Comment on Quantum Transition State Theory

Stuart A. Rice,* Soonmin Jang, and Meishan Zhao

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637

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In a previous paper (*J. Phys. Chem.* **1994**, *98*, 3444), we showed, within the framework of the reaction coordinate representation of the dynamics of a chemical reaction, that application of a complex scaling transformation to the reaction coordinate leads naturally to the definition of transition states with complex energies and to the definition of an operator whose expectation values are the lifetimes of these states. That analysis has the unphysical feature of not eliminating the dependence of the lifetime operator on the positive angle parameter of the unitary transformation that generates the scaling of the reaction coordinate. In this paper, we reexamine the approach used earlier and remove this unphysical feature of the analysis. We recover the results of our earlier analysis and provide an interpretation of other related results in the literature.

I. Introduction

Considerable effort has been devoted to the development of a quantum transition state theory of reaction rate which is complementary to the classical transition state theory of reaction rate.

Consider, first, the classical version of the theory.[1−14] In this case the transition state is a dividing surface in phase space which both defines the separate subspaces of reactants and products and has the property that a system trajectory which crosses it does not recross. In the most widely used version of the classical theory[15] the dividing surface is defined in the many-body configuration space, but that definition does not always satisfy the condition that system trajectories can cross only once. The most recent versions of classical transition state theory[16−35] identify the dividing surface with the system separatrix, which is difficult to determine in a many-body system but which does satisfy the requirement that a system trajectory can only cross once. The use of the separatrix for the dividing surface also properly incorporates the nonlinear dynamics of the system.

All of the preceding leads to the inference that if the conventional definition of the dividing surface in configuration space is adopted, classical transition state theory will be most accurate if the reaction occurs by passage over a simple barrier on the potential energy surface, without the intervention of long-lived collision complexes. Nevertheless, classical transition state theory is also useful to describe reactions in which long-lived collision complexes occur,[35] although in such cases it is better to define the dividing surface as the system separatrix. Leaving aside the need to use quantum mechanics to describe a molecular system, it can be said that the principal difficulty associated with treating reactions that involve a long-lived collision complex can be avoided by proper choice of the dividing surface in the full phase space of the system.

Consider, now, the quantum version of transition state theory.[31,37−42] If a long-lived collision complex exists, the states of the complex have eigenenergies of the form $E_j^{\mathrm{res}} = E_j - i\Gamma_j/2$ corresponding to the fact that these states are metastable. Of course, in the scattering theory description of the reaction, these metastable states appear as scattering resonances. Seideman and Miller[43,44] have shown that for a direct bimolecular reaction, which involves penetration through a simple barrier on a potential energy surface and for which there are no metastable states, the eigenenergies have the same form as do the Siegert eigenenergies associated with scattering resonances. Starting from a different point of view, Truhlar and Garrett[45] have used the fact that the cumulative reaction probabilities obtained from accurate quantum mechanical calculations of several direct bimolecular reactions have features that can be associated with resonances as a motivation for reformulating transition state theory for bimolecular reactions in terms of the properties of resonances.[46,47] Given this formulation, it is useful to have a convenient method for calculating the widths of transition state resonances.

In a previous paper, we showed,[48] within the framework of the reaction coordinate representation of the dynamics of a chemical reaction, that application of a complex scaling transformation to the reaction coordinate leads naturally to the identification of transition states as resonances, where we use the term "resonance" to indicate that the energy of a state is complex. That analysis, which also leads to the definition of a resonance width operator whose expectation values are the lifetimes of the resonances, has the unphysical feature of not eliminating the dependence of the transition width operator on the positive angle parameter of the unitary transformation that generates the scaling of the reaction coordinate. In this paper, we reexamine the approach used earlier and remove this unphysical feature of the analysis. We recover the results of our earlier analysis and provide an interpretation of other related results in the literature.

II. Complex Scaling of the Reaction Coordinate

The complex scaling transformation of a dynamical system is based on replacement of the ordinary coordinates with complex coordinates via the substitution[49−54]

$$r \rightarrow r\,\exp\{\mathrm{i}\theta\} \qquad (2.1)$$

The transformation is carried out by use of the unitary scaling operator

$$\hat{U}(\theta) = \exp\{\mathrm{i}\hat{S}\theta\} \qquad (2.2)$$

where $\hat{S}$ is the generator of the scaling transformation and θ is a positive angle parameter. Under the dilatation transformation (2.1) the wave function is defined by

$$\hat{U}(\theta)\,\psi(\mathbf{r}) = \exp\left\{\mathrm{i}\left(\frac{n}{2}\right)\theta\right\}\psi(\mathbf{r}\mathrm{e}^{\mathrm{i}\theta}) \qquad (2.3)$$

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where **r** is an n-dimensional vector. It is easy to show that

$$\frac{\mathrm{d}}{\mathrm{d}\theta}[\hat{U}(\theta)\ \psi(\mathbf{r})]_{\theta=0} = \mathrm{i}\hat{S}\psi(\mathbf{r}) \quad (2.4)$$

A direct evaluation of (2.4) yields

$$\frac{\mathrm{d}}{\mathrm{d}\theta}[\hat{U}(\theta)\psi(\mathbf{r})]|_{\theta=0} = \frac{\mathrm{d}}{\mathrm{d}\theta}\left[\exp\left\{\mathrm{i}\left(\frac{n}{2}\right)\theta\right\}\psi(\mathbf{r}\mathrm{e}^{\mathrm{i}\theta})\right]\Big|_{\theta=0}$$

$$= \left[\frac{\mathrm{i}}{2}\exp\left\{\mathrm{i}\left(\frac{n}{2}\right)\theta\right\}\psi(\mathbf{r}\mathrm{e}^{\mathrm{i}\theta}) + \mathrm{i}\exp\left\{\mathrm{i}\left(\frac{n}{2}\right)\theta\right\}\frac{\mathrm{d}\psi(\mathbf{r}\mathrm{e}^{\mathrm{i}\theta})}{\mathrm{d}\theta}\right]\Big|_{\theta=0} \quad (2.5)$$

Inserting the identities

$$\frac{\mathrm{d}\psi(\mathbf{r}\mathrm{e}^{\mathrm{i}\theta})}{\mathrm{d}\theta}|_{\theta=0} = \nabla\psi(\mathbf{r})\cdot\mathbf{r} \quad (2.6a)$$

$$\nabla\cdot[\psi(\mathbf{r})\mathbf{r}] = \psi(\mathbf{r}) + \nabla\psi(\mathbf{r})\cdot\mathbf{r} \quad (2.6b)$$

into (2.5) we find

$$\frac{\mathrm{d}}{\mathrm{d}\theta}[\hat{U}(\theta)\psi(\mathbf{r})]|_{\theta=0} = \frac{\mathrm{i}}{2}[\nabla\cdot\mathbf{r} + \mathbf{r}\cdot\nabla]\psi(\mathbf{r}) \quad (2.7)$$

A comparison of (2.7) with (2.4) yields the following form for the generator S:

$$\hat{S} = {}^{1}/_{2}[\nabla\cdot\mathbf{r} + \mathbf{r}\cdot\nabla] \quad (2.8)$$

If **r** is a Cartesian coordinate (2.8) can also be written in the form

$$\hat{S} = \frac{\mathrm{i}}{2\hbar}[\mathbf{p}\cdot\mathbf{r} + \mathbf{r}\cdot\mathbf{p}] \quad (2.9)$$

after introduction of the conjugate momentum operator $\mathbf{p} = (\hbar/\mathrm{i})\nabla$.

We suppose that all atomic motion except that along the reaction coordinate is bounded. This assumption is valid both for a direct bimolecular reaction and for the penetration of a barrier on the potential energy surface. We choose to apply complex scaling only to the reaction coordinate, denoted s. Use of (2.2) then leads to

$$\hat{U}(\theta)\ \psi(s,\mathbf{x}) = \mathrm{e}^{\mathrm{i}\theta/2}\psi(s\mathrm{e}^{\mathrm{i}\theta},\mathbf{x}) \quad (2.10)$$

where **x** represents all coordinates except the reaction coordinate. The specific form of the dilatation operator which generates a transformation of only the reaction coordinate is

$$\hat{S} = \frac{1}{2}\left[\frac{\mathrm{d}}{\mathrm{d}s}s + s\frac{\mathrm{d}}{\mathrm{d}s}\right] \quad (2.11)$$

which can also be written

$$\hat{S} = \frac{\mathrm{i}}{2\hbar}[\hat{p}_s s + s\hat{p}_s] \quad (2.12)$$

when we make the identification $\hat{p}_s = (\hbar/\mathrm{i})(\mathrm{d}/\mathrm{d}s)$. We now substitute (2.12) into (2.2) to obtain an explicit expression for the complex scaling operator:

$$\hat{U}(\theta) = \exp\{\mathrm{i}\hat{S}\theta\} = \exp\left\{\frac{-\theta}{2\hbar}[\hat{p}_s s + s\hat{p}_s]\right\} \quad (2.13)$$

S is an invariant of the motion which, we shall see, is directly related to the virial.

