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$\hbar^2$ corrections to semiclassical transmission probabilities

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- Kemble derived a semiclassical expression for the energy dependent transmission probability through a potential barrier :

$$T_{\text{usc}}(E) = \frac{1}{1 + \exp\left[\frac{S(E)}{\hbar}\right]}$$

where $S(E)$ is the Euclidean action on the upside-down potential energy surface .

There is however a fundamental problem with Kemble's expression for the energy dependent transmission probability $T_{usc}(E)$. When the energy E equals the barrier height $V^{\ddagger}$, the action $S(E = V^{\ddagger}) = 0$ and the resulting transmission probability is $\frac{1}{2}$, which we call the half point .

This is independent of the form of the barrier . However , in reality this is not the case, implying that an improvement of the uniform theory is needed.

Miller's VPT2 theory

- Miller and co-workers used the uniform expression in conjunction with vibrational perturbation theory (VPT) to evaluate transmission probabilities for various systems .

- In the VPT2 theory , the action of the unstable orbit , whether the energy is above or below the barrier height , is obtained from the quadratic expansion of the energy about the saddle point energy in terms of the action of the orbit using the quantum second order vibrational perturbation theory .

$$E - V^{\ddagger} = E_0 + \sum_{k=1}^{N} \hbar\omega_k^{\ddagger}\left(n_k + \frac{1}{2}\right) + \sum_{k=1}^{N}\sum_{j=1}^{N} \hbar x_{kj}\left(n_k + \frac{1}{2}\right)\left(n_j + \frac{1}{2}\right) - \frac{S(E)}{2\pi}\left[\omega^{\ddagger} + \sum_{j=1}^{N} x_{k,N+1}\left(n_k + \frac{1}{2}\right)\right] + \frac{x_{N+1,N+1}}{4\pi^2}(S(E))^2$$

E_0 : zero point energy shift , which modifies the barrier height of the potential.

$\omega_k^{\ddagger}$ - defines the stable normal mode frequencies

Def : $E_v^{\ddagger}(n) = \sum_{k=1}^{N} \hbar\omega_k^{\ddagger}\left(n_k + \frac{1}{2}\right) + \sum_{k=1}^{N}\sum_{j=1}^{N} \hbar x_{kj}\left(n_k + \frac{1}{2}\right)\left(n_j + \frac{1}{2}\right)$

$$S(E,n) = \frac{4\pi\left[V^{\ddagger} - \left\{E - E_0 - E_v^{\ddagger}(n)\right\}\right]}{\Omega^{\ddagger}(n)\left[1 + \sqrt{1 + \frac{4x_{N+1,N+1}\left\{V^{\ddagger} - \left(E - E_0 - E_v^{\ddagger}(n)\right)\right\}}{\hbar\Omega_n^{\ddagger 2}(n)}}\right]}$$

$$\Omega^{\ddagger}(n) = \omega^{\ddagger} + \sum_{k=1}^{N} x_{k,N+1}\left(n_k + \frac{1}{2}\right)$$ is the “effective barrier frequency” .

However , we know that the VPT2 theory is not precise for the deep tunneling regime , especially when the potential is asymmetric .

Yasumori - Fueki Thought

Alternatively, especially for the Eckart barrier , Yasumori and Fueki (YF) used Eckart's idea to replace the $\cosh(x)$ terms in the exact transmission probability of the Eckart barrier with the $\exp(x)/2$ leading to an expression which gives thermal transmission coefficients which are better than Kemble's expression using the Euclidean action.

For the symmetric Eckart barrier the YF modification is as follows $\left(\eta = \frac{E}{V^{\ddagger}}\ ;\ \alpha = \frac{2\pi V^{\ddagger}}{\hbar\omega^{\ddagger}}\right)$

$$T(E) = \frac{\cosh\left(2\alpha\sqrt{\eta}\right) - 1}{\cosh\left(2\alpha\sqrt{\eta}\right) + \cosh\left[\sqrt{4\alpha^2 - \pi^2}\right]} \sim \frac{\exp\left(2\alpha\sqrt{\eta}\right) - 2}{\exp\left(2\alpha\sqrt{\eta}\right) + \exp\left[\sqrt{4\alpha^2 - \pi^2}\right]}$$

$$\simeq \frac{1}{1 + \exp\left[\sqrt{4\alpha^2 - \pi^2} - 2\alpha\sqrt{\eta}\right]}$$

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- **Wigner (1932)** : derived a leading order $\hbar^2$ correction term for the thermal transmission coefficient $(\kappa(\beta))$

