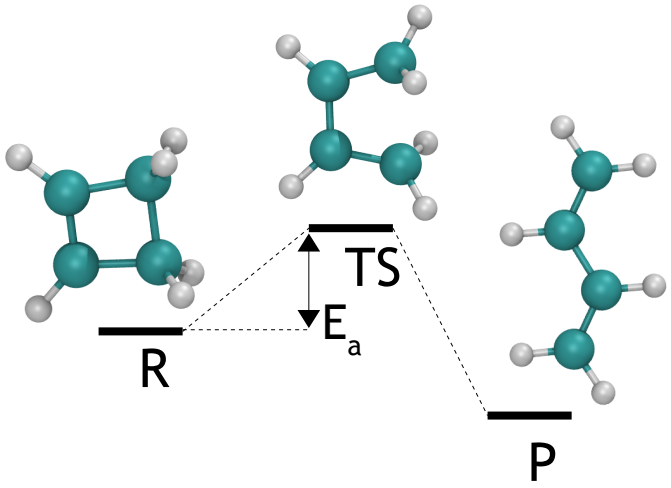
- R3: [1,5]-Cope rearrangement of the 1,5-hexadiene molecule

  16 atoms

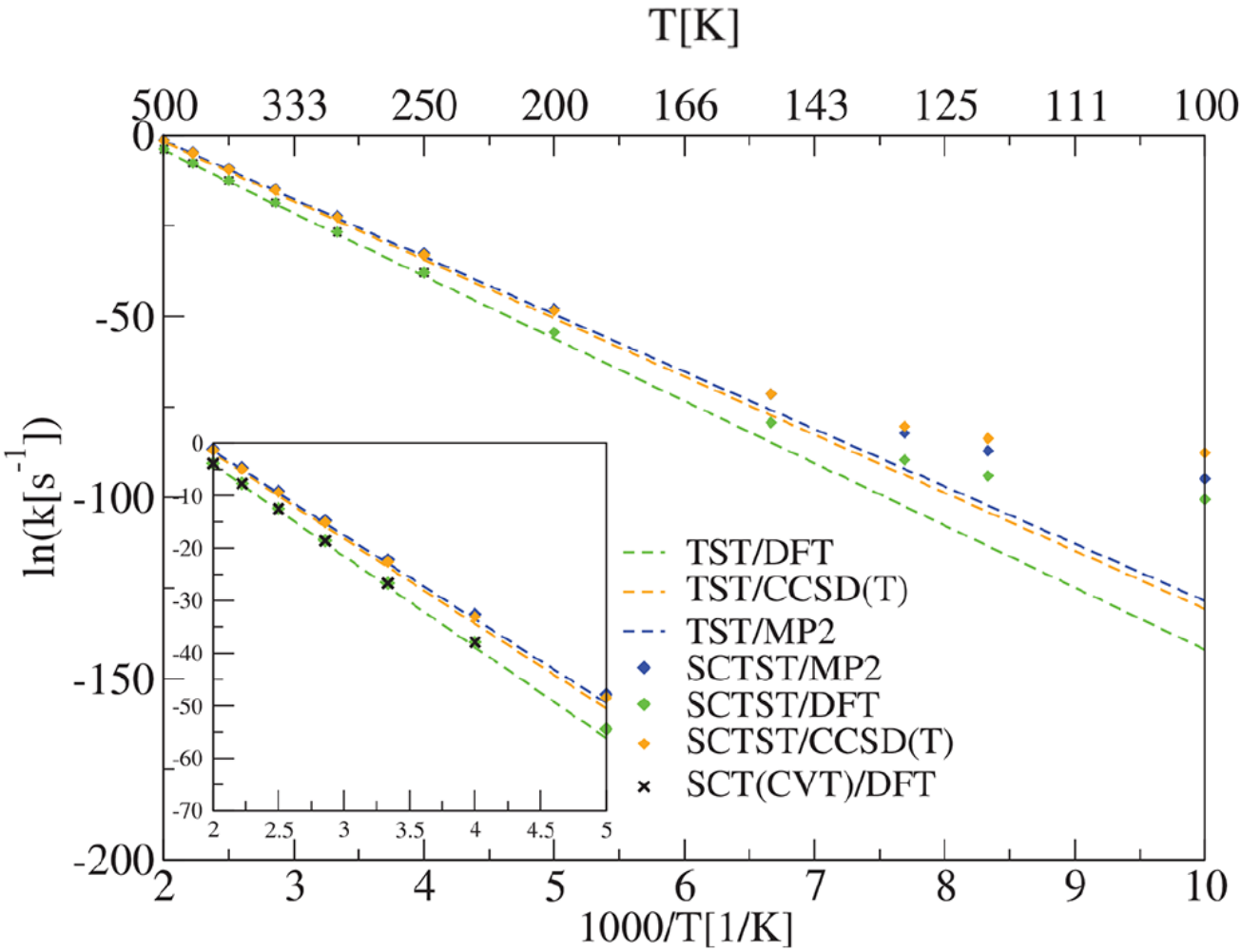


C. Doubleday, R. Armas, D. Walker, C. V. Cosgriff, E.M. Greer *Angew. Chem.* **129**,13279 (2017); C. Castro, W. L. Karney *Angew. Chem. Int. Ed.* **59**, 8355 (2020).

R1: 10-atom HAT Reaction up to CCSD(T) level of theory



level of theory/basis set	E_a [kcal/mol]
B3LYP/6-31G*	33.9
MP2/aug-cc-pVDZ	31.2
CCSD(T)/aug-cc-pVDZ	31.7
experiment (8−14 Torr)	32.5 ± 0.5
experiment (100 Torr)	32.5 ± 0.4
experiment (1500 Torr)	32.9 ± 0.7
experiment (5 Torr)	32.7 ± 0.2



G. Mandelli, C. Aieta, M. Ceotto *J. Chem. Theory Comput.* **18**, 623 (2022). C. Doubleday, R. Armas, D. Walker, C. V. Cosgriff, E.M. Greer *Angew. Chem.* **129**,13279 (2017);