III. The Complex-Scaled Hamiltonian

Consider the reaction path Hamiltonian operator

$$\hat{H}(s,\mathbf{x}) = \frac{1}{2\mu}(\hat{\mathbf{p}}^2 + \hat{p}_s^{\,2}) + V(s,\mathbf{x}) \quad (3.1)$$

where μ is the reduced mass. Because the reaction coordinate is the only coordinate relevant to our discussion, in the following we omit reference to the other coordinates unless otherwise specified.

The complex scaled Hamiltonian operator takes the form

$$\hat{H}_\theta(s) = \hat{U}(\theta)\ \hat{H}(s)\ \hat{U}^{-1}(\theta) = \mathrm{e}^{\mathrm{i}\hat{S}\theta}\hat{H}(s)\mathrm{e}^{-\mathrm{i}\hat{S}\theta} = \hat{H}(s\mathrm{e}^{\mathrm{i}\hat{S}\theta}) \quad (3.2)$$

We now expand $\hat{H}_\theta(s)$ in powers of θ by employing the operator identity[55]

$$\mathrm{e}^{\hat{A}}\hat{B}\mathrm{e}^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!}[\hat{A}, [\hat{A}, \hat{B}]] + \frac{1}{3!}[\hat{A}, [\hat{A}, [\hat{A}, \hat{B}]]] + \ldots \quad (3.3)$$

and the following commutation relations:

$$[s\hat{p}_s, H(s)] = [\hat{p}_s s, H(s)] \quad (3.4a)$$

$$[s\hat{p}_s, H(s)] = \left[s\hat{p}_s, \frac{\hat{p}_s^{\,2}}{2\mu} + V(s,\mathbf{x})\right] = \left[s\hat{p}_s, \frac{\hat{p}_s^{\,2}}{2\mu}\right] + [s\hat{p}_s, V(s,\mathbf{x})]$$

$$= [s, \hat{p}_s^{\,2}]\frac{\hat{p}_s}{2\mu} + s[\hat{p}_s, V(s,\mathbf{x})]$$

$$= \hat{p}_s[s, \hat{p}_s]\frac{\hat{p}_s}{2\mu} + [s, \hat{p}_s]\frac{\hat{p}_s^{\,2}}{2\mu} + s[\hat{p}_s, V(s,\mathbf{x})]$$

$$= \mathrm{i}\hbar\frac{\hat{p}_s^{\,2}}{\mu} - \mathrm{i}\hbar s\frac{\partial V(s,\mathbf{x})}{\partial s} \quad (3.4b)$$

Let

$$\hat{A} = \mathrm{i}\hat{S}\theta = \frac{-\theta}{2\hbar}[\hat{p}_s s + s\hat{p}_s] \quad (3.5a)$$

$$\hat{B} = \hat{H}(s) = \sum_j \frac{\hat{p}_j^{\,2}}{2\mu} + \frac{\hat{p}_s^{\,2}}{2\mu} + V(s,\mathbf{x}) \quad (3.5b)$$

whereupon we find that

$$[\hat{A}, \hat{B}] = (-\mathrm{i}2\theta)\left[\frac{\hat{p}_s^{\,2}}{2m} - \frac{1}{2}s\frac{\partial V(s,\mathbf{x})}{\partial s}\right] = (-\mathrm{i}2\theta)\hat{H}_1$$

$$[A, [\hat{A}, \hat{B}]] = (-\mathrm{i}2\theta)^2\left[\frac{\hat{p}_s^{\,2}}{2m} - \frac{1}{2}s\frac{\partial V_1(s,\mathbf{x})}{\partial s}\right] = (-\mathrm{i}2\theta)^2\hat{H}_2$$

......

$$[\hat{A},...[\hat{A}, \hat{B}]] = (-\mathrm{i}2\theta)^n\left[\frac{\hat{p}_s^{\,2}}{2m} - \frac{1}{2}s\frac{\partial V_{n-1}(s,\mathbf{x})}{\partial s}\right] = (-\mathrm{i}2\theta)^n\hat{H}_n \quad (3.6)$$

and

$$\hat{H}_n = \frac{\hat{p}_s^{\,2}}{2m} + V_n(s,\mathbf{x}), \quad n = 1, 2, 3, ..., \infty \quad (3.7)$$

$$V_1(s,\mathbf{x}) = -\frac{1}{2}s\frac{\partial V(s,\mathbf{x})}{\partial s}$$

$$V_n(s,\mathbf{x}) = -\frac{1}{2}s\frac{\partial V_{n-1}(s,\mathbf{x})}{\partial s}, \quad n = 2, 3, ..., \infty \quad (3.8)$$

Finally, applying (3.3)−(3.8) to (3.2), the complex-scaled Hamiltonian operator takes the form

$$\hat{H}_\theta(s) = \hat{H} + (-\mathrm{i}2\theta)\hat{H}_1(s) + \frac{(-\mathrm{i}2\theta)^2}{2!}\hat{H}_2(s) + \frac{(-\mathrm{i}2\theta)^3}{3!}\hat{H}_3(s) + ... + \frac{(-\mathrm{i}2\theta)^n}{n!}\hat{H}_n(s) + ... \quad (3.9)$$

This representation of the transformed Hamiltonian operator has several advantages. The complex virial theorem,[56] i.e., the analog of the conventional virial theorem,[57] can be obtained directly from (3.9). Furthermore, it is obvious from the form of the expansion displayed in (3.9) why the transformation (2.1) leads to a rotation of the continuum energy spectrum to the lower complex energy plane by an angle (2θ).

IV. Variational Stationary Point and the Complex Viral Theorem

Given the complex-scaled Hamiltonian operator $\hat{H}_\theta(s)$ and a resonance state $\Phi(s)$, the expectation value of the resonance energy is a functional of the scaling parameter:

$$W(\theta) = \langle\Phi(s)|\hat{H}_\theta(s)|\Phi(s)\rangle \quad (4.1)$$

The stationary point of $W(\theta)$ with respect to variation of θ determines the true resonance energy. We write

$$\left.\frac{\mathrm{d}W(\theta)}{\mathrm{d}\theta}\right|_{\theta=\theta_\mathrm{c}} = 0, \quad E_\mathrm{res} = W(\theta_\mathrm{c}) \quad (4.2)$$

where θ_c is the stationary point value of θ. Since $W(\theta)$ is, in general, a complex functional of θ, we write

$$W(\theta) = W_\mathrm{R}(\theta) - \mathrm{i}W_\mathrm{i}(\theta) \quad (4.3)$$

where $W_\mathrm{R}(\theta)$ and $W_\mathrm{i}(\theta)$ are real numbers for a given θ. Using (4.3), (4.2) becomes

$$\left.\frac{\mathrm{d}W_\mathrm{R}(\theta)}{\mathrm{d}\theta}\right|_{\theta=\theta_\mathrm{R}} = 0, \quad \left.\frac{\mathrm{d}W_\mathrm{i}(\theta)}{\mathrm{d}\theta}\right|_{\theta=\theta_\mathrm{i}} = 0 \quad (4.4)$$

We must expect to find that $\theta_\mathrm{R} \neq \theta_\mathrm{i}$ for a trial wave function which is not an eigenfunction.

To locate the variational minimum (4.4) we return to the complex-scaled Hamiltonian

$$\hat{H}_\theta(s) = \sum_{n=0}^{\infty}\frac{(-\mathrm{i}2\theta)^n}{n!}\hat{H}_n(s), \quad \hat{H}_0(s) = \hat{H}(s) \quad (4.5)$$

and calculate the derivative

$$\frac{\mathrm{d}\hat{H}_\theta(s)}{\mathrm{d}(-\mathrm{i}2\theta)} = \sum_{n=0}^{\infty}\frac{(-\mathrm{i}2\theta)^n}{n!}\hat{H}_{n+1}(s) = \hat{H}_1(s\mathrm{e}^{\mathrm{i}\theta}) \quad (4.6a)$$

which can be rewritten in the form

$$\frac{\mathrm{d}\hat{H}_\theta(s)}{\mathrm{d}(-\mathrm{i}2\theta)} = U(\theta)\left[\frac{\hat{p}_s^{\,2}}{2m} - \frac{1}{2}s\frac{\partial V(s,\mathbf{x})}{\partial s}\right]\hat{U}^{-1}(\theta) \quad (4.6b)$$

Application of the stationary condition (4.2) to (4.6) leads to

$$\left.\frac{\mathrm{d}W(\theta)}{\mathrm{d}\theta}\right|_{\theta=\theta_\mathrm{c}} = \left.\left\langle\frac{\mathrm{d}\hat{H}_\theta(s)}{\mathrm{d}(-\mathrm{i}2\theta)}\right\rangle\right|_{\theta=\theta_\mathrm{c}} = \left.\left\langle\Phi(s)\middle|U(\theta)\left(\frac{\hat{p}_s^{\,2}}{2m} - \frac{1}{2}s\frac{\partial V(s,\mathbf{x})}{\partial s}\right)\hat{U}^{-1}(\theta)\middle|\Phi(s)\right\rangle\right|_{\theta=\theta_\mathrm{c}} = 0 \quad (4.7)$$

Equation 4.7 is the complex analog of the virial theorem which requires that, in a stationary state, the expectation value of the potential energy is equal to the negative of twice the expectation value of the kinetic energy.