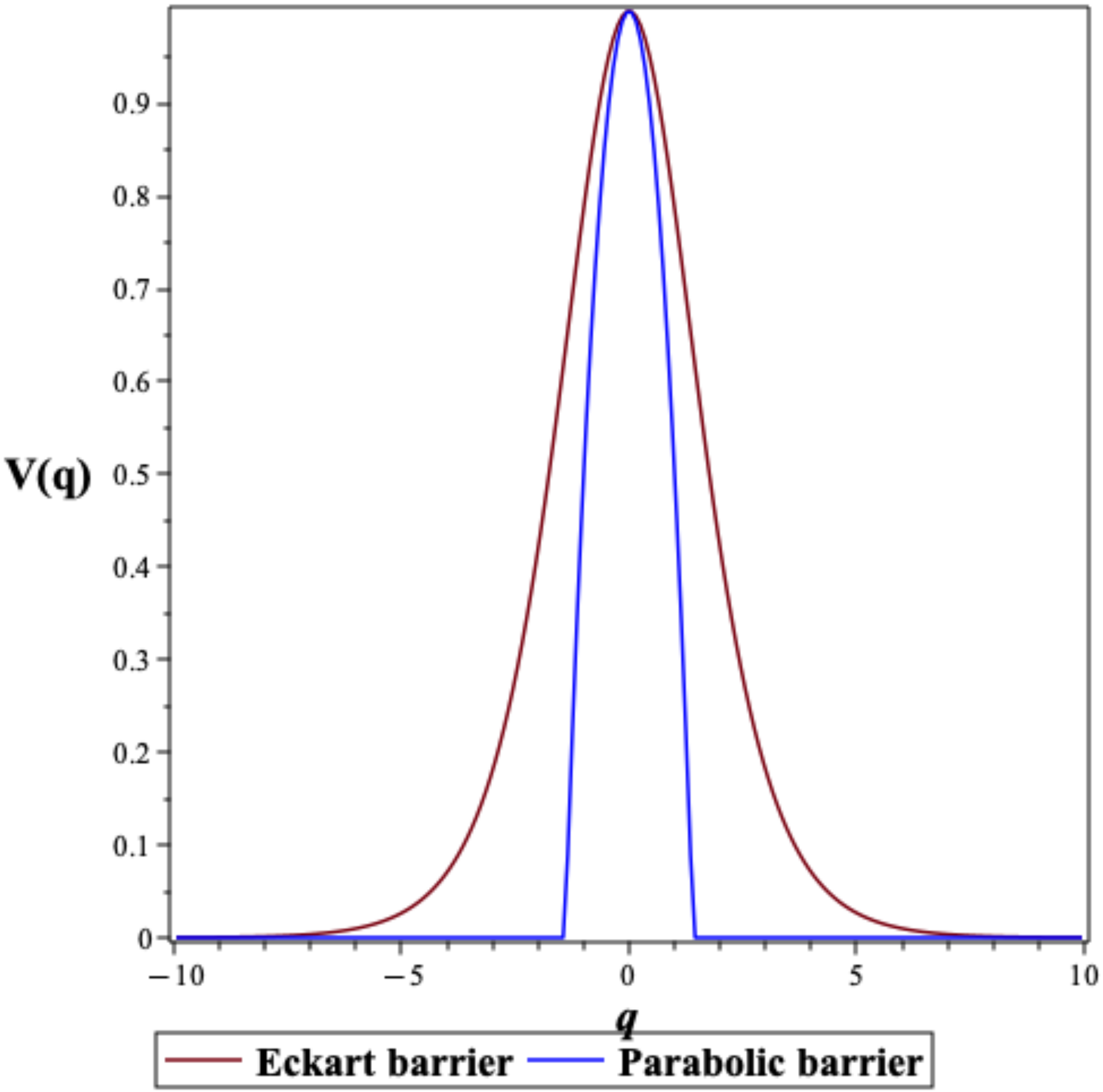
(Consider V_n as the n^{th} derivative of the potential at the barrier top)

$$\kappa\left(\beta\right) = 1 + \frac{\hbar^2\beta^2\omega^{\ddagger 2}}{24}\left[1 + \frac{V_4}{4\beta V_2^2}\right]$$ (valid only for symmetric barriers)

- **Pollak and Cao (2022)** : Generalised the above expression for any barrier

$$\kappa\left(\beta\right) = 1 + \frac{\hbar^2\beta^2\omega^{\ddagger 2}}{24}\left[1 + \frac{1}{4}\left\{\frac{V_4}{\beta V_2^2} - \frac{V_3^2}{3\beta V_2^3}\right\}\right] + O(\hbar^4)$$

Note that $V_2 < 0$: both the leading order asymmetric and symmetric anharmonic terms lead to an increase of the thermal transmission factor , as compared to the parabolic barrier result.



V(q)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
−10
−5
0
5
10
q
Eckart barrier
Parabolic barrier

- **Modified VPT2 theory (mVPT2)**

$$T_{mVPT2}(E) = \frac{1}{1 + \exp\left[\frac{S(E - E')}{\hbar}\right]}$$

After some tedious algebra, we find the energy shift to be $E' = E_0 = -\frac{\hbar^2 \omega^{\ddagger 2}}{64}\left[\frac{V_4}{V_2^2} - \frac{7V_3^2}{9V_2^3}\right]$(which is the correct $\hbar^2$ dependent parameter) which is just the zero point energy shift observed in the VPT2 theory defined by Miller !

- **Modified Yasumori-Fueki theory (mYF)**

$$T_{mYF}(E) = \frac{1}{1 + \exp\left[\frac{S(E) + \Delta S}{\hbar}\right]}$$

where $\Delta S = \frac{2\pi E_0}{\omega^{\ddagger}}$ is also dependent on $\hbar^2$.