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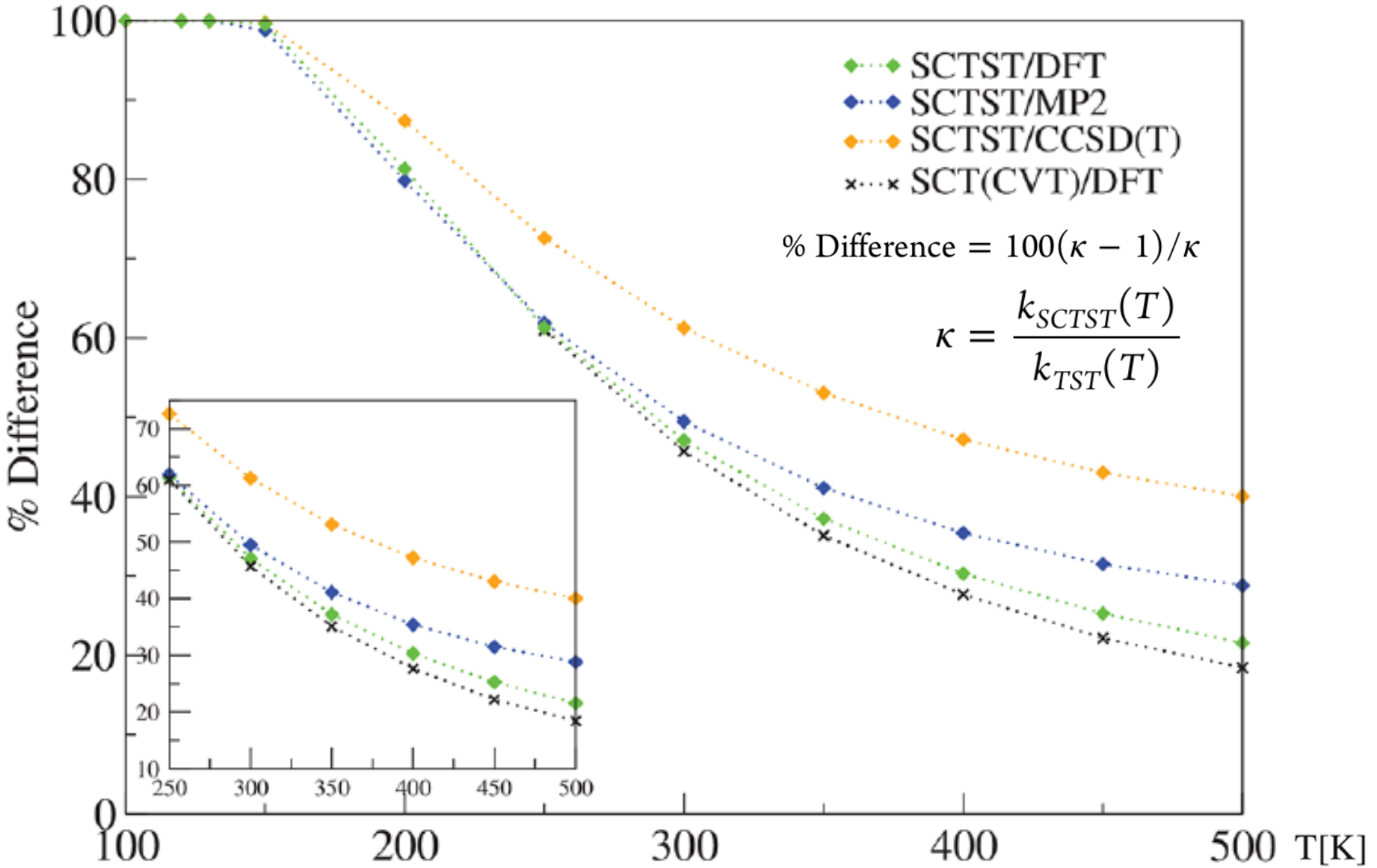
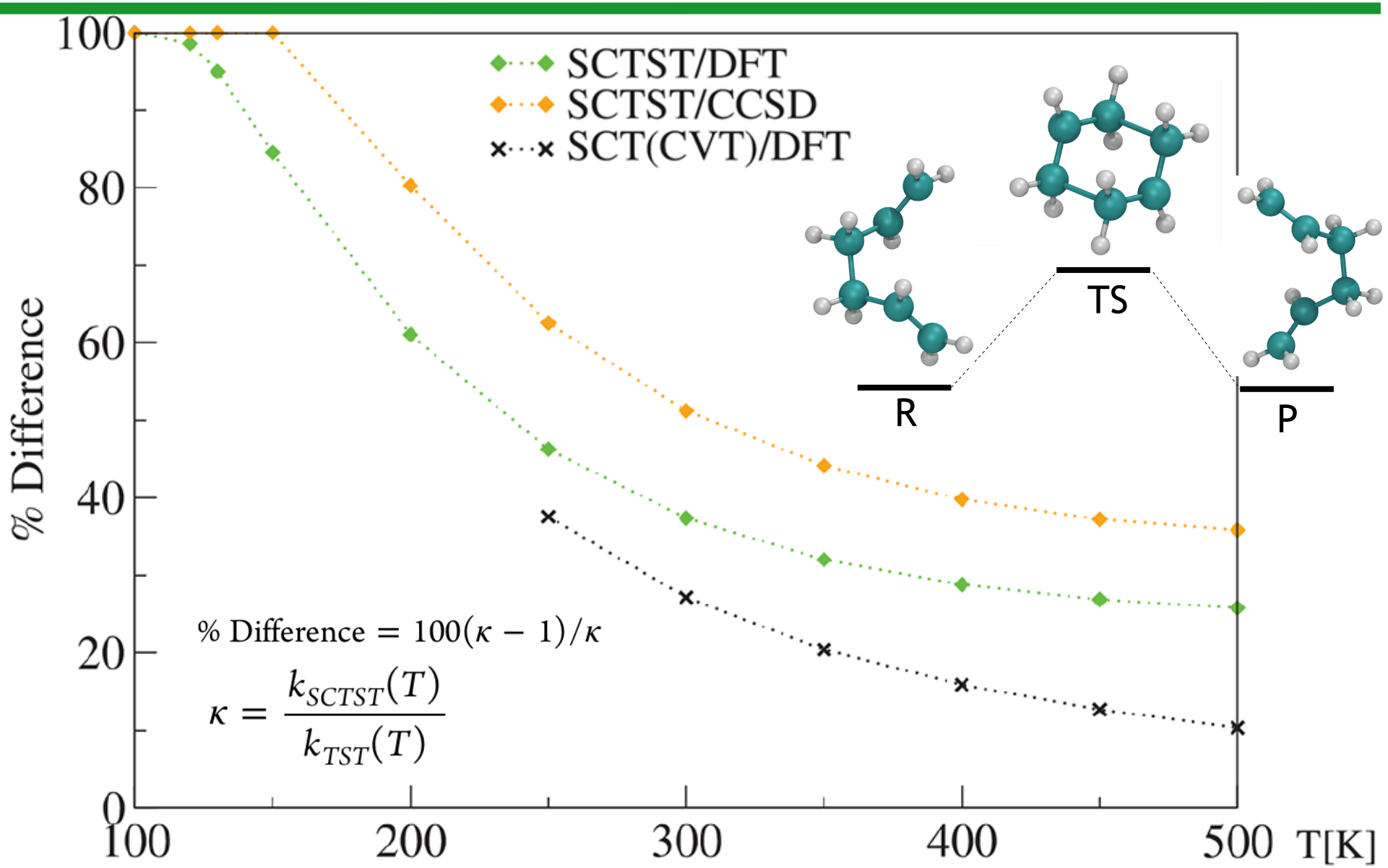