We now use the complex virial theorem (4.7) to determine the stationary point θ_c. For convenience, we express the complex virial theorem in the alternative form

$$\left\langle\frac{\hat{p}_s^{\,2}}{2m}\right\rangle\mathrm{e}^{-\mathrm{i}2\theta_\mathrm{c}} - \left\langle\left(\frac{1}{2}s'\frac{\partial V(s',\mathbf{x})}{\partial s'}\right)_{s'=s\mathrm{e}^{-\mathrm{i}\theta_\mathrm{c}}}\right\rangle = 0 \quad (4.8)$$

Then θ_c can be obtained from the implicit relation

$$\mathrm{e}^{-\mathrm{i}2\theta_\mathrm{c}} = \frac{\left\langle\left(\frac{1}{2}s'\frac{\partial V(s',\mathbf{x})}{\partial s'}\right)_{s'=s\mathrm{e}^{-\mathrm{i}\theta_\mathrm{c}}}\right\rangle}{\left\langle\frac{\hat{p}_s^{\,2}}{2m}\right\rangle} \quad (4.9)$$

by iteration.

V. Time Evolution of the Resonance States

A scattering resonance is conveniently described as a state with finite lifetime; for the cases of interest to us it can be represented as a superposition of bound and continuum states with complex energy

$$E_j^\mathrm{res} = E_j - \mathrm{i}\Gamma_j/2 \quad (5.1)$$

where E_j is the energy of the isolated narrow resonance and Γ_j is the full width at half-maximum (fwhm) of this resonance.

The time evolution of a state with complex energy is $\exp\{-i(E_j - i\Gamma_j/2)t/\hbar\}$, and its amplitude decays as $\exp\{-(\Gamma_j/2)t/\hbar\}$.

The complex scaling transformation described in the last section localizes the resonance states and isolates them from the continuum part of the spectrum. Indeed, a transformed scattering resonance acts like a bound state with square integrable wave function. Under the complex scaling operation the Hamiltonian of the system assumes the form

$$\hat{H}_\theta(s) = \hat{U}(\theta)\,\hat{H}(s)\,\hat{U}^{-1}(\theta) \tag{5.2}$$

The time evolution of the system after complex scaling is described by the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi_\theta(s,t) = \hat{H}_\theta(s)\,\Psi_\theta(s,t) \tag{5.3}$$

The formal solution to (5.3) is

$$\Psi_\theta(s,t) = \exp\left\{-\frac{i}{\hbar}\hat{H}_\theta(s)t\right\}|\Psi_\theta(s,0) \tag{5.4}$$

which has exactly the same form as for the unscaled system evolution.

The time evolution operator in (5.4) can also been expanded in powers of θ by use of the operator identities

$$e^{\hat{A}}e^{\hat{B}} = \exp\{A + B + {}^1/_2[A,B] + ...\} \tag{5.5}$$

and

$$\exp\left\{-\frac{i}{\hbar}\hat{H}_\theta(s)t\right\} = \exp\{-i\hat{S}\theta\}\exp\left\{-\frac{i}{\hbar}\hat{H}(s)t\right\}\exp\{i\hat{S}\theta\} \tag{5.6}$$

A direct evaluation of the operators yields

$$\exp\left\{-\frac{i}{\hbar}\hat{H}_\theta(s)t\right\} = \exp\left\{-\frac{i}{\hbar}\sum_{n=0}^{\infty}\frac{(-i2\theta)^n}{n!}\hat{H}_n(s)t\right\} \tag{5.7}$$

with $\hat{H}_0(s) = \hat{H}(s)$, and

$$\hat{H}_\theta(s) = \hat{H} + (-i2\theta)\hat{H}_1(s) + \frac{(-i2\theta)^2}{2!}\hat{H}_2(s) + \frac{(-i2\theta)^3}{3!}\hat{H}_3(s) + ... + \frac{(-i2\theta)^n}{n!}\hat{H}_n(s) + ... \tag{5.8}$$

as before.

If the initial state is a resonance state $\Psi_n(s)$ with eigenenergy $(E_n - i\Gamma_n/2)$, then

$$\psi_n(s,t) = \exp\left\{-\frac{i}{\hbar}\left(E_n - i\frac{\Gamma_n}{2}\right)t\right\}\psi_n(s)$$

and the norm $\|\psi_n(s,t)\| = \exp\{-(\Gamma_n t/\hbar)\}\|\psi_n(s,0)\|$ decays exponentially with a life time $\tau = \hbar\Gamma_n^{-1}$.

VI. The Resonance Energy

The scaled Hamiltonian operator can be formally separated into real and imaginary parts:

$$\hat{H}_\theta(s) = \left[\hat{H}_0 - \frac{(2\theta)^2}{2!}\hat{H}_2(s) + \frac{(2\theta)^4}{4!}\hat{H}_4(s) + ... + \frac{(-1)^n(2\theta)^{2n}}{(2n)!}\hat{H}_{2n}(s) + ...\right] - i\left[(2\theta)\hat{H}_1(s) - \frac{(2\theta)^3}{3!}\hat{H}_3(s) + ... + \frac{(-1)^{n-1}(2\theta)^{2n-1}}{(2n-1)!}\hat{H}_{2n-1}(s) + ...\right] \tag{6.1}$$

With this separation, and noting that all the $\hat{H}_n(s)$ should have real expectation values, we define the resonance energy and resonance width operators by, respectively,

$$\hat{E}_{res}(\theta) = \hat{H}_0 - \frac{(2\theta)^2}{2!}\hat{H}_2(s) + \frac{(2\theta)^4}{4!}\hat{H}_4(s) + ... = \sum_{n=0}^{\infty}\frac{(-1)^n(2\theta)^{2n}}{(2n)!}\hat{H}_n(s) \tag{6.2}$$

$$\frac{\hat{\Gamma}(\theta)}{2} = (2\theta)\hat{H}_1(s) - \frac{(2\theta)^3}{3!}\hat{H}_3(s) + \frac{(2\theta)^5}{5!}\hat{H}_5(s) + ... = \sum_{n=1}^{\infty}\frac{(-1)^{n-1}(2\theta)^{2n-1}}{(2n-1)!}\hat{H}_{2n-1}(s) \tag{6.3}$$

Assuming that the expansion displayed in (6.3) is convergent, for potential functions satisfying

$$\hat{H}_n \ll \hat{H}_{n-1} \tag{6.4}$$

the resonance width operator may be approximated by

$$\frac{\hat{\Gamma}(\theta)}{2} = (2\theta)\left(\frac{\hat{p}^2}{2\mu} - \frac{1}{2}s\frac{dV(s)}{ds}\right) \tag{6.5}$$

and the angle parameter may be approximated by

$$\frac{d}{d(2\theta)}\left[(2\theta)\hat{H}_1(s) - \frac{(2\theta)^3}{3!}\hat{H}_3(s)\right] = 0 \tag{6.6}$$

which then gives

$$(2\theta) = \left(\frac{2\hat{H}_1(s)}{\hat{H}_3(s)}\right)^{1/2} \tag{6.7}$$

Equations 6.5−6.7 are also a useful approximation for the calculation of resonance energy and width in systems with a nearly harmonic potential energy surface.

Note that $\hat{E}_{res}(\theta)$ and $\hat{\Gamma}(\theta)$ are determined simultaneously, so have the same eiegenfunctions, i.e., when $\theta = \theta_c$ the operators $\hat{E}_{res}(\theta)$ and $\hat{\Gamma}(\theta)$ commute.

Although (6.2) and (6.3) are complicated, there are some special cases which are simple to analyze.