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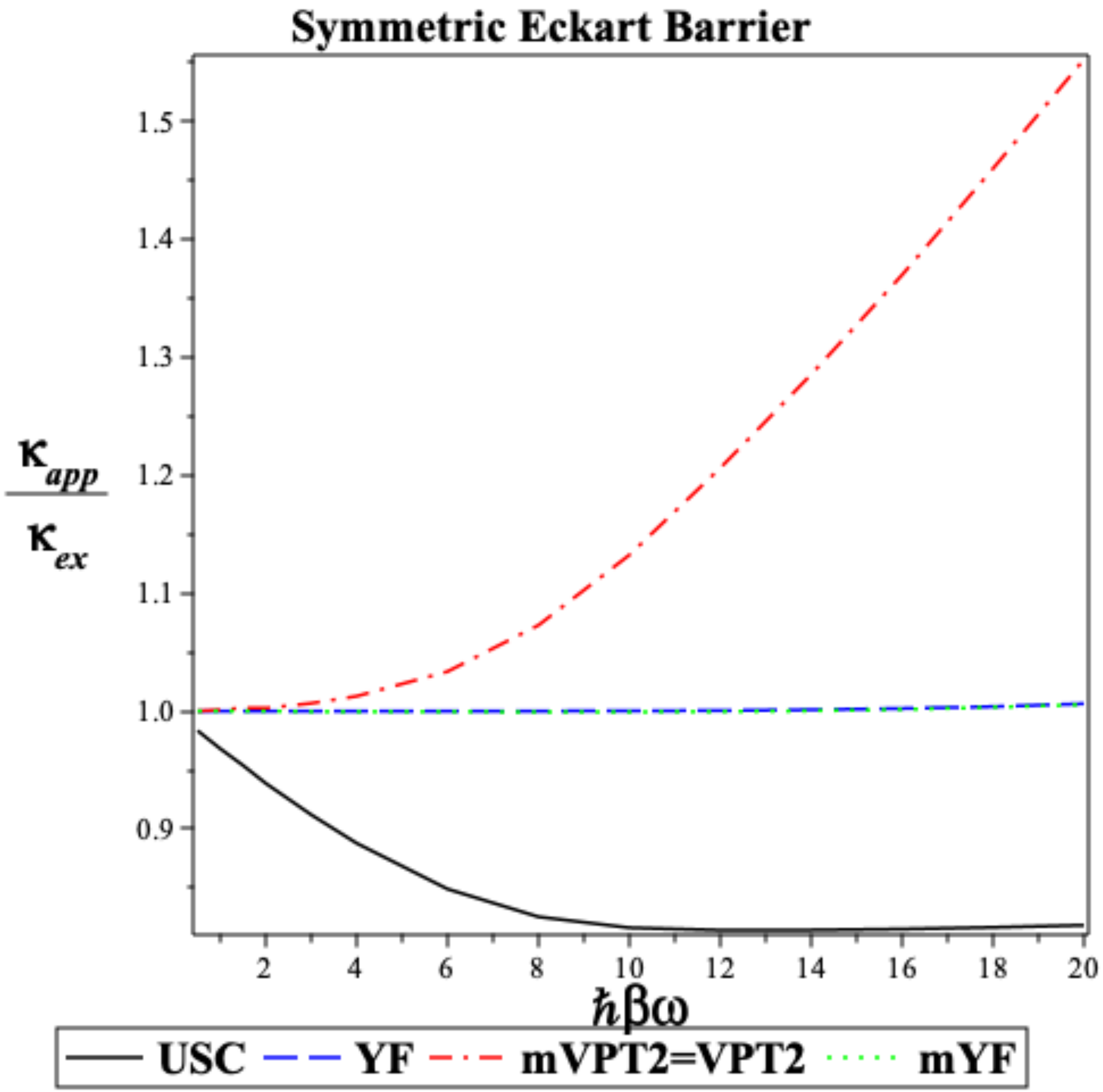
We note that the fourth derivative for the Eckart barrier is positive ($V_4 > 0 \implies E_0 < 0$) . Using this information , the expressions for the transmission probability are

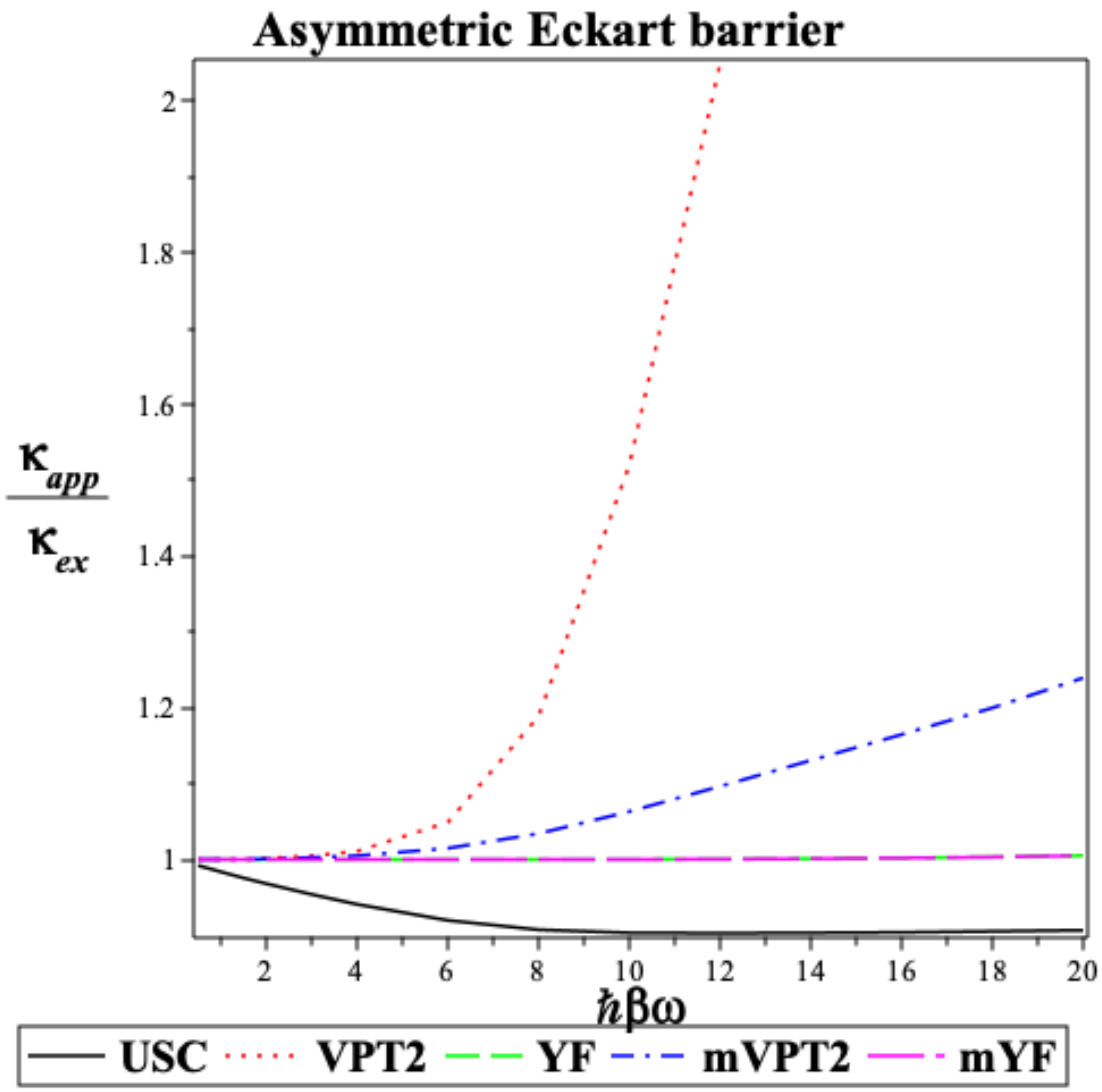
$$T_{mVPT2}\left(E, V_4 \geq 0\right) = \begin{cases} \dfrac{1}{1+\exp\left[\frac{S(E-E_0)}{\hbar}\right]} & E \leq V^{\ddagger} + E_0 \\ \dfrac{1}{1+\exp\left[\frac{S_{VPT2}(E)}{\hbar}\right]} & E \geq V^{\ddagger} + E_0 \end{cases}$$