G. Mandelli, C. Aieta, M. Ceotto *J. Chem. Theory Comput.* **18**, 623 (2022). C. Doubleday, R. Armas, D. Walker, C. V. Cosgriff, E.M. Greer *Angew. Chem.* **129**,13279 (2017).

R3: 16-atom HAT Reaction up to CCSD level of theory

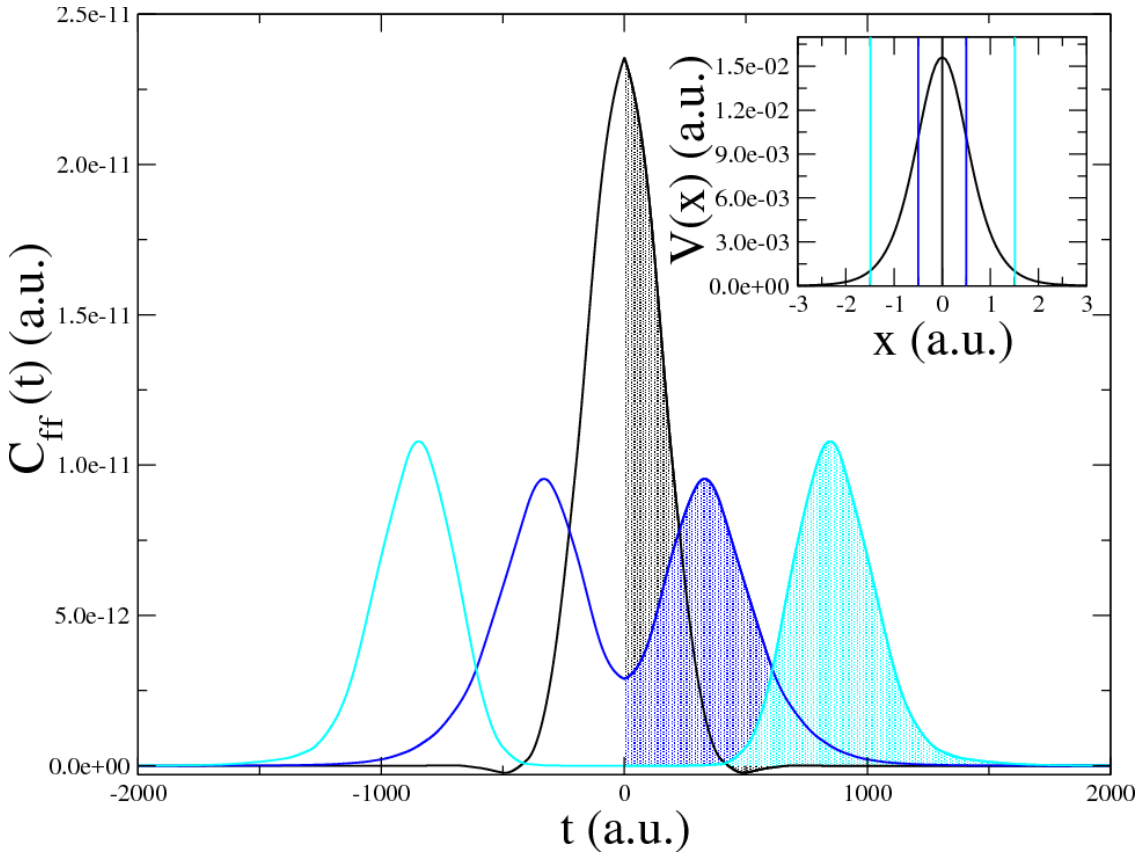


G. Mandelli, C. Aieta, M. Ceotto *J. Chem. Theory Comput.* **18**, 623 (2022). C. Doubleday, R. Armas, D. Walker, C. V. Cosgriff, E.M. Greer *Angew. Chem.* **129**,13279 (2017).

Real Time Quantum Instanton - Derivation

1) The shape of the flux-flux correlation function changes with respect to the position of the two dividing surfaces defined by the two flux operators, and is an even function of time.

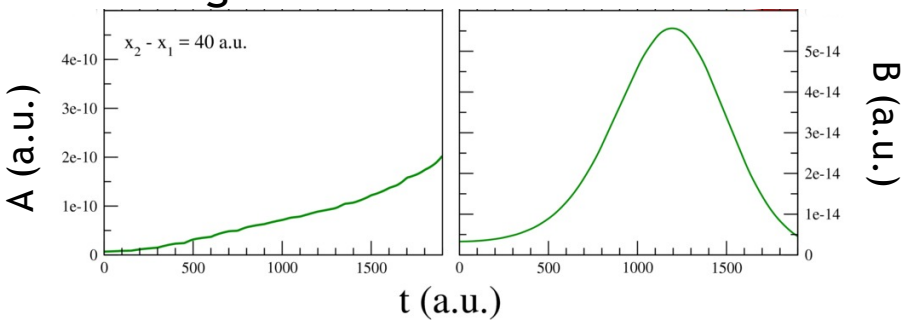
$$k(T)\,Q_r(T) = \int_0^{\infty} dt C_{ff}(t) \Rightarrow k(T)\,Q_r(T) = \frac{1}{2}\int_{-\infty}^{+\infty} dt C_{ff}(t)$$



Real Time Quantum Instanton - Derivation

2) Stationary phase approximation to evaluate the integral.

$$k\left(T\right)Q_r\left(T\right)=\frac{1}{2}\int_{-\infty}^{+\infty}dtC_{ff}\left(t\right)$$



$$k\left(T\right)Q_r\left(T\right)=\frac{1}{2}\int_{-\infty}^{+\infty}dt\underbrace{\frac{C_{ff}\left(t\right)}{\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle\right|^2}}_{\text{A: Slow}}\underbrace{e^{\ln\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle\right|^2}}_{\text{B: Fast}}$$