Consider the harmonic potential $V(s) = ks^2/2$. It is easy to show that

$$\hat{H}_0 = \hat{H}_2 = \hat{H}_4 = ... = \hat{H}_{2n} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}ks^2 \quad (6.8a)$$

$$\hat{H}_1 = \hat{H}_3 = \hat{H}_5 = ... = \hat{H}_{2n-1} = \frac{\hat{p}^2}{2\mu} - \frac{1}{2}ks^2 \quad (6.8b)$$

so that the corresponding resonance energy and width operators are

$$\hat{E}_{\mathrm{res}}(\theta) = \left(\frac{\hat{p}^2}{2\mu} + \frac{1}{2}ks^2\right)\sum_{n=0}^{\infty}\frac{(-1)^n(2\theta)^{2n}}{(2n)!} = \left(\frac{\hat{p}^2}{2\mu} + \frac{1}{2}ks^2\right)\cos(2\theta) \quad (6.9a)$$

$$\frac{\hat{\Gamma}(\theta)}{2} = \left(\frac{\hat{p}^2}{2\mu} - \frac{1}{2}ks^2\right)\sum_{n=1}^{\infty}\frac{(-1)^{n-1}(2\theta)^{2n-1}}{(2n-1)!}\hat{H}_{2n-1}(s) = \left(\frac{\hat{p}^2}{2\mu} - \frac{1}{2}ks^2\right)\sin(2\theta) \quad (6.9b)$$

It is obvious that the harmonic oscillator wave function is a joint eigenfunction of these operators with expectations values

$$\langle\hat{E}_{\mathrm{res}}(\theta)\rangle = \left\langle\left(\frac{\hat{p}^2}{2\mu} + \frac{1}{2}ks^2\right)\right\rangle\cos(2\theta) \quad (6.10a)$$

$$\left\langle\frac{\hat{\Gamma}(\theta)}{2}\right\rangle = = \left\langle\left(\frac{\hat{p}^2}{2\mu} - \frac{1}{2}ks^2\right)\right\rangle\sin(2\theta) \quad (6.10b)$$

The stationary point with respect to variation of θ is determined by

$$\frac{\mathrm{d}\langle\hat{E}_{\mathrm{res}}(\theta)\rangle}{\mathrm{d}\theta} = -2\left\langle\left(\frac{\hat{p}^2}{2\mu} + \frac{1}{2}ks^2\right)\right\rangle\sin(2\theta) = 0, \quad \theta = 0, \frac{\pi}{2} \quad (6.11a)$$

$$\frac{\mathrm{d}}{\mathrm{d}\theta}\left\langle\frac{\hat{\Gamma}(\theta)}{2}\right\rangle = 2\left\langle\left(\frac{\hat{p}^2}{2\mu} - \frac{1}{2}ks^2\right)\right\rangle\cos(2\theta) = 0, \quad \theta = \frac{\pi}{4} \quad (6.11b)$$

The possible choices of θ are restricted to $\theta = 0$ and $\theta = \pi/4$ because $\theta = \pi/2$ is nonphysical by definition. We note that

$$\left\langle\left(\frac{\hat{p}^2}{2\mu} + \frac{1}{2}ks^2\right)\right\rangle_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad \left\langle\left(\frac{\hat{p}^2}{2\mu} - \frac{1}{2}ks^2\right)\right\rangle_n = 0 \quad (6.12)$$

and for either $\theta = 0$ or $\theta = \pi/4$ one obtains

$$E_{\mathrm{res}} = (n + {}^1/_2)\hbar\omega, \quad \Gamma_n = 0 \quad (6.13)$$

Thus, as expected, complex scaling does not alter the physical nature of a bound state of the system.

We now consider scattering by the parabolic barrier $V(s) = -ks^2/2$. The resonance energy and width operators are

$$\hat{E}_{\mathrm{res}}(\theta) = \hat{H}\cos(2\theta) \quad (6.14a)$$

$$\hat{\Gamma}(\theta)/2 = \hat{H}_1\sin(2\theta) \quad (6.14b)$$

As before, the harmonic oscillator wave function is a joint eigenfunction of these operators, and the stationary point with respect to variation of θ is obtained from

$$\frac{\mathrm{d}\langle\hat{E}_{\mathrm{res}}(\theta)\rangle}{\mathrm{d}\theta} = -2\langle\hat{H}\rangle\sin(2\theta) = 0, \quad \theta = 0, \frac{\pi}{2} \quad (6.15a)$$

$$\frac{\mathrm{d}}{\mathrm{d}\theta}\left\langle\frac{\hat{\Gamma}(\theta)}{2}\right\rangle = 2\langle\hat{H}_1\rangle\cos(2\theta) = 0, \quad \theta = \frac{\pi}{4} \quad (6.15b)$$

The only physical solution is $\theta = \pi/4$. Note that this solution also satisfies (6.15a). The substitution of $\theta = \pi/4$ into (6.14) yields

$$\frac{\hat{\Gamma}}{2} = \left(\frac{\hat{p}^2}{2\mu} - \frac{1}{2}s\frac{\mathrm{d}V(s)}{\mathrm{d}s}\right) \quad (6.16)$$

which is the resonance width operator for scattering over a parabolic potential barrier.[48,58]

Consider, now, the anharmonic potential function[59]

$$V(s) = {}^1/_2\mu\omega^2 s^2 - \beta s^4 \quad (6.17)$$

Depending on the value of β, this potential supports both bound and resonant states. It is easy to show that for the potential function (6.17)

$$\hat{H}_1 = \frac{\hat{p}^2}{2\mu} - \frac{1}{2}\mu\omega^2 s^2 + 2\beta s^4$$

$$\hat{H}_3 = \frac{\hat{p}^2}{2\mu} - \frac{1}{2}\mu\omega^2 s^2 + 8\beta s^4 \quad (6.18)$$

The resonance width operator is approximated by

$$\frac{\hat{\Gamma}(\theta)}{2} \approx (2\theta)\left(\frac{\hat{p}^2}{2\mu} - \frac{1}{2}\mu\omega^2 s^2 + 2\beta s^4\right) \quad (6.19)$$

with

$$(2\theta) \approx \left(\frac{2\hat{H}_1(s)}{\hat{H}_3(s)}\right)^{1/2} \quad (6.20)$$

To proceed further we choose a set of near harmonic basis functions ϕ_n, such that

$$\left\langle\phi_n\left|\frac{\hat{p}^2}{2\mu} - \frac{1}{2}\mu\omega^2 s^2\right|\phi_n\right\rangle = c_1 \quad (6.21)$$

$$\langle\phi_n|s^4|\phi_n\rangle = c_2 \quad (6.22)$$

where c_1 and c_2 are constants. Because the ϕ_n are close to but not exact harmonic oscillator functions, c_1 is small but not zero. Using (6.21) and (6.22) we find

$$\left\langle\phi_n\left|\frac{2\hat{H}_1(s)}{\hat{H}_3(s)}\right|\phi_n\right\rangle = \frac{c_1 + 2c_2\beta}{c_1 + 8c_2\beta} \quad (6.23)$$

If $c_1 \ll c_2$

$$\left\langle\phi_n\left|\frac{2\hat{H}_1(s)}{\hat{H}_3(s)}\right|\phi_n\right\rangle = \frac{1}{4\left(1 + \frac{c_1}{8c_2\beta}\right)} \quad (6.24)$$

Since

$$e^{-\epsilon} = 1 - \epsilon + \frac{1}{2}\epsilon^2 - ...$$

$$\frac{1}{1+\epsilon} = 1 - \epsilon + \epsilon^2 - ...$$

for small ϵ, when $c_1 \ll c_2$ we may write (6.24) in the form

$$\left\langle \phi_n \left| \frac{2\hat{H}_1(s)}{\hat{H}_3(s)} \right| \phi_n \right\rangle \approx \frac{1}{4} \exp\left\{-\frac{c_1}{8c_2\beta}\right\} \tag{6.25}$$

Using (6.25) in (6.20) leads to

$$(2\theta) \approx \frac{1}{2} \exp\left\{-\frac{c_1}{4c_2\beta}\right\} \tag{6.26}$$

and from (6.19) we then find the resonance width

$$\Gamma \approx (c_1 + 2\beta c_2) \exp\left\{-\frac{c_1}{4c_2\beta}\right\} \tag{6.27}$$

As expected, when β is approaches zero the resonance width approaches zero (note the singularity in $1/\beta$ as β approaches zero).

VII. Relationship between the Quickert−LeRoy−Miller Semiclassical Theory of Tunneling and Complex Scaling

Quickert, LeRoy, and Miller have suggested that the semiclassical analysis[60] of tunneling through a barrier can be formally transformed into the analysis of bounded motion in the *inverted barrier potential*. QLM's suggestion follows from analysis of the system dynamics in imaginary time, in which case the conjugate momentum is pure imaginary:

$$t = -i\tau$$

$$\bar{p} = \mu\frac{dq}{d\tau} = -ip \tag{7.1}$$

Using τ as the time, Newton's equation of motion reads

$$\mu\frac{d^2q(\tau)}{d\tau^2} = \frac{dV(q)}{dq} \tag{7.2}$$

which implies that the system dynamics is governed by the new Hamiltonian

$$H = \frac{p^2}{2\mu} - V(q) \tag{7.3}$$

If $V(q)$ is a potential barrier, so that $-V(q)$ is a potential well, (7.3) supports bounded motion. By virtue of the transformation (7.1), the energies of the bound states in the inverted potential correspond to the imaginary parts of the complex energies in the original problem hence correspond to resonance widths from which lifetimes can be obtained.