$$T_{mYF}\left(E, V_4 \geq 0\right) = \begin{cases} \dfrac{1}{1+\exp\left[\frac{S(E)+\Delta S}{\hbar}\right]} & E \leq V^{\ddagger} + E_0 \\ \dfrac{1}{1+\exp\left[\frac{S_{VPT2}(E)+S^{*}_{VPT2}}{\hbar}\right]} & E \geq V^{\ddagger} + E_0 \end{cases}$$

where $S^{*}_{VPT2} = S\left(V^{\ddagger} + E_0\right) + \Delta S$ is defined to ensure that the transmission coefficient is continuous at $E = V^{\ddagger} + E_0$.



Symmetric Eckart Barrier
κapp / κex
1.5
1.4
1.3
1.2
1.1
1.0
0.9
2
4
6
8
10
12
14
16
18
20
ħβω
USC
YF
mVPT2=VPT2
mYF



Asymmetric Eckart barrier
κ_app / κ_ex
2
1.8
1.6
1.4
1.2
1
2 4 6 8 10 12 14 16 18 20
ħβω
USC
VPT2
YF
mVPT2
mYF

Multidimensional mVPT2 and mYF theories

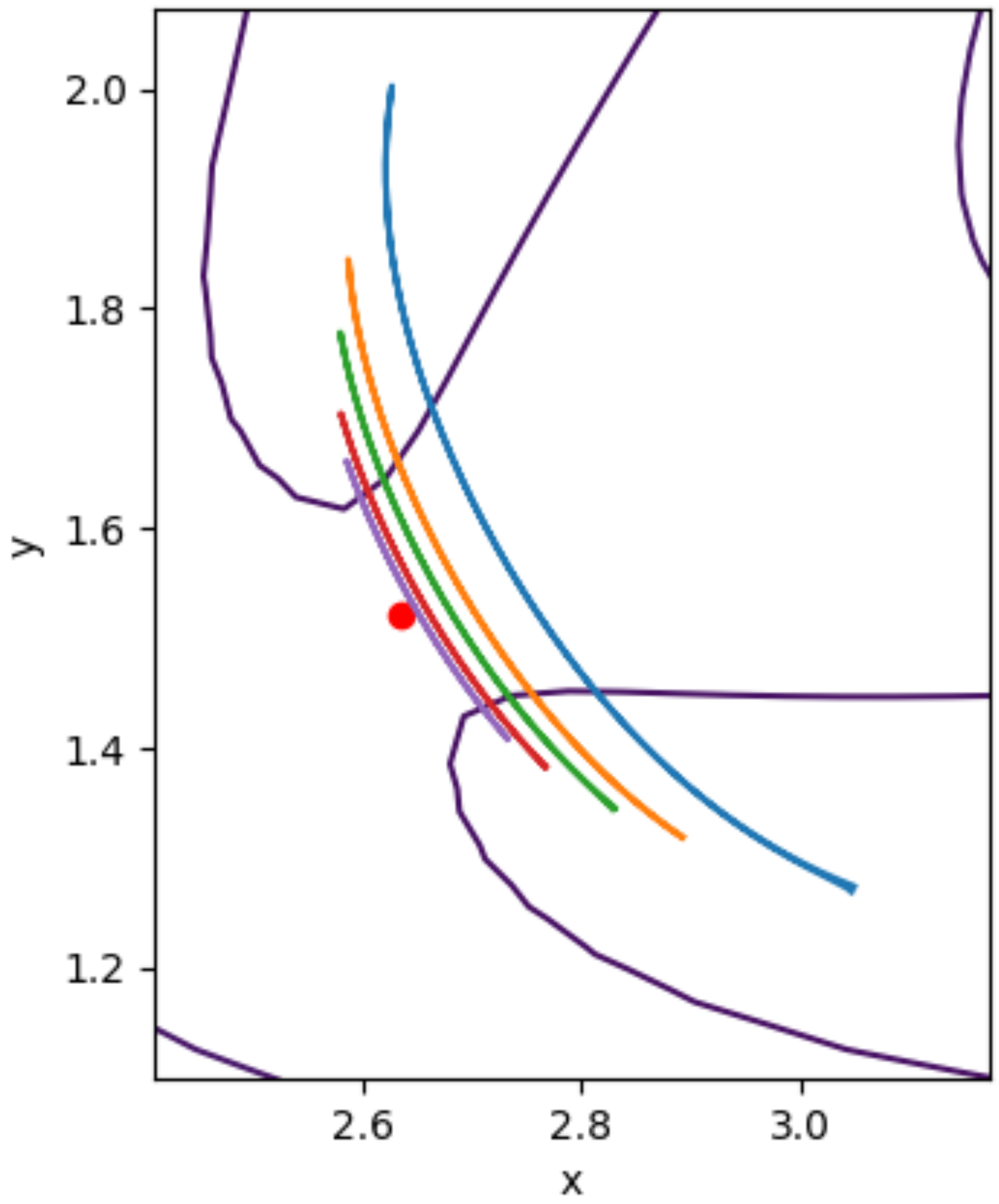
$$P_{mVPT2}(E) = \begin{cases} \sum_{\mathbf{n}=0}^{\infty} \frac{1}{1+\exp\left[\frac{S\left(E-E^*(\mathbf{n})-E_0\right)}{\hbar}\right]} & E \le V^\ddagger + E_0 + E_v^\ddagger(\mathbf{n}) \\ \sum_{\mathbf{n}=0}^{\infty} \frac{1}{1+\exp\left[\frac{S_{VPT2}(E,\mathbf{n})}{\hbar}\right]} & E \ge V^\ddagger + E_0 + E_v^\ddagger(\mathbf{n}) \end{cases}$$