Stationary phase condition:

$$\frac{\partial}{\partial t}\ln\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle\right|^2=0$$

$$\Im\left[\frac{\left\langle x_1\left|\hat{H}e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle}{\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle}\right]=0$$

$$\Im\left[E\left(\beta,t\right)\right]=0\rightarrow\left\{t_0\right\}$$

Real Time Quantum Instanton - Derivation

2) Stationary phase approximation to evaluate the integral.

$$k\left(T\right)Q_r\left(T\right)=\frac{1}{2}\int_{-\infty}^{+\infty}dt\frac{C_{ff}\left(t\right)}{\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle\right|^2}e^{\ln\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle\right|^2}$$

$$\ln\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle\right|^2\simeq\ln\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle\right|^2\Big|_{t=t_0}+$$

$$\cancel{\left(t-t_0\right)\frac{\partial}{\partial t}\ln\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle\right|^2\Big|_{t=t_0}}+$$

$$\frac{\left(t-t_0\right)^2}{2}\frac{\partial^2}{\partial t^2}\ln\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}}\right|x_2\right\rangle\right|^2\Big|_{t=t_0}$$

Stationary phase condition

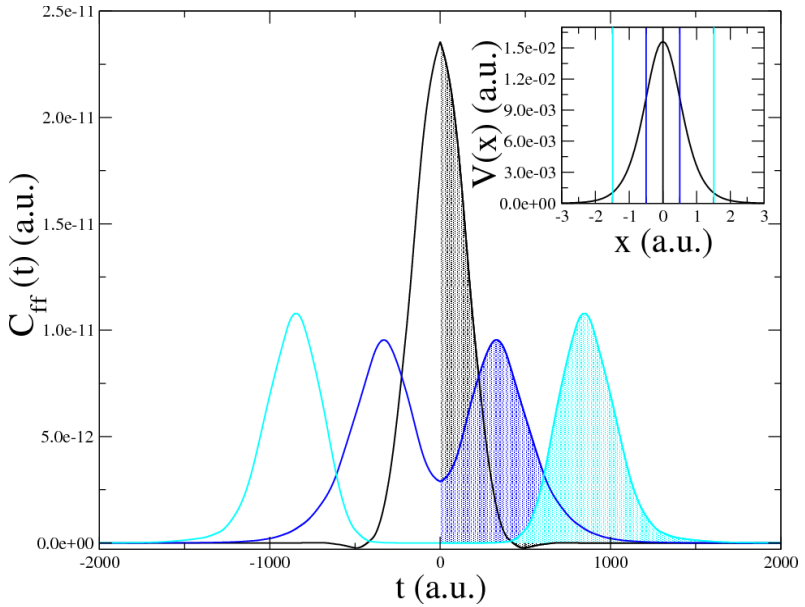
$$k\left(T\right)Q_r\left(T\right)=\sum_{t_0}\frac{1}{2}\int_{-\infty}^{+\infty}dt\frac{C_{ff}\left(t_0\right)}{\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}}\right|x_2\right\rangle\right|^2}e^{\ln\left|\left\langle x_1\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}}\right|x_2\right\rangle\right|^2+\frac{\left(t-t_0\right)^2}{2}\left(-\frac{2}{\hbar^2}\Re\Delta H^2(\beta,t_0)\right)}$$

Gaussian Integral

Real Time Quantum Instanton - Derivation

$$k(T)\,Q_r(T) \approx \sum_{t_0} \frac{1}{2} \frac{\hbar\sqrt{\pi}}{\sqrt{\Re\left[\Delta H^2(\beta,t_0)\right]}} C_{ff}(t_0)$$

$$\Delta H^2(\beta,t_0) = \frac{\left\langle x_1 \left| \hat{H}^2 e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}} \right| x_2 \right\rangle}{\left\langle x_1 \left| e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}} \right| x_2 \right\rangle} - \left(\frac{\left\langle x_1 \left| \hat{H} e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}} \right| x_2 \right\rangle}{\left\langle x_1 \left| e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}} \right| x_2 \right\rangle} \right)^2$$



- $\Im\left[E(\beta,t)\right]$ is an odd function of time.
- $\Re\Delta H^2(\beta,t)$ is an even function of time.
- Surfaces sufficiently far such that $C_{ff}(0) = 0$
- $C_{ff}(t)$ is an even function of time.

$$k(T)\,Q_r(T) \approx \frac{1}{2}\frac{\hbar\sqrt{\pi}C_{ff}(t_0=0)}{\sqrt{\Re\Delta H^2(\beta,t_0=0)}} + \frac{1}{2}\frac{\hbar\sqrt{\pi}C_{ff}(t_0)}{\sqrt{\Re\Delta H^2(\beta,t_0)}} + \frac{1}{2}\frac{\hbar\sqrt{\pi}C_{ff}(-t_0)}{\sqrt{\Re\Delta H^2(\beta,-t_0)}}$$

$$= \frac{1}{2}\frac{\hbar\sqrt{\pi}C_{ff}(t_0=0)}{\sqrt{\Re\Delta H^2(\beta,t_0=0)}} + \frac{\hbar\sqrt{\pi}C_{ff}(t_0)}{\sqrt{\Re\Delta H^2(\beta,t_0)}}$$

Real Time Quantum Instanton - Derivation

$$k\left(T\right)Q_{r}\left(T\right)=\int_{0}^{\infty}dtC_{ff}\left(t\right)$$

$$k\left(T\right)Q_{r}\left(T\right)=\frac{\hbar\sqrt{\pi}}{\sqrt{\Re\left[\Delta H^{2}\left(\beta,t_{0}\right)\right]}}C_{ff}\left(t_{0}\right)$$

$$\Delta H^{2}\left(\beta,t_{0}\right)=\frac{\left\langle x_{1}\left|\hat{H}^{2}e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_{0}}{\hbar}}\right|x_{2}\right\rangle}{\left\langle x_{1}\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_{0}}{\hbar}}\right|x_{2}\right\rangle}-\left(\frac{\left\langle x_{1}\left|\hat{H}e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_{0}}{\hbar}}\right|x_{2}\right\rangle}{\left\langle x_{1}\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_{0}}{\hbar}}\right|x_{2}\right\rangle}\right)^{2}$$