The relationship between the complex-scaling approach described in this paper and the QLM analysis of tunneling can be developed as follows. We first rewrite the resonance width operator defined earlier by taking advantage of the relations

$$\hat{H}_1 = \frac{\hat{p}^2}{2\mu} + \left(-\frac{1}{2}s\frac{d}{ds}\right)V(s)$$

$$\hat{H}_2 = \frac{\hat{p}^2}{2\mu} + \left(-\frac{1}{2}s\frac{d}{ds}\right)^2V(s)$$

$$......$$

$$\hat{H}_n = \frac{\hat{p}^2}{2\mu} + \left(-\frac{1}{2}s\frac{d}{ds}\right)^nV(s) \tag{7.4}$$

Inserting (7.4) into the width operator

$$\frac{\hat{\Gamma}(\theta)}{2} = \sum_{n=1}^{\infty}\frac{(-1)^{n-1}(2\theta)^{2n-1}}{(2n-1)!}\hat{H}_{2n-1}(s)$$

yields

$$\frac{\hat{\Gamma}(\theta)}{2} = \sum_{n=1}^{\infty}\frac{(-1)^{n-1}(2\theta)^{2n-1}}{(2n-1)!}\left[\frac{\hat{p}^2}{2\mu} + \left(-\frac{1}{2}s\frac{d}{ds}\right)^{2n-1}V(s)\right] \tag{7.5}$$

which can be simplified to

$$\frac{\hat{\Gamma}(\theta)}{2} = \frac{\hat{p}^2}{2\mu}\sum_{n=1}^{\infty}\frac{(-1)^{n-1}(2\theta)^{2n-1}}{(2n-1)!} + \sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{(2n-1)!}\left(-\theta s\frac{d}{ds}\right)^{2n-1}V(s)$$

or

$$\frac{\hat{\Gamma}(\theta)}{2} = \sin(2\theta)\frac{\hat{p}^2}{2\mu} - \sin\left(\theta s\frac{d}{ds}\right)V(s) \tag{7.6}$$

As shown in the last section, for a harmonic motion $\theta = \pi/4$ at the stationary point, whereupon eq 7.6 becomes

$$\frac{\hat{\Gamma}(\theta)}{2} = \frac{\hat{p}^2}{2\mu} - V(s) \tag{7.7}$$

which is identical with the result of the QLM semiclassical theory.

VIII. Model Calculations

A. Threshold Resonances for Barrier Crossing Dynamics. As an example of the use of the resonance width operator we describe a very simple scheme for locating resonances near the energy threshold for barrier crossing. Specifically, we use our analysis to estimate the threshold resonance energy and width for an unsymmetric potential that resembles the first vibrationally excited adiabatic one-dimensional potential energy surface for the O + H_2 reaction. The one-dimensional asymmetric potential barrier

$$V(x) = \frac{V_1e^{\alpha(x-x_1)}}{[1+e^{\alpha(x-x_1)}]^2} + \frac{V_2e^{\alpha(x-x_2)}}{[1+e^{\alpha(x-x_2)}]^2} \tag{8.1}$$

is a modified Eckart potential.[47−48,61] With $V_1 = 870.75$ meV, $V_2 = 598.64$ meV, $\alpha = 3\ a_0^{-1}$, and $x_2 = -x_1 = 0.6\ a_0$, eq 8.1

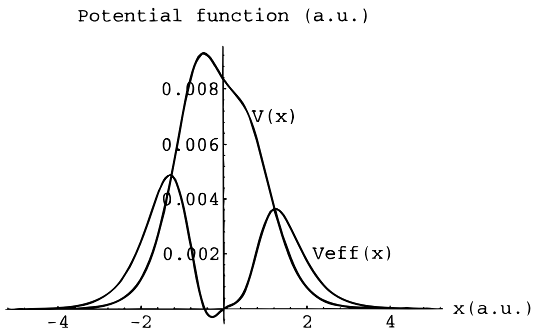

Figure 1. Schematic plot of the modified Eckart potential function (eq 8.1) and the corresponding effective potential function (eq 8.4). Specifically, in this plot, the potential parameter $\alpha = 2.4\ a_0^{-1}$.

resembles the first vibrationally excited adiabatic potential surface for the one-dimensional $O + H_2$ reaction. We take the reduced mass in this system to be $\mu = 6526.3m_e$, where m_e is the mass of the electron. The parameter α will be varied to modify the potential shape. The resonances supported by eq 8.1 have been studied by Friedman and Truhlar,[47] with whose results we will compare our calculations.

Since this potential is very near harmonic for the parameters we use, a harmonic approximation gives very satisfying results. The resonance width operator takes the form

$$\frac{\hat{\Gamma}}{2} = \left[\frac{\hat{p}^2}{2m} + V_{\text{eff}}(x)\right] \qquad (8.2)$$

where the effective potential is given by

$$V_{\text{eff}}(x) = -\frac{1}{2}x\frac{\mathrm{d}V(x)}{\mathrm{d}x} \qquad (8.3)$$

Specifically, we find

$$V_{\text{eff}}(x) = -\frac{2\alpha V_1 e^{2\alpha(x-x_1)}}{[1+e^{\alpha(x-x_1)}]^3} + \frac{\alpha V_1 e^{\alpha(x-x_1)}}{[1+e^{\alpha(x-x_1)}]^2} - \frac{2\alpha V_2 e^{2\alpha(x-x_2)}}{[1+e^{\alpha(x-x_2)}]^3} + \frac{\alpha V_2 e^{\alpha(x-x_2)}}{[1+e^{\alpha(x-x_2)}]^2} \qquad (8.4)$$

The expectation value of the operator in (8.2) gives the resonance width. A system potential function and an effective potential are displayed in Figure 1.

The effective potential can be expanded in a Taylor series

$$V_{\text{eff}}(x) = V_{\text{eff}}(x_0) + \frac{1}{2}k(\alpha)(x-x_0)^2 + \frac{1}{3!}\left(\frac{\mathrm{d}^3V_{\text{eff}}(x)}{\mathrm{d}x^3}\right)_{x=x_0}(x-x_0)^3 + \ldots \qquad (8.5)$$

and the harmonic frequency, for the given parameter α, can be evaluated from

$$\omega(\alpha) = [k(\alpha)/\mu]^{1/2} \qquad (8.6)$$

whereupon the resonance width is $\Gamma(\alpha) = \hbar\omega(\alpha)$, and the resonance lifetime is $\tau(\alpha) = \hbar/\Gamma(\alpha) = 1/\omega(\alpha)$.

The potential parameters for the systems studied are listed in Table 1. Table 2 lists the resonance widths obtained from eq 8.6 using the harmonic approximation for the ground state vibrational frequency; it also lists the results from Truhlar's calculations.

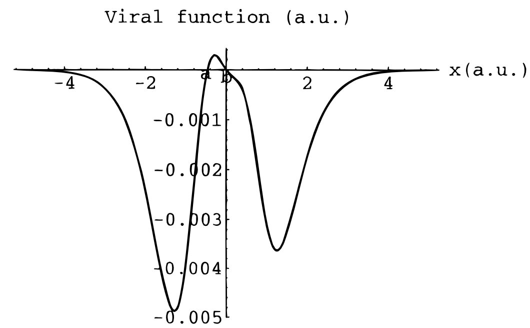

Figure 2. Virial function, $W(x)$, for the quasibound state and the effective potential function. $x = a$ and $x = b$ are the turning points of the $W(x)$ function.

TABLE 1: Critical Positions for the Resonances in Configuration Space on the Modified Eckart Potential Energy Surface (Eq 8.1)[a]

α (a_0^{-1})	a (a_0)	b (a_0)	x_0 (a_0)	$V(x_0)$ (meV)
2.4	−0.463 931	0	−0.287 116	246.542
2.3	−0.440 269	0	−0.268 359	251.845
2.2	−0.413 118	0	−0.246 746	257.496
2.0	−0.349 953	0	−0.197 636	269.858
1.8	−0.283 930	0	−0.151 223	283.452
1.7	−0.254 362	0	−0.132 720	290.538

[a] x_0 is the minimum position of the effective potential; $x = a$ and $x = b$ are the turning points of the virial function $W(x)$ as given in Figure 1.

TABLE 2: Resonance Widths (meV) of the Modified Eckart Potential Function As Generated from the Harmonic Frequency As Defined in Eq 8.6

α (a_0^{-1})	$\Gamma(\alpha)$	ref 47
2.4	40.8	44.2
2.3	37.5	43.1
2.2	34.5	37.8
2.0	29.8	31.0
1.8	27.9	28.9
1.7	27.6	28.5

To evaluate the real part of the resonance energy we note that the complex scaling transformation creates a pseudobound state. According to the virial theorem, for any bound state motion the average kinetic energy of a system is equal to its virial, i.e., $\langle\hat{T}\rangle = \langle{}^1\!/_2 x(\mathrm{d}V(x)/\mathrm{d}x)\rangle$. We conclude that the virial for the pseudobound state generated from the transformed resonance must have a positive value.