$$k_{mVPT2}(T) = \left[2\pi\hbar Q_r(T)\right]^{-1} \int_0^\infty \exp\left(-\beta E\right) P_{mVPT2}(E)\ dE$$

$$P_{mYF}(E) = \begin{cases} \sum_{\mathbf{n}=0}^{\infty} \frac{1}{1+\exp\left[\frac{S\left(E-E^*(\mathbf{n})\right)+\Delta S}{\hbar}\right]} & E \le V^\ddagger + E_0 + E_v^\ddagger(\mathbf{n}) \\ \sum_{\mathbf{n}=0}^{\infty} \frac{1}{1+\exp\left[\frac{S_{VPT2}(E,\mathbf{n})+S^*_{VPT2}(\mathbf{n})}{\hbar}\right]} & E \ge V^\ddagger + E_0 + E_v^\ddagger(\mathbf{n}) \end{cases}$$

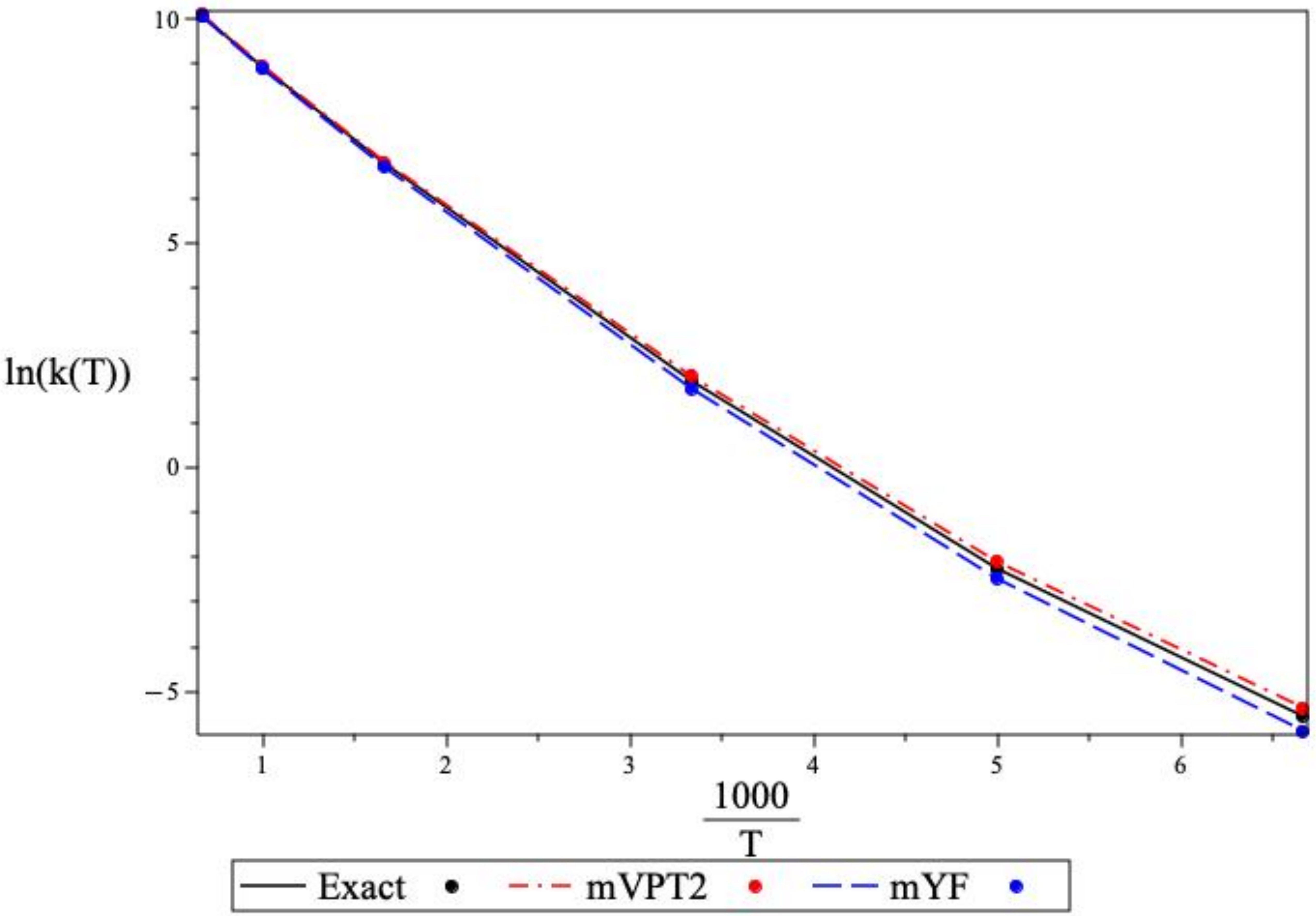
$$k_{mYF}(T) = \left[2\pi\hbar Q_r(T)\right]^{-1} \int_0^\infty \exp\left(-\beta E\right) P_{mYF}(E)\ dE$$