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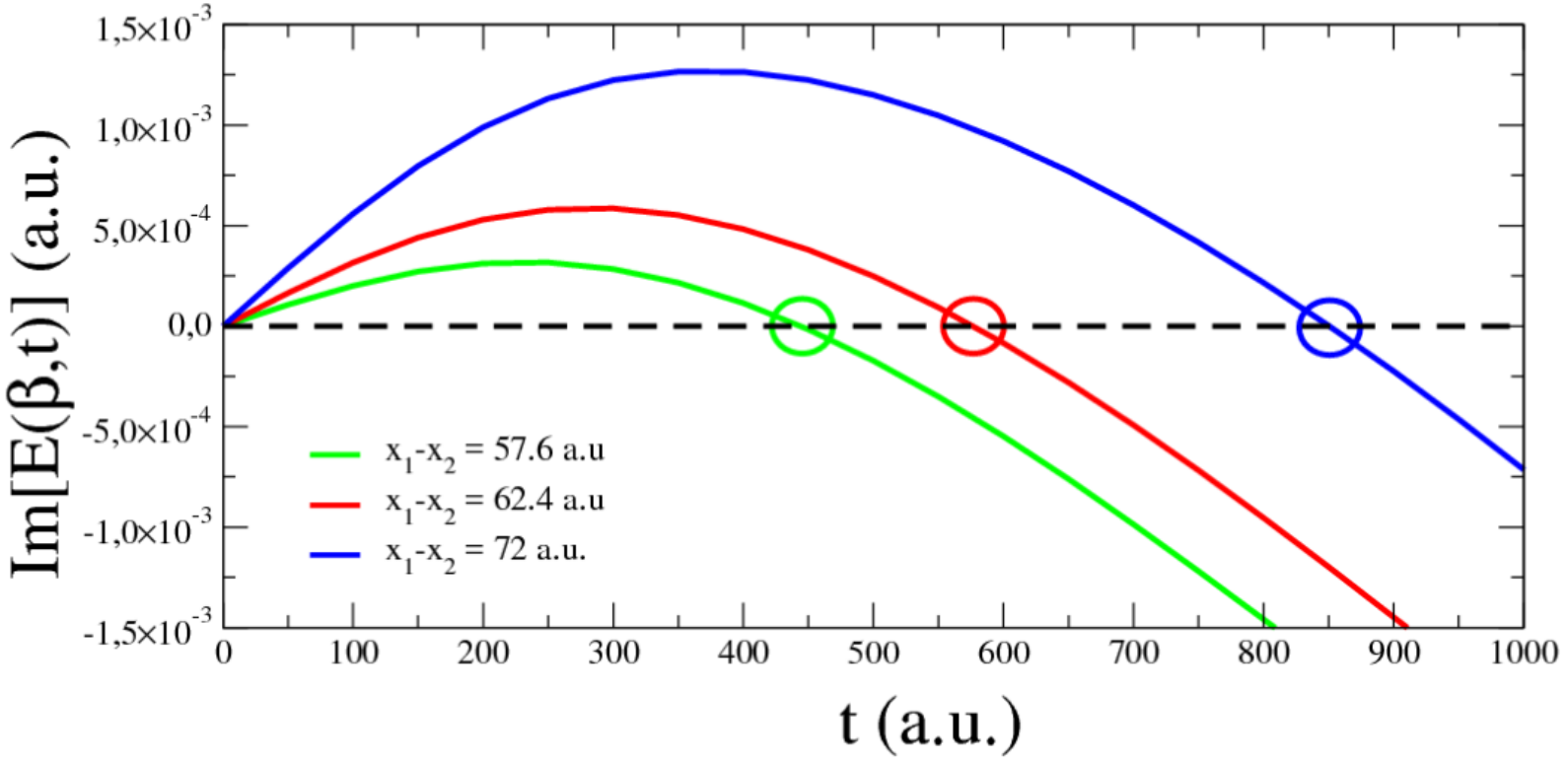
Practical Implementation

Discrete variable representation

$$\Im\left[\frac{\left\langle x_1 \left| \hat{H} e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}} \right| x_2 \right\rangle}{\left\langle x_1 \left| e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t}{\hbar}} \right| x_2 \right\rangle}\right] = 0$$

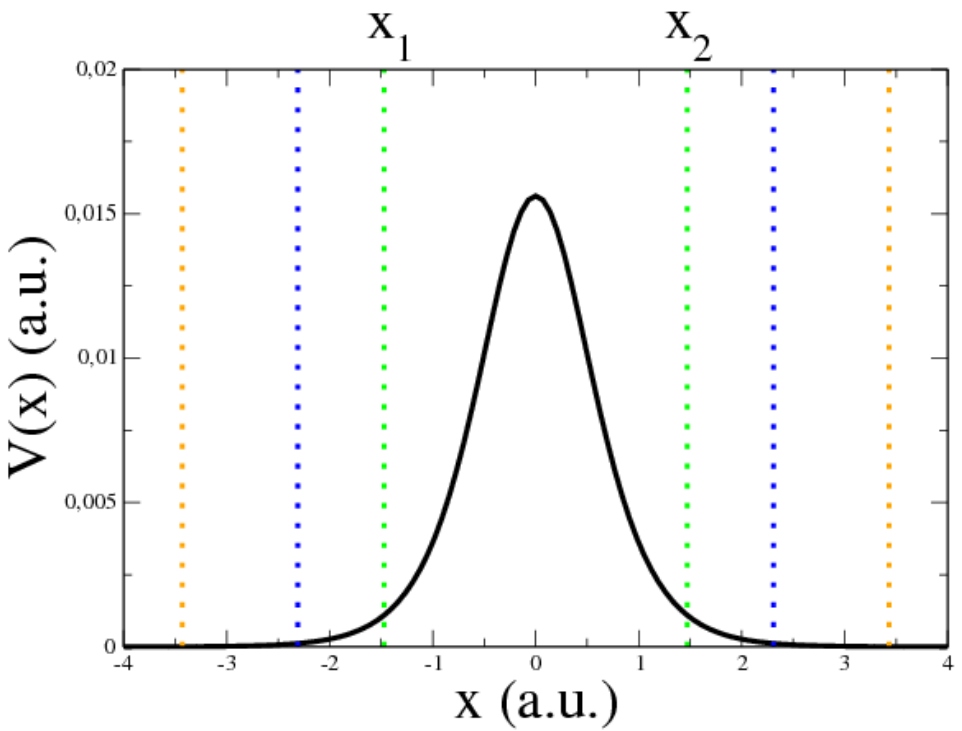
$$k(T)\,Q_r(T) = \frac{\hbar\sqrt{\pi}}{\sqrt{\Re\left[\Delta H^2(\beta,t_0)\right]}} C_{ff}(t_0)$$

$$\Delta H^2(\beta,t_0) = \frac{\left\langle x_1 \left| \hat{H}^2 e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}} \right| x_2 \right\rangle}{\left\langle x_1 \left| e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}} \right| x_2 \right\rangle} - \left(\frac{\left\langle x_1 \left| \hat{H} e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}} \right| x_2 \right\rangle}{\left\langle x_1 \left| e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}} \right| x_2 \right\rangle} \right)^2$$



At a fixed temperature, the special time t_0 increases with the distance between the dividing surfaces positioned at x_1 and x_2.