The resonance center is given by the expectation value

$$\langle\hat{E}_R\rangle = \langle\hat{T}\rangle + \langle V(x)\rangle \qquad (8.7)$$

from which we find the real part of the energy to be

$$E_R = \langle V(x)\rangle + \left\langle\frac{1}{2}x\frac{\mathrm{d}V(x)}{\mathrm{d}x}\right\rangle \qquad (8.8)$$

For convenience, we have defined the virial operator as a function of reaction coordinate

$$W(x) = \frac{1}{2}x\frac{\mathrm{d}V(x)}{\mathrm{d}x}$$

which is displayed in Figure 2. We note that the virial is only positive for a small range of x, namely from $x = a$ to $x = b$ with a maximum at $x = x_0$ (the position of the minimum of the effective potential). Figure 2 also shows why the scheme proposed in this paper is only useful for locating resonances near threshold. Clearly, the condition that the virial be positive is only useful as a locator of a resonance if the energy domain

TABLE 3: Resonance Energy Center, $E_R(\alpha)$ (meV), of the Modified Eckart Potential Function As Generated from the Harmonic Frequency

α (a_0^{-1})	$\langle\hat{T}\rangle$	$\langle V(x)\rangle$	$E_R(\alpha)$	ref 47
2.4	4.989	242.107	247.10	251.38
2.3	4.053	248.330	252.38	254.38
2.2	3.239	254.789	257.83	258.01
2.0	2.000	268.383	270.38	270.83
1.8	1.231	282.683	283.92	284.65
1.7	0.978	289.966	290.94	291.64

over which the virial is positive is small, which is the case near threshold but not far above threshold.

The evaluation of the expectation values in eq 8.8 is carried out using the ground state harmonic wave function derived from the effective potential for the resonance width, with the fundamental frequency given in (8.6)

$$\langle V(x)\rangle = \int_a^b V(x)|\phi(x,\alpha)|^2\, dx$$

$$\left\langle \frac{1}{2}x\frac{dV(x)}{dx}\right\rangle = \frac{1}{2}\int_a^b x\frac{dV(x)}{dx}|\phi(x,\alpha)|^2\, dx$$

$$\phi(x,\alpha) = A\exp\left\{-\frac{\mu\omega(\alpha)}{2\hbar}(x-x_0)^2\right\} \quad (8.9)$$

where A is a normalization constant. Table 3 lists the resonance energies calculated from eq 8.8 and, for comparison, the results of Truhlar's calculations.

The simple scheme described here for the calculation of the resonance energy is seen to be quite accurate, our results differing from Friedman and Truhlar's calculations by only ~0.24 to 1.7%. The resonance widths are also accurate, being smaller than Truhlar's by ~3 to 8%. The discrepancy between our results and Truhlar's is due, for the most part, to our use of the harmonic approximation.

B. A Simple Realistic Model: Collinear Reaction between H and H_2. We now examine the calculation of the expectation value of the resonance width operator for the collinear reaction of H with H_2. Specifically, we consider a special two-dimensional representation of this reaction on the LSTH potential surface.[62] We label the atoms H, H′, and H″ and define q_1 to be the H−H′ separation, q_2 to be the H′−H″ separation, and $q_3 = q_1 + q_2$ to be the H−H″ separation. The Cartesian coordinates are mass scaled such that $x_1 = \mu^{1/2}q_1$, $x_2 = \mu^{1/2}q_2$, and

$$\mu = \frac{m_H(m_{H'} + m_{H''})}{m_H + m_{H'} + m_{H'}} = \frac{2}{3}m_H$$

We now use the Miller−Handy−Adams[63] reaction path formalism to reduce the description of the dynamics of a many degree of freedom polyatomic molecule to an effective reaction path analysis. In the reaction path formalism the reactive trajectory is determined by the minimum energy path, and small displacements from that path, on the potential energy surface. The usual analysis keeps the full dimensionality of the reacting system, albeit with a focus on motion along and orthogonal to the minimum energy path.[63,64] However, we consider the definition of a reaction path in a reduced dimensionality representation.

The Hamiltonian for an N-particle molecular system is, in Cartesian coordinates,

$$H(p,x) = \sum_{i=1}^{3N}\frac{p_i^2}{2m_i} + V(x_1,...,x_{3N}) \quad (8.10)$$

where **x** and **p** are the 3N-dimensional coordinate and conjugate momentum vectors. Let $\mathbf{a} = (a_1,...,a_{3N})$ be a vector on the reaction path. Then the potential energy function $V(\mathbf{x})$ can be expanded near the reaction path in powers of $(\mathbf{x}-\mathbf{a})$. When only terms to second order are retained

$$V(\mathbf{x}) \approx V(\mathbf{a}) + \nabla V(\mathbf{a})\cdot(\mathbf{x}-\mathbf{a}) + \frac{1}{2}(\mathbf{x}-\mathbf{a})\cdot\mathbf{F}\cdot(\mathbf{x}-\mathbf{a}) \quad (8.11)$$

where **F** is the force constant matrix. Because the displacement vector $(\mathbf{x}-\mathbf{a})$ is orthogonal to $\nabla V(\mathbf{a})$ in the 3N-dimensional vector space, the linear term in eq 3.70 vanishes. For simplicity, and because they are not of interest for our purposes, the motions corresponding to molecular rotations and translation of the center of mass are removed by use of the projector

$$\mathbf{F}^P = (1 - \mathbf{P}^{GRT})\cdot\mathbf{F}\cdot(1 - \mathbf{P}^{GRT}) \quad (8.12)$$

where $\mathbf{P}^{GRT}$ is the projection operator for the translational and rotational motions. Following the application of $\mathbf{P}^{GRT}$, a normal-mode analysis is carried out.

A normal-mode representation of the Hamiltonian for the reduced system involves the diagonalization of the projected force constant matrix, which in turn generates a reduced dimension potential energy surface in terms of the mass-weighed coordinates of the reaction path:[30]

$$V(s,Q_1,...,Q_{3N-7}) = V(s) + \sum_{k=1}^{3N-7}\frac{1}{2}\omega_k^2(s)Q_k^2 \quad (8.13)$$

In (8.13), the Q_k $\{k = 1, ..., 3N - 7\}$ are the generalized normal coordinates and the $\omega_k(s)$ $\{k = 1, ..., 3N - 7\}$ are the corresponding normal-mode frequencies. The kinetic energy is then

$$T = \sum_{k=1}^{3N-7}\frac{1}{2}P_k^2 + \frac{1}{2}\frac{[p_s - \sum_{k,l=1}^{3N-7}Q_kB_{kl}(s)P_l]^2}{[1 + \sum_{k=1}^{3N-7}Q_kB_{k(3N-6)}(s)]^2} \quad (8.14)$$

where the B_{kl}'s are coupling constants.

With this analysis, the reaction path Hamiltonian for the two-dimensional representation on the LSTH potential surface is given by

$$H = \frac{p_s^2}{2(1+\kappa(s)q)} + \frac{p_q^2}{2} + \frac{1}{2}\omega^2(s)q^2 + V(s) \quad (8.15)$$

where q is a perpendicular motion coordinate, p_s and p_q are their conjugate momenta, $\omega(s)$ is the vibrational frequency associated with motion along q, $\kappa(s)$ is the curvature of the reaction path, and $V(s)$ is the potential energy along the reaction path. Figure 3 displays $V(s)$ as a function of s and Figure 4

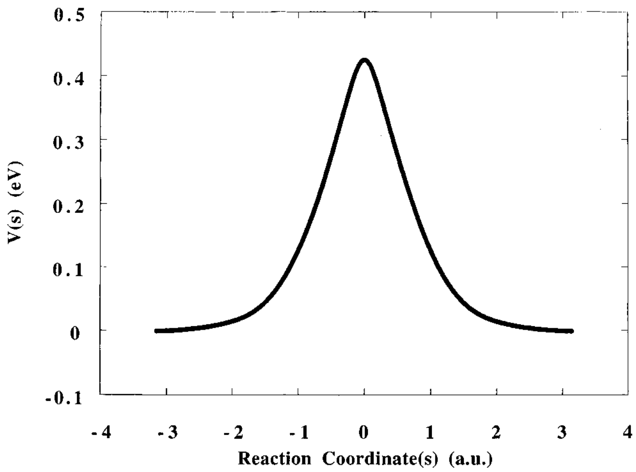

Figure 3. Potential energy along the reaction path on the LSTH potential energy surface.