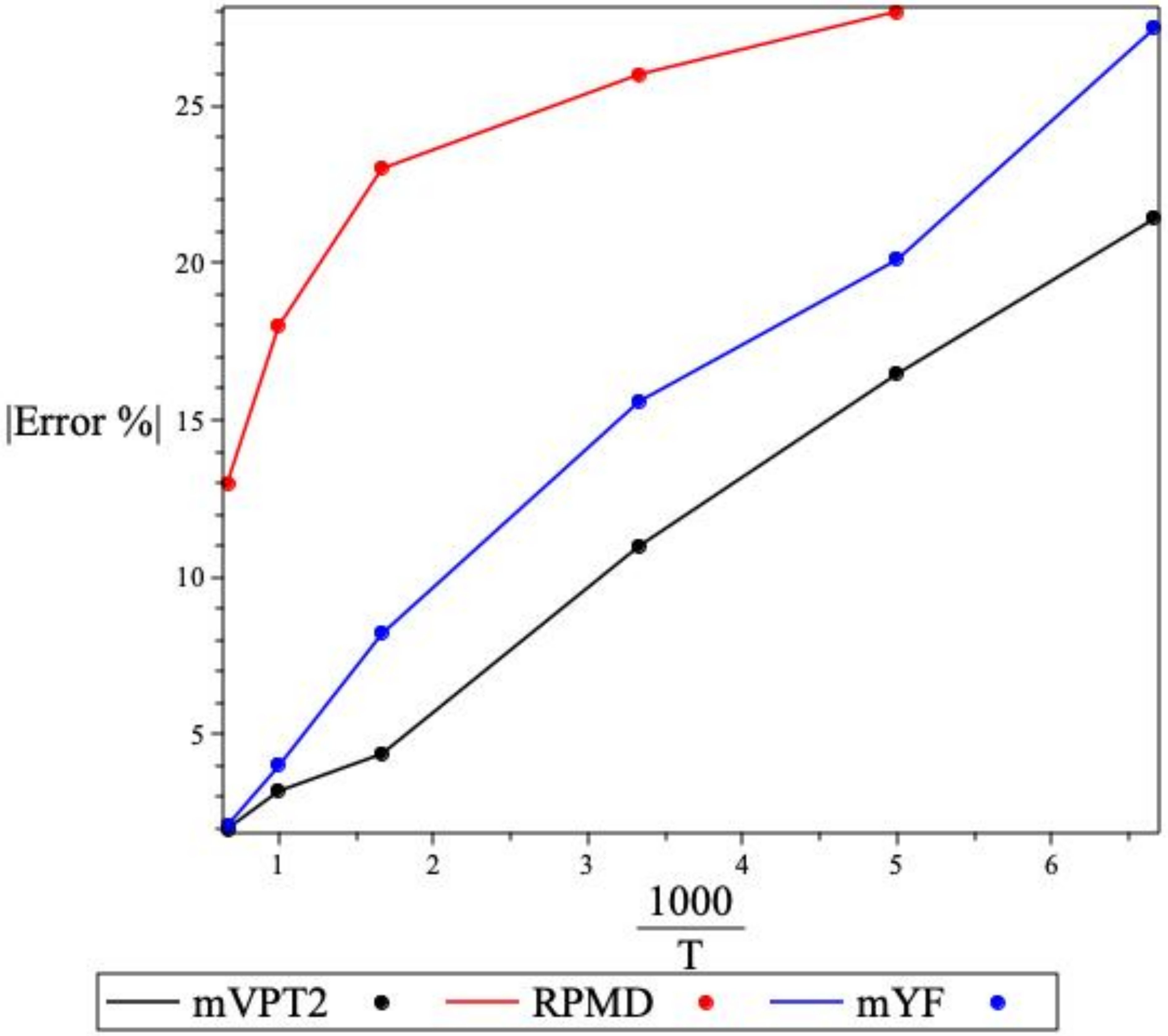
Collinear $H + H_2$ reaction



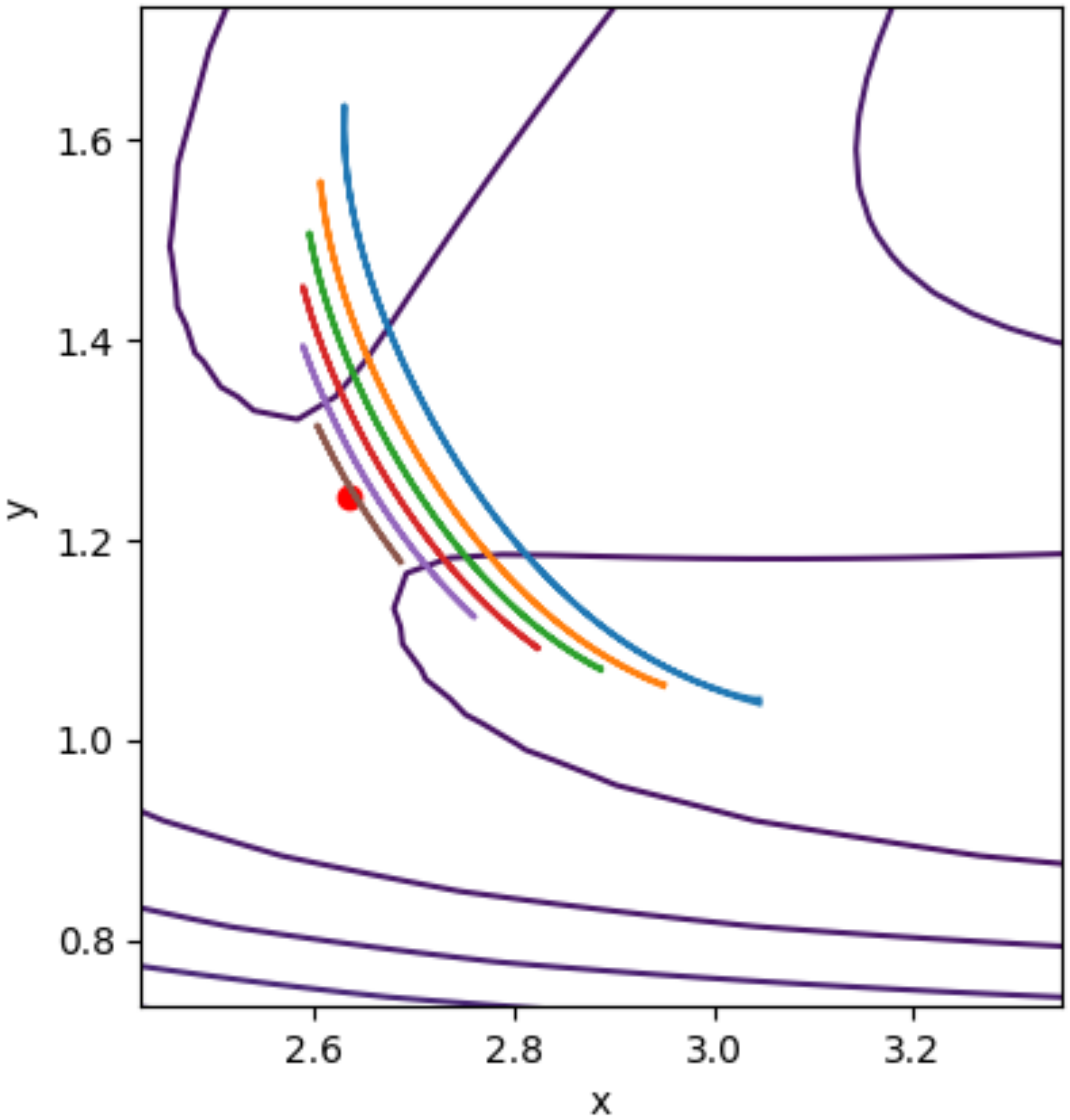
Instanton energy (eV)	Color code
0.30	Blue
0.35	Orange
0.37	Green
0.39	Red
0.40	Purple