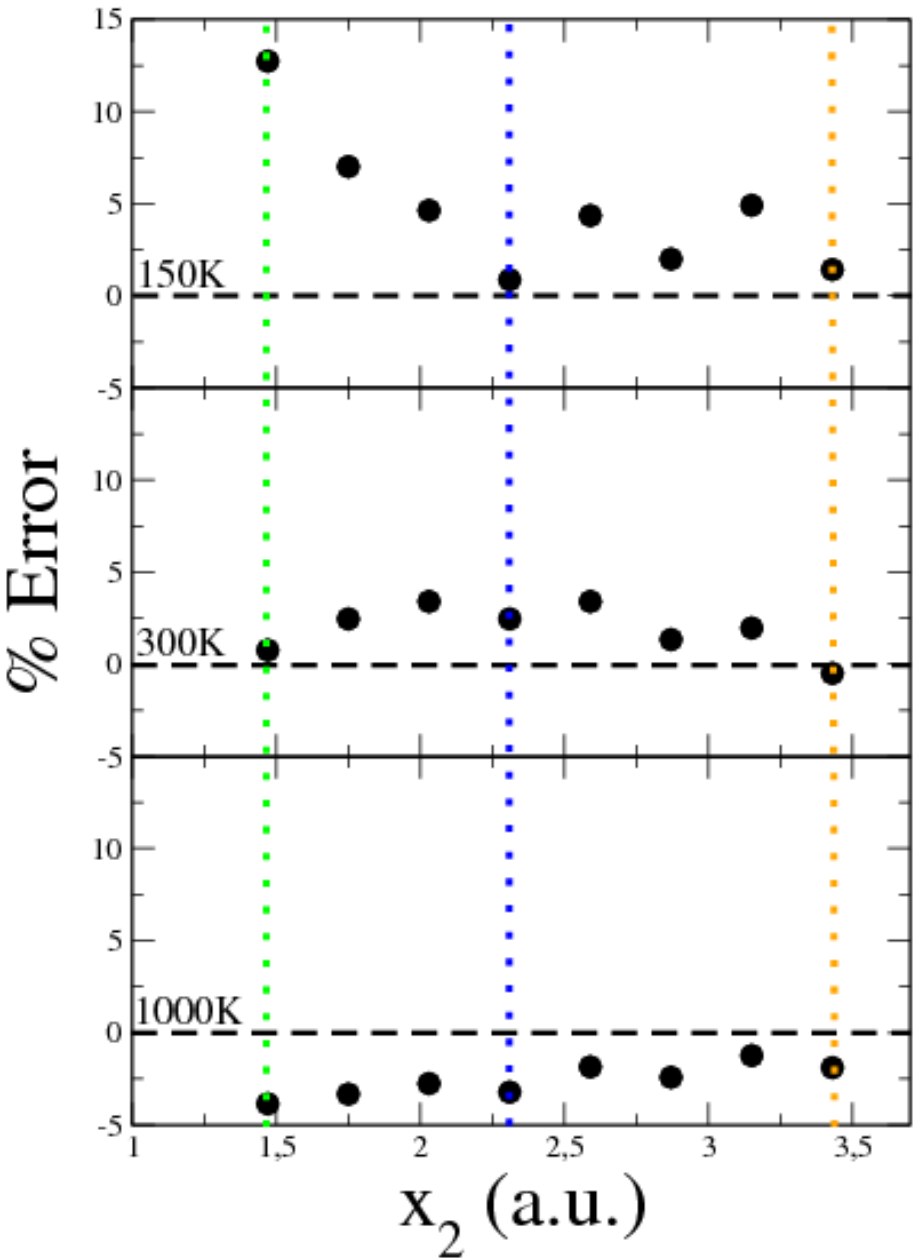
Symmetric 1D Eckart Barrier



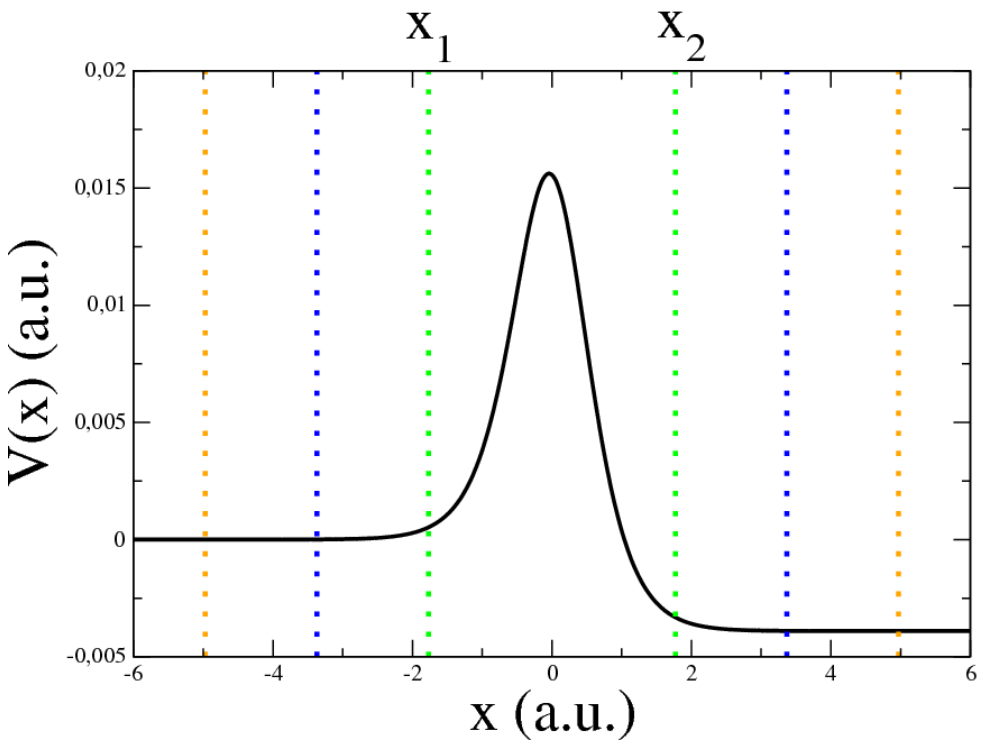
$$V(x) = V_0 \mathrm{sech}^2(ax)$$

V_0(a.u.)	0.01562
a (a.u.)	1.3624
m (a.u.)	1060

Rate Constant Estimates



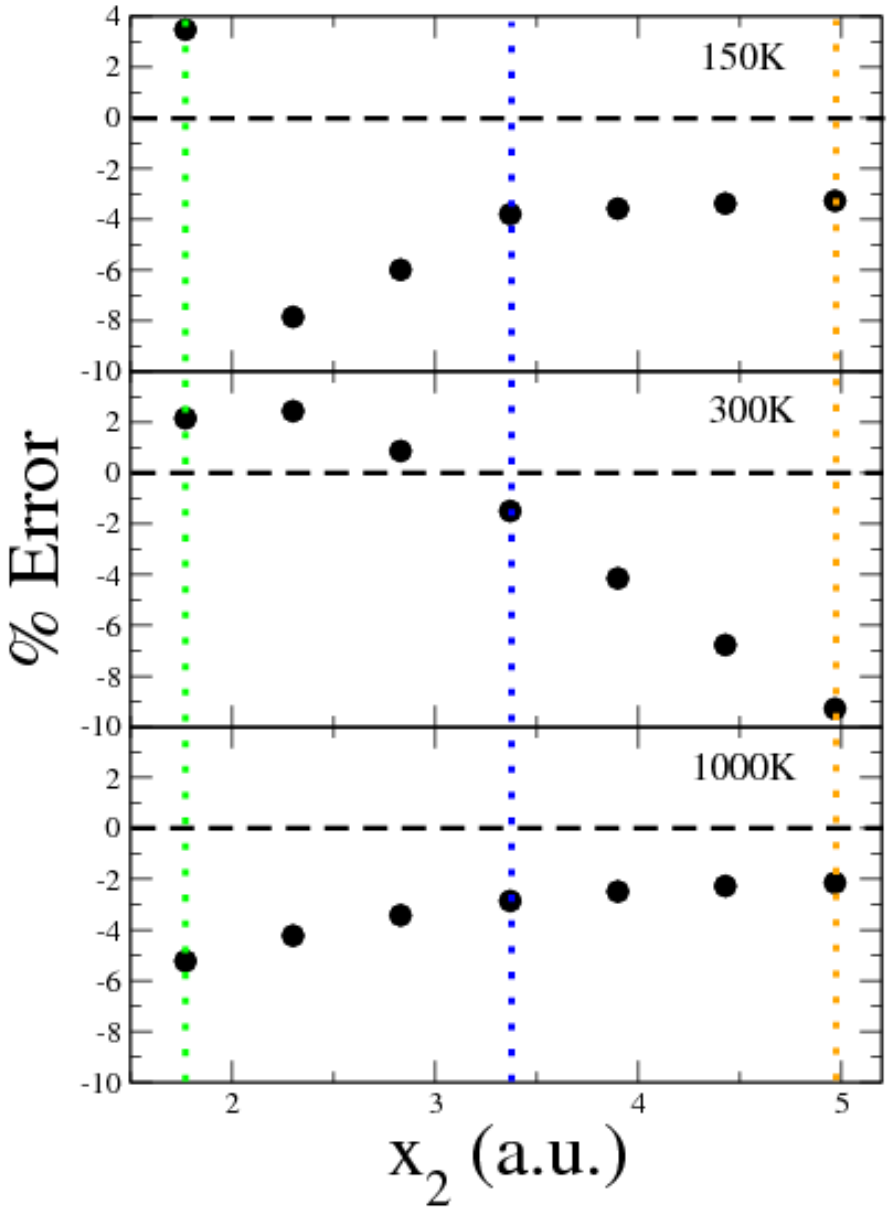
Asymmetric 1D Eckart Barrier



$$V(x) = \frac{V_0(1-\alpha)}{1+e^{-2ax}} + \frac{V_0(1+\sqrt{\alpha})^2}{4\cosh^2(ax)}$$