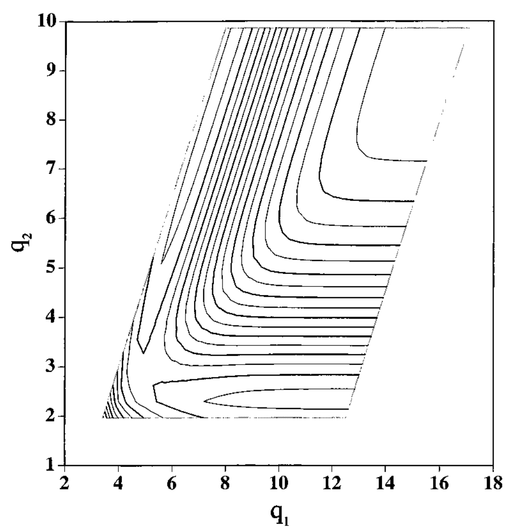

Figure 4. Contour plot of the LSTH potential energy surface along the reaction path. q_1 and q_2 are defined in the text of the paper. The skewed coordinates are defined by $r_1 = (q_1 - q_2)$, $r_2 = \alpha q_2 \sec \theta$. For the present system, $\alpha = 1$, $\theta = 30°$.

displays a contour plot of the LSTH potential surface along the reaction path. If the curvature function of eq 8.15 is expanded

$$\frac{1}{1 + \kappa(s)q} = 1 - \kappa(s)q + \kappa^2(s)q^2 - ... \qquad (8.16)$$

then (8.15) can also be written as

$$H = \frac{p_s^{\ 2}}{2} + \frac{p_q^{\ 2}}{2} + \frac{1}{2}\omega^2(s)q^2 + V(s) + U(s,q) \qquad (8.17)$$

with $U(s,q) \ll V(s)$.

The reaction path (defined as the minimum energy path on the potential energy surface) is followed by solving the equations[65]

$$\frac{d\mathbf{x}(s)}{ds} = -\frac{\nabla V(\mathbf{x})}{|\nabla V(\mathbf{x})|} \qquad (8.18)$$

where s is the reaction coordinate and $\mathbf{x}(s)$ is the reaction path.

Equation 8.17 is the simplified Hamiltonian function we have used for the numerical calculation of the resonance widths for the collinear H + H_2 reaction on the LSTH potential energy surface. It is well-known that the reaction path potential on the LSTH surface is very nearly harmonic at the saddle point.

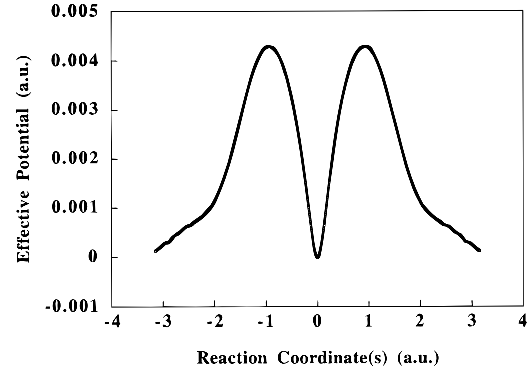

Figure 5. Effective potential for resonance width analysis along the reaction path on the LSTH potential energy surface.

TABLE 4: Resonance Lifetime for Collinear H−H_2 Reaction on LSTH Potential Energy Surface[a]

	potential inversion	complex scaling	time correlation
Δt (fs)	14.2	15.6	16

[a] Δt is defined as $\Delta t = \hbar/\mathrm{Im}(E) = 2\tau$.

We find that the effective potential (8.3) obtained from the complex-scaling analysis is also nearly harmonic at the bottom of the well (Figure 5). Accordingly, we have carried out calculations of the resonance widths and lifetimes for the collinear H + H_2 reaction using Miller's semiclassical potential-inversion analysis and the complex-scaling analysis using the harmonic approximation discussed in sections VI and VII. The results of these calculations are listed in Table 4. Note that the lifetime is defined here as $\Delta t = \hbar/\mathrm{Im}(E) = 2\tau$. We find that both the semiclassical potential-inversion analysis and the complex-scaling analysis are in good agreement with the value obtained by Sadeghi and Skodje[66] from a time correlation function analysis using a slightly different double-many-body-expansion (DMBE) potential energy surface.[67] In particular, the resonance width obtained from the complex scaling analysis is in nearly perfect agreement with that obtained by Sadeghi and Skodje.

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References and Notes

(1) Wigner, E. P. *Z. Phys. Chem. (Munich)* **1932**, *B19*, 203.
(2) Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107. Glasstone, S.; Laidler, K.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941. Eyring, H.; Walter, J.; Kimball, G. E. *Quantum Chemistry*; John Wiley & Sons: New York, 1944.
(3) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1935**, *31*, 875.
(4) Eliason, M. A.; Hirschfelder, J. O. *J. Chem. Phys.* **1959**, *30*, 1426.
(5) Johnson, H. S. *Gas Phase Reaction Rate Theory*; Ronald Press: New York, 1966.
(6) Marcus, R. A. *J. Chem. Phys.* **1966**, *43*, 1598, 2138. Marcus, R. A. *J. Phys. Chem.* **1979**, *83*, 204.
(7) Gardiner, W. C., Jr. *Rates and Mechanisms of Chemical Reactions*; W. A. Benjamin: Menlo Park, CA, 1969.
(8) Kreevoy, M. M.; Truhlar, D. G. In *Investigation of Rates and Mechanisms of Reactions*, 4th ed.; Bernsaconi, C. F., Ed.; John Wiley & Sons: New York, 1986; Part I, p 13.
(9) Porter, R. N.; Karplus, M.; Sharma, R. D. *J. Chem. Phys.* **1965**, *43*, 1426.
(10) Schatz, G. C.; Kuppermann, A. *J. Chem. Phys.* **1976**, *65*, 4668. Schatz, G. C. *J. Chem. Phys.* **1989**, *90*, 3582, 4847. Schatz, G. C. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1729.
(11) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987; p 89.
(12) Rice, O. K.; Ramsperger, H. C. *J. Am. Chem. Soc.* **1927**, *49*, 1616; **1928**, *50*, 617. Kassel, L. S. *J. Phys. Chem.* **1928**, *32*, 225. Rice, O. K.; Ramsperger, H. C. *Kinetics of Homogeneous Gas Reactions*; Reinhold: New York, 1932; Chapter 5.

(13) Marcus, R. A.; Rice, O. K. *J. Phys. Colloid Chem.* **1951**, *55*, 894. Marcus, R. A. *J. Chem. Phys.* **1952**, *20*, 359. Wieder, G. M.; Marcus, R. A. *J. Chem. Phys.* **1962**, *37*, 1835. Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 2658.

(14) See, for example: Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: London, 1972. Forst, W. *Theory of Unimolecular Reactions*; Academic: New York, 1973; Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987.

(15) See, for a recent review: Truhlar, D. G.; Garrett, B. C. *Annu. Rev. Phys. Chem.* **1984**, *35*, 159−189.

(16) Davis, M. J. *J. Chem. Phys.* **1985**, *83*, 1016; *Chem. Phys. Lett.* **1984**, *110*, 491. Davis, M. J.; Wagner, A. F. In *Resonances in Electron-Molecular Scattering, van der Waals Complexes, and Reactive Chemical Dynamics*; ACS Symposium Series 263; Truhlar, D. G., Ed.; American Chemical Society: Washington, DC, 1984; p 337.

(17) Davis, M. J.; Gray, S. K. *J. Chem. Phys.* **1986**, *84*, 5389.

(18) See, for example: Lichtenberg, A. J.; Lieberman, M. A. *Regular and Stochastic Motion*; Springer-Verlag: New York, 1983. Arrowsmith, D. K.; Place, C. M. *An Introduction to Dynamical Systems*; Cambridge University Press: Cambridge, U.K., 1990.

(19) Mackay, R. S.; Meiss, J. D.; Percival, I. C. *Physica* **1984**, *D13*, 55; **1987** *D27*, 1. Bensimon, D.; Kadanoff, L. P. *Physica* **1984**, *D13*, 65. Dana, I.; Murray, N. V.; Percival, I. C. *Phys. Rev. Lett.* **1988**, *62*, 233.

(20) See, for example: Hale, J.; Kocak, H. *Dynamics and Bifurcations*; Springer-Verlag: New York, 1991. Zaslavsky, G. M. *Chaos in Dynamic Systems*; Harwood Academic: New York, 1985. Zaslavsky, G. M.; Sagdeev, R. Z.; Usikov, D. A.; Chernikov, A. A. *Weak Chaos and Quasi-Regular Patterns*; Cambridge Press: New York, 1991.

(21) Gray, S. K.; Rice, S. A.; Davis, M. J. *J. Phys. Chem.* **1986**, *90*, 3470.

(22) Zhao, M.; Rice, S. A. *J. Chem. Phys.* **1992**, *96*, 3541, 6654, 7483.

(23) Jang, S.; Zhao, M.; Rice, S. A. *J. Chem. Phys.* **1992**, *97*, 8188.

(24) Zhao, M.; Rice, S. A. *J. Chem. Phys.* **1992**, *97*, 943; **1993**, *98*, 3824.