T(K)	Exact Rates	mVPT2 Rates	mYF Rates
1500	23931	24410 (2%)	23421 (2.1%)
1000	7482.1	7721.4 (3.2%)	7182.8 (4%)
600	867.67	905.46 (4.36%)	796.53 (8.2%)
300	6.9109	7.6711 (11%)	5.8327 (15.6%)
200	0.10482	0.12197 (16.36%)	0.08381(20.1%)
150	3.8991E-03	4.7349E-03 (21.41%)	2.8282E-03 (27.47%)



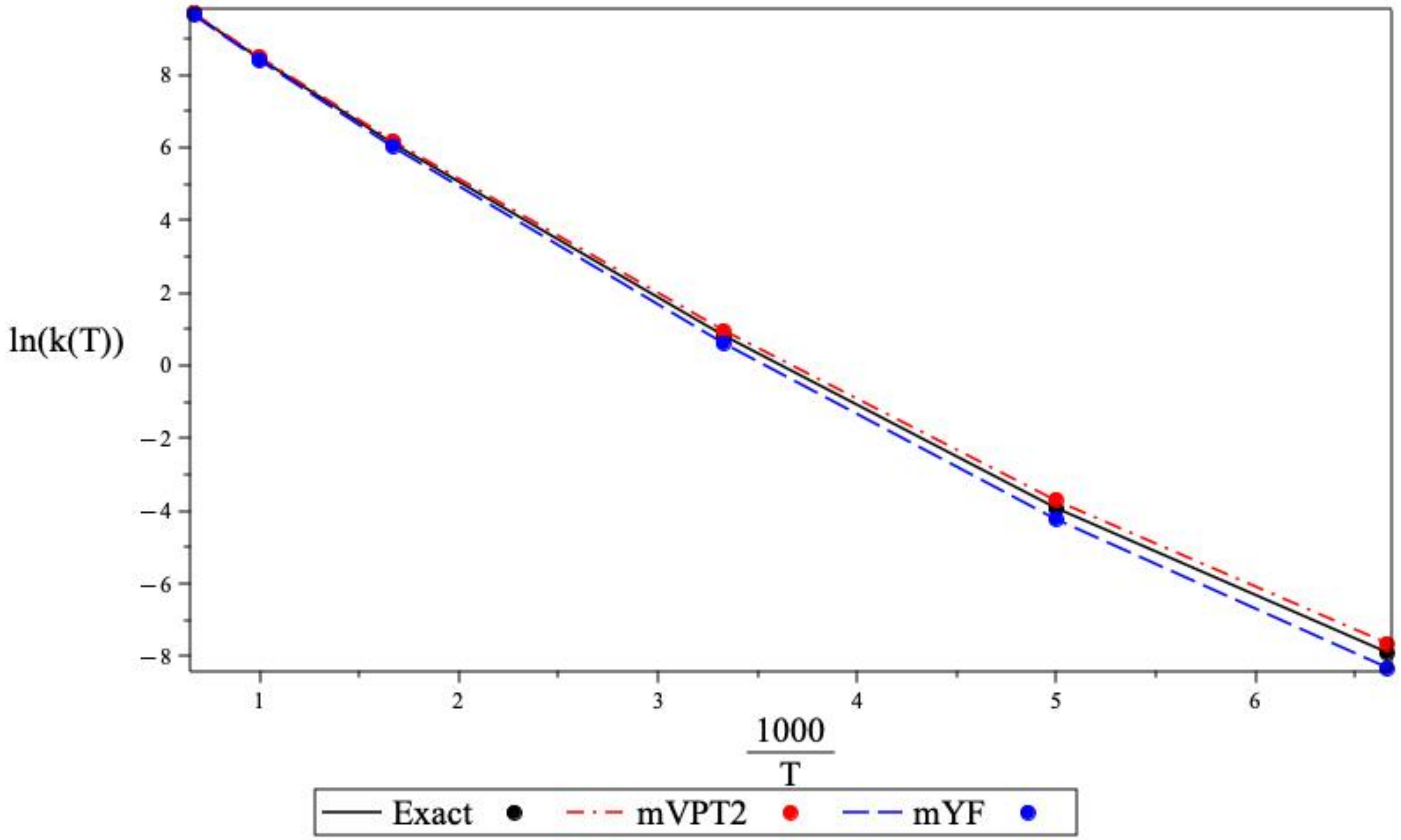


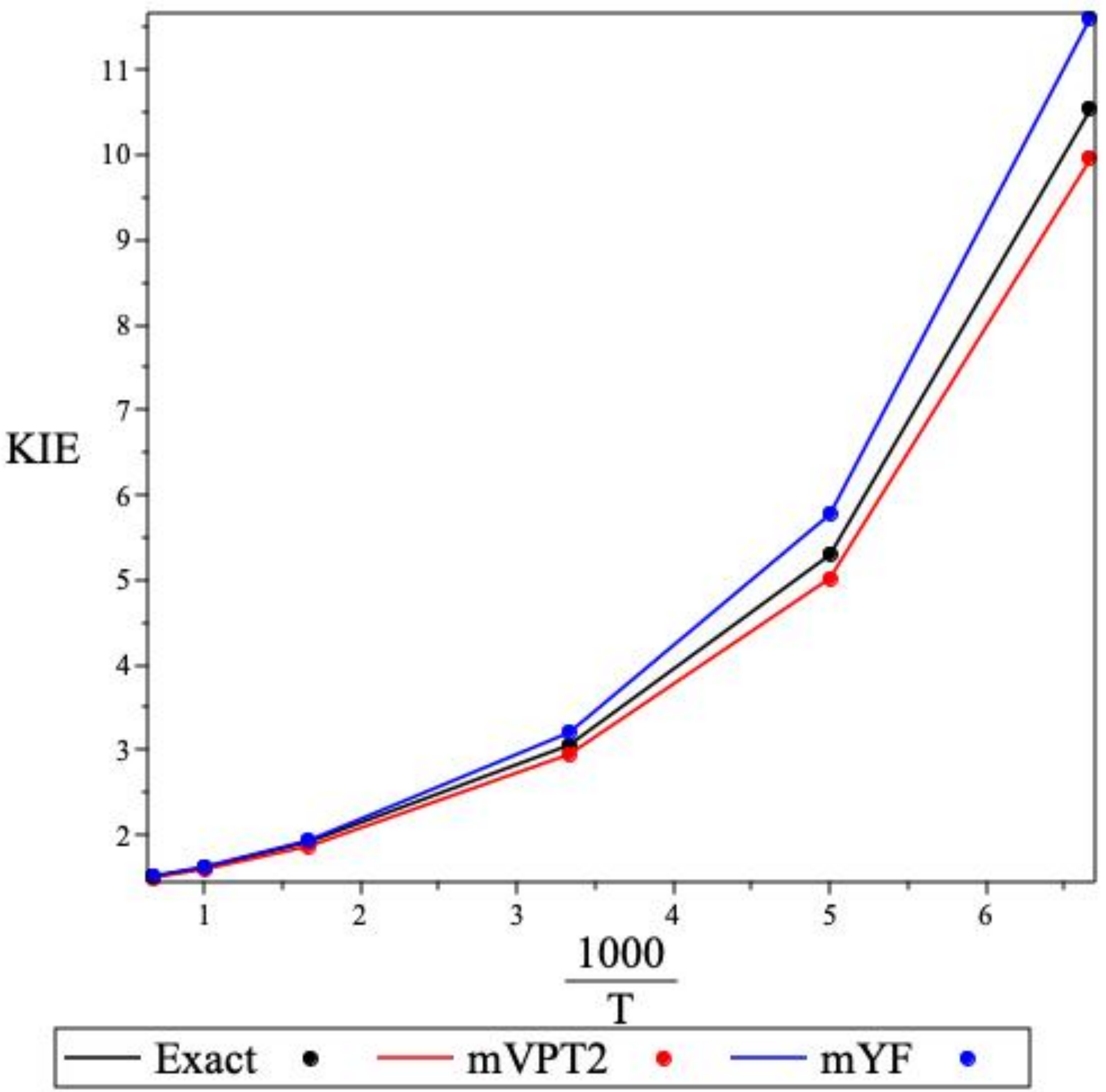
Collinear $D + H_2$ reaction



Instanton energy (eV)	Color code
0.30	Blue
0.33	yellow
0.35	green
0.37	red
0.39	purple
0.41	brown

T(K)	Exact Rates	mVPT2 Rates	mYF Rates
1500	**15867**	16265 (2.5%)	15540 (2.7%)
1000	**4633.1**	4832.3 (4.3%)	4418.5 (4.6%)
600	**452.18**	484.74 (7.2%)	411.48 (9%)
300	**2.2595**	2.6014 (15%)	1.8202 (20.4%)
200	**1.9798E-02**	2.3757E-02 (22.74%)	1.4519E-02 (29.61%)
150	**3.70228E-04**	4.6467E-04 (29.7%)	2.4351E-04 (34.23%)





KIE
1000/T
Exact
mVPT2
mYF

Summary

- The half point problem inherent to Kemble's expression has been solved.

- Two solutions have been presented : one which shifts the energy scale of the action (mVPT2) and one which shifts the action directly (mYF).

- Importance of E_0 , which is a correction term dependent on $\hbar^2$ appearing in the VPT2 theory is seen.

- Application to Eckart barriers shows the power of the mVPT2 and mYF theories.

- Both mVPT2 and mYF theories have been extended to calculate thermal rates of collinear chemical reactions "on-the-fly". Results indicate that the mVPT2 and mYF theories account for the correct $\hbar^2$ limit at high temperatures. In low temperatures as well , the rates are better than the RPMD rates , atleast for the $H + H_2$ case , exemplifying the importance of E_0 .

- One can in principle calculate the $\hbar^4$ expansion for the thermal transmission coefficient , but it will require derivatives of the potential up to eighth order at the barrier top. This has been implemented at least in 1D cases , however implementing it in more than 1D "on the fly" requires that the derivatives up to eighth order be accurate and implementing this with the present level of quantum chemistry codes is in itself a challenging problem.