V_0(a.u.)	0.01562
a (a.u.)	1.3624
α (a.u.)	1.25
m (a.u.)	1060

Rate Constant Estimates



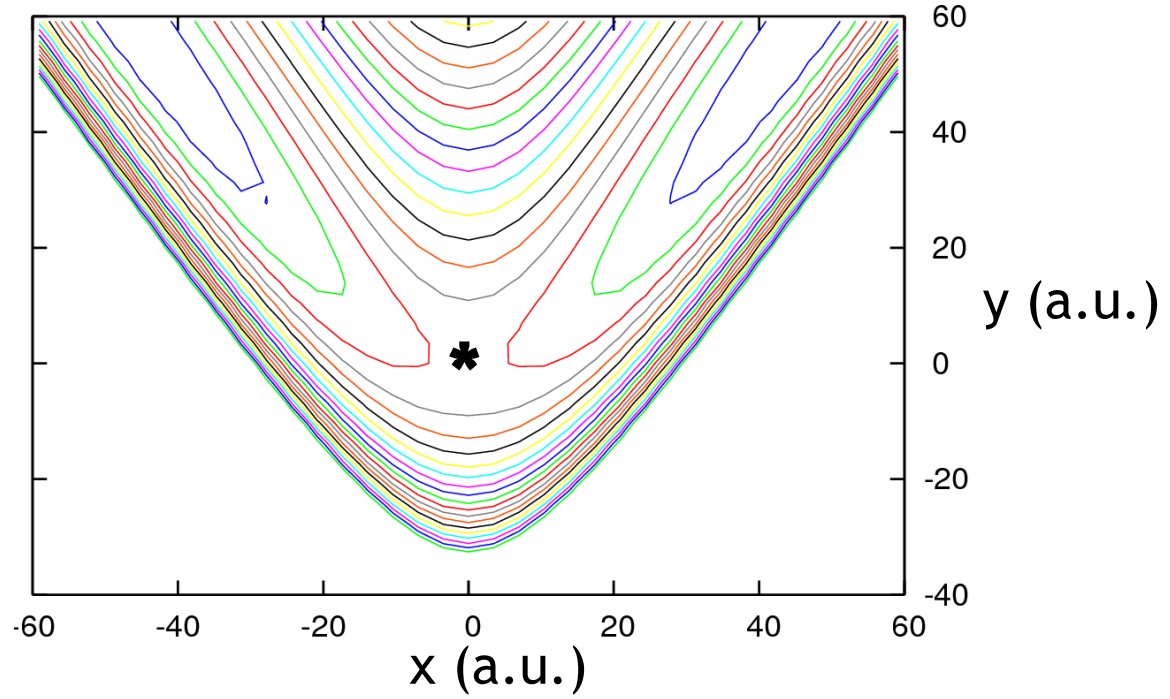
Multidimensional Generalization

$$k\left(T\right)Q_r\left(T\right)=\frac{\hbar\sqrt{\pi}}{\sqrt{\Re\left[\Delta H^2\left(\beta,t_0\right)\right]}}C_{ff}\left(t_0\right)$$