(25) Tang, H.; Jang, S.; Zhao, M.; Rice, S. A. *J. Chem. Phys.* **1994**, *101*, 1.

(26) Jang, S.; Rice, S. A. *J. Chem. Phys.* **1994**, *99*, 9585.

(27) Arnold, V. I. *Dokl. Akad. Nauk SSSR* **1964**, *156*, 9.

(28) Bensimon, D.; Kadanoff, L. P. *Physica D* **1984**, *13*, 82.

(29) Gillilan, R. E.; Ezra, G. S. *J. Chem. Phys.* **1991**, *94*, 2648.

(30) Gray, S. K.; Rice, S. A.; Noid, D. W. *J. Chem. Phys.* **1986**, *84*, 3745.

(31) Kay, K. G. *J. Chem. Phys.* **1976**, *65*, 3813.

(32) Gray, S. K.; Rice, S. A. *Faraday Discuss. Chem. Sci.* **1986**, *82*, 307.

(33) Gray, S. K. In *Dynamics of Polyatomic van der Waals Complexes*; Halberstardt, N., Janda, K. C., Eds.; Plenum Press: New York, 1990; p 81.

(34) Gray, S. K.; Rice, S. A. *J. Chem. Phys.* **1985**, *83*, 2818; **1987**, *86*, 2020.

(35) Gaspard, P.; Rice, S. A. *J. Phys. Chem.* **1989**, *93*, 6947.

(36) De Leon, N.; Berne, B. J. *J. Chem. Phys.* **1981**, *75*, 3495. De Leon, N. *J. Chem. Phys.* **1992**, *96*, 285. De Leon, N.; Marston, C. C. *J. Chem. Phys.* **1989**, *91*, 3405. Marston, C. C.; De Leon, N. *J. Chem. Phys.* **1989**, *91*, 3392.

(37) Kuppermann, A. *J. Phys. Chem.* **1979**, *83*, 171.

(38) Yamamoto, T. *J. Chem. Phys.* **1960**, *33*, 281.

(39) Miller, W. H. *J. Chem. Phys.* **1971**, *54*, 5386.

(40) Garrett, B. C.; Truhlar, D. G. *J. Phys. Chem.* **1979**, *83*, 1079.

(41) Miller, W. H. In *Potential Energy Surfaces and Dynamics Calculations*; Truhlar, D. G., Ed.; Plenum: New York, 1981.

(42) Miller, W. H. *J. Chem. Phys.* **1970**, *61*, 1823. Miller, W. H.; Schwartz, S.; Tromp, J. W. *J. Chem. Phys.* **1983**, *79*, 4889.

(43) Seideman, T.; Miller, W. H. *J. Chem. Phys.* **1991**, *95*, 1768; **1992**, *97*, 2499.

(44) See, for example: Makri, N.; Miller, W. H. *J. Chem. Phys.* **1987**, *86*, 1451. Waite, B. A.; Miller, W. H. *J. Chem. Phys.* **1980**, *73*, 3713. Waite, B. A. *J. Phys. Chem.* **1984**, *88*, 5076. Gray, S. K.; Miller, W. H.; Yamaguchi, Y.; Schaefer III, H. F. *J. Chem. Phys.* **1980**, *73*, 2733.

(45) Truhlar, D. G.; Garrett, B. C. *J. Phys. Chem.* **1992**, *96*, 6515.

(46) Day, P. N.; Truhlar, D. G. *J. Chem. Phys.* **1990**, *94*, 2045. Mielke, S. L.; Lynch, G. C.; Truhlar, D. G.; Schwenke, D. W. *Chem. Phys. Lett.* **1993**, 441. Chatfield, D. C.; Friedman, R. S.; Truhlar, D. G.; Garrett, B. C.; Schwenke, D. W. *J. Am. Chem. Soc.* **1991**, *113*, 486. Chatfield, D. C.; Truhlar, D. G.; Schwenke, D. W. *Faraday Discuss. Chem. Soc.* **1991**, *91*, 289. Chatfield, D. C.; Friedman, R. S.; Schwenke, D. W.; Truhlar, D. G. *J. Phys. Chem.* **1992**, *96*, 2414. Chatfield, D. C.; Friedman, R. S.; Lynch, G. C.; Truhlar, D. G. *Faraday Discuss. Chem. Soc.* **1991**, *91*, 398. Chatfield, D. C.; Friedman, R. S.; Lynch, G. C.; Truhlar, D. G. *J. Phys. Chem.* **1992**, *96*, 57.

(47) Friedman, R. S.; Truhlar, D. G. *Chem. Phys. Lett.* **1991**, *183*, 539. Friedman, R. S.; Hullinger, V. D.; Truhlar, D. G. *J. Phys. Chem.* **1995**, *99*, 3184.

(48) Zhao, M.; Rice, S. A. *J. Phys. Chem.* **1994**, *98*, 3444.

(49) Balslev, E.; Combes, J. M. *Commun. Math. Phys.* **1971**, *22*, 280.

(50) See, for example: Brändas, E. In *Resonances*; Elander, N., Eds.; Springer-Verlag: Sweden, 1987; p 345. *Resonances-Models and Phenomena*; Albeverio, S., Ferreira, L. S., Streit, L., Eds.; Springer-Verlag: New York, 1984.

(51) Obcemea, Ch.; Brändas, E. *Ann. Phys.* **1983**, *151*, 383. Chatyid-inmitriou-Dreismann, C. A. *Adv. Chem. Phys.* **1991**, *80*, 201.

(52) Reinhardt, W. P. In *Mathematical Frontiers in Computational Chemical Physics*; Truhlar, D. G., Ed.; Springer-Verlag: New York, 1988; p 41; Chu, S. In Resonances in *Electron-Molecular Scattering, van der Waals Complexes, and Reactive Chemical Dynamics*; Truhlar, D. G., Ed.; American Chemical Society: Washington, DC, 1984; p 263.

(53) Truhlar, D. G.; Mead, C. A. *Phys. Rev. A* **1990**, *42*, 2593.

(54) Moiseyev, N.; Friedland, S.; Certain, P. R. *J. Chem. Phys.* **1981**, *74*, 4739. Moiseyev, N.; Certain, P. R.; Weinhold, F. *Mol. Phys.* **1987**, *36*, 1614. Moiseyev, N.; Corcoran, C. T. *Phys. Rev. A* **1979**, *20*, 814. Moiseyev, N.; Certain, P. R.; Weinhold, F. *Int. J. Quantum Chem.* **1978**, *14*, 727. Moiseyev, N.; Friedland, S. *Phys. Rev. A* **1980**, *22*, 618.

(55) See, for example: Merzbacher, E. *Quantum Mechanics*, 2nd ed.; John Wiley & Sons: New York, 1970.

(56) Brandas, E.; Froelich, P. *Phys. Rev. A* **1977**, *16*, 2207.

(57) Marion, J. B. *Classical Dynamics of Particles and Systems*, 2nd ed.; Academic Press: New York, 1970.

(58) Atabek, O.; Lefebvre, R.; Garcia Sucre, M.; Gomez-Llorente, J.; Taylor, H. S. *Int. J. Quantum. Chem.* **1991**, *40*, 211.

(59) Park, D. A. *Introduction to the Quantum Theory*, 2nd ed.; McGraw-Hill: New York, 1974.

(60) Miller, W. H. *J. Chem. Phys.* **1975**, *62*, 1899 and references therein.

(61) Eckart, C. *Phys. Rev.* **1930**, *35*, 1303.

(62) Truhlar, D. G.; Horowitz, C. J. *J. Chem. Phys.* **1978**, *68*, 2466. Liu, B. *J. Chem. Phys.* **1973**, *68*, 1925. Seigbahn, P.; Liu, B. *J. Chem. Phys.* **1978**, *68*, 2457.

(63) Miller, W. H.; Handy, N. C.; Adams, J. E. *J. Chem. Phys.* **1980**, *72*, 99.

(64) Rice, S. A.; Zhao, M. In *Laser Techniques for State-Selected and State-to-State Chemistry II*; Hepburn, J. W., Ed.; SPIE-The International Society for Optical Engineering: California, 1994.

(65) Truhlar, D. G.; Isaacson, A. D.; Garrett, B. C. *Theory of Chemical Reaction Dynamics*; Baer, M., Ed.; Chemical Rubber Co.: Boca Raton, FL, 1985. Heidrich, D.; Kliesch, W.; Quapp, W. *Properties of Chemically Interesting Potential Energy Surfaces*; Springer-Verlag: New York, 1991. Skodje, R. T.; Truhlar, D. G.; Garrett, B. C. *J. Chem. Phys.* **1982**, *77*, 5955.

(66) Sadeghi, R.; Skodje, R. T. *J. Chem. Phys.* **1993**, *98*, 9208.

(67) Varandas, A. J. C.; Brown, F. B.; Mead, C. A.; Truhlar, D. G.; Blais, N. C. *J. Chem. Phys.* **1987**, *86*, 6258.

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