$$\Delta H^2\left(\beta,t_0\right)=\frac{\int d\mathbf{Q_1}\int d\mathbf{Q_2}\left[\left\langle x_1\mathbf{Q_1}\left|\hat{H}^2e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}}\right|x_2\mathbf{Q_2}\right\rangle\left\langle x_1\mathbf{Q_1}\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}}\right|x_2\mathbf{Q_2}\right\rangle\right]}{\int d\mathbf{Q_1}\int d\mathbf{Q_2}\left(\left\langle x_1\mathbf{Q_1}\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}}\right|x_2\mathbf{Q_2}\right\rangle\right)^2}+$$

$$-\frac{\int d\mathbf{Q_1}\int d\mathbf{Q_2}\left[\left(\left\langle x_1\mathbf{Q_1}\left|He^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}}\right|x_2\mathbf{Q_2}\right\rangle\right)^2\right]}{\int d\mathbf{Q_1}\int d\mathbf{Q_2}\left(\left\langle x_1\mathbf{Q_1}\left|e^{-\frac{\beta\hat{H}}{2}-\frac{i\hat{H}t_0}{\hbar}}\right|x_2\mathbf{Q_2}\right\rangle\right)^2}$$

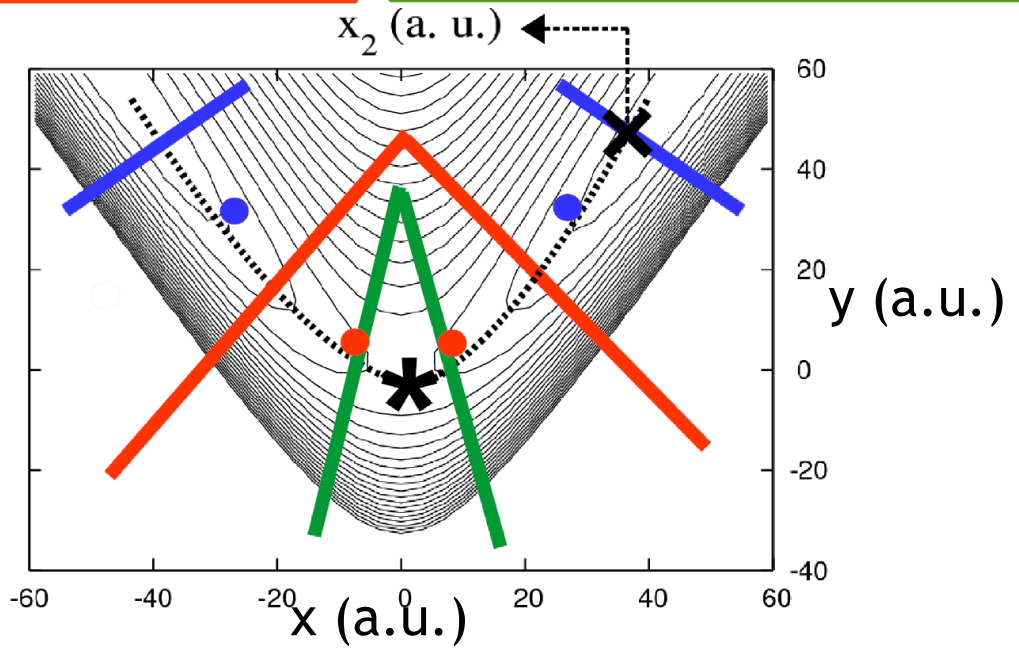
LSTH PES
Collinear
$H + H_2$



$H + H_2$ Collinear Reaction

Rate Constant Estimates

150 K		300 K		600 K		1000 K	
x_2	%Err	x_2	%Err	x_2	%Err	x_2	%Err
35	−0.9	20	−4.9	20	−1.5	9	+4.1
40	+0.4	22	−9.3	22	−2.4	12	+0.6
45	+1.8	24	−10.3	25	−7.7	15	+7.7
50	+3.4	26	−10.0	30	−7.0	18	+2.2
55	+4.0	28	−9.5	32	−4.1	21	+7.4
60	+6.1	30	−9.2	35	−3.4	24	−4.2



Comparison with Other Approaches to Thermal Rate Constant Calculations

Eckart barrier	LSC-IVR[13]	SC-VV-IVR[13]	RPMD[14]	QI[15]	HD-QI[16]	RTQI
150 K	~ -62	~ -33	-	+1.7 (-3.2)	$\sim +2$	+12.7
200K	~ -37	~ -16	~ -45	+2.5 (-1.6)	~ -4	+10.7
300 K	~ -11	$\sim +3$	~ -25	+19.5 (+15.8)	$\sim +2$	+3.4
1000 K	~ -7	$\sim +3$	~ -5	+21.4 (+2.5)	~ -2	-4

$H + H_2$	QTST[17]	MQCLT[18]	QI[15]	RTQI
150 K	-	-	+10	+6.1
200K	+270	+270	-4.2	-15.3
300 K	+91	+29.5	+9.8	-10.3
1000 K	-6	+3.6	+3	-10.9

[13] C. Venkataraman and W. H. Miller, J. Chem. Phys. 126, 094104 (2007); [14] I. R. Craig and D. E. Manolopoulos, J. Chem. Phys. 122, 084106 (2005); [15] W. H. Miller, Y. Zhao, M. Ceotto, and S. Yang, J. Chem. Phys. 119, 1329 (2003); [16] M. Ceotto, S. Yang, and W. H. Miller, J. Chem. Phys. 122, 044109 (2005); [17] J.-L. Liao and E. Pollak, J. Phys. Chem. A 104, 1799 (2000); [18] Y. Zheng and E. Pollak, J. Chem. Phys. 114, 9741 (2001).

Summary and Conclusions

- We implemented **SCTST** as a practical approach for high level rate constants predictions for high dimensional systems.

- We developed the **RTQI** method that includes real time information into rate estimates with flexible choice of the position of the dividing surfaces and without the need of a full quantum time evolution.

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