Final Technical Report
Department of Energy
Basic Energy Sciences

Project Title: Theoretical Chemical Dynamics Studies of Elementary
Combustion Reactions

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Abstract

The purpose of this research was the development and application of theoretical/computational methods for accurate predictions of the rates of reactions in many-atom systems. The specific aim was to improve computational methods for studying the chemical dynamics of large, complex systems and to obtain a better understanding of the chemical reactions involving large polyatomic molecules and radicals. The focus was on the development an automatic potential energy surface generation algorithm that takes advantage of high-performance computing environments; e.g., software for rate calculations that direct quantum chemistry codes to produce *ab initio* predictions of reaction rates and related dynamics quantities. Specifically, we developed interpolative moving least-squares (IMLS) methods for accurately fitting *ab initio* energies to provide global PESs and for use in direct dynamics simulations.

I. Introduction

The specific objectives of the research were:
- Develop improved methods that take advantage of modern high-performance computing capabilities for using *ab initio* potential energy surfaces (PESs) in many-atom chemical dynamics simulations and rate calculations.
- Develop better methods for simulating chemical reactions using classical molecular dynamics (with particular emphasis on developing a better understanding of the validity of the classical approximation and correcting for it where appropriate).

The central focus of the work was the development of better methods for computing reaction rates that take advantage of the current state-of-the-art quantum chemistry capabilities and high-performance computers; specifically, the development of an automatic PES generation algorithm that directs quantum chemistry codes to produce *ab initio* predictions of reaction rates and related dynamics quantities. We developed an interpolative moving least-squares (IMLS) method for accurately fitting *ab initio* energies to provide global PESs and for use in direct dynamics simulations. The chemical emphasis was on full-dimenional, atomic-level treatments of complex chemical reactions involving polyatomic molecules and radicals.

II. Completed Work

A. Publications

The papers resulting from the work during the grant period reflect the two components of the project designed to develop better methods for theoretical predictions of chemical dynamics and kinetics quantities: (1) Studies of classical and semiclassical methods for studying fundamental reaction dynamics and (2) development of PES fitting methods specifically designed to take advantage of modern high-performance computing capabilities. The work performed during the previous grant period resulted in the following publications and manuscripts:

- Yin Guo and Donald L. Thompson, "*Semiclassical Calculations of Tunneling Splitting in Hydrogen Peroxide and Its Deuterated Isotopomers*," J. Phys. Chem. A **106**, 8374-8377 (2002). (Part of Don W. Setser Festschrift)

- Yin Guo and Donald L. Thompson, "*A Theoretical Study of Cis-Trans Isomerization in HONO Using an Empirical Valence Bond Potential*," J. Chem. Phys. **118**, 1673-1678 (2003).

- Gia G. Maisuradze and Donald L. Thompson, "*Interpolating Moving Least-Squares Method for Fitting Potential Energy Surfaces: Illustrative Approaches and Applications*,"
J. Phys. Chem. A **107**, 7118-7124 (2003). (Part of Donald J. Kouri Festschrift)

- Gia G. Maisuradze, Donald L. Thompson, Albert F. Wagner, and Michael Minkoff, "*Interpolating Moving Least-Squares Method for Fitting Potential Energy Surfaces:*

Detailed Analysis of One Dimensional Applications," J. Chem. Phys. **119**, 10002-10014 (2003).

- Yin Guo and Donald L. Thompson, "*A Classical Trajectory Study of Bond Dissociation in HONO and HOOH,*" Chem. Phys. Letters 382, 654-660 (2003).
- Akio Kawano, Yin Guo, Donald L. Thompson, Albert F. Wagner, and Michael Minkoff, "*Improving the Accuracy of Interpolated Potential Energy Surfaces by Using an Analytical Zeroth-Order Potential Function,*" J. Chem. Phys. **120**, 6414-6422 (2004).
- Yin Guo, Akio Kawano, Donald L. Thompson, Albert F. Wagner, and Michael Minkoff, "*Interpolating Moving Least-Squares Methods for Fitting Potential Energy Surfaces: Applications to Classical Dynamics Calculations,*" J. Chem. Phys. **121**, 5091-5097 (2004).
- Gia G. Maisuradze, Donald L. Thompson, Albert F. Wagner, and Michael Minkoff, "*Interpolating Moving Least-Squares Methods for Fitting Potential Energy Surfaces: Analysis of Application to a Six-Dimensional System*" J. Chem. Phys. 121, 10329-10338 (2004).

B. Development of IMLS Fitting Methods

Formulating accurate PESs based on *ab initio* calculations has been a major obstacle to the extension of molecular dynamics to chemical reactions involving large polyatomic molecules and radicals. There are several reasons for this:

- *Ab initio* calculations of chemical accuracy can be quite expensive. Consequently only a few *ab initio* points are often fit to a global function with the parameters determined so that the general features, especially the critical points, are in accord with the available experimental data for the reaction. The analytical form used in such fits has the serious disadvantage of not being sufficiently flexible to fit increased numbers of *ab initio* points; that is, flexibility and accuracy are sacrificed for simplicity. This was our motivation for suggesting in the 1970's that local fitting functions should be used to fit *ab initio* energies.   The particular approach we proposed was based on cubic splines,[i] which provide the desired flexibility to yield accurate smooth first and second derivatives but requires a fairly dense grid of *ab initio* points. Thus, it has been used mainly for relatively small systems.[ii-vii]

- Typically each PES is largely "handmade." Fitting a global PES is as much an art as a science; it is extremely tedious and not readily "generalizable," thus a huge investment of human labor is required in each case. This is the pragmatic reason for the popularity of *ab initio* dynamics simulations[viii] and direct kinetics calculations,[ix] where *ab initio* points are used directly without fitting to advance trajectories or evaluate integral expressions for rate constants. Since the *ab initio* points are not fit, they cannot be readily reused in subsequent studies. Relatively straightforward, "art-less" fitting methods that are broadly applicable and flexible would find ready use in many reaction dynamics simulations.

During the past 30 years, and especially in the past decade, a variety of PES fitting methods have been developed.[x] These methods can be categorized as weighted or unweighted. Unweighted methods include: least-squares fitting methods,[xi] spline methods,[xii] reproducing Kernel Hilbert space (RKHS) interpolation methods,[xiii] and hybrid methods like Morse-spline[xiv] and rotated Morse-spline.[xv] With such methods, the

fit at each PES geometry is determined by all the *ab initio* points. Weighted methods include the modified Shepard interpolation method[xvi-xix] and the interpolated moving least-squares (IMLS) method explored by others[xx-xxiii] and developed by us[xxiv-xxvi] in the present project.

The modified Shepard methods suggested by Ischtwan and Collins[xvi] in 1994 is the most relevant to IMLS development, which is the focus of this proposal. The *un*modified Shepard method suffers from the "flat-spot" phenomenon; i.e., the derivative of the interpolant is zero at every data point. Ischtwan and Collins avoided this problem by modifying the Shepard method by interpolating a second-order Taylor expansion instead of just the potential energy at each data point. They have combined their modified Shepard interpolation method with classical trajectory simulations in an iterative scheme for successively and automatically improving the PES. This procedure selects the data points for additional *ab initio* calculations in regions of configuration space that are dynamically important. The procedure is simple and readily automated but has the drawback that gradients and Hessians are required at every point. This is expensive, but most important, Hessians are generally not readily available in high-level *ab initio* calculations. This approach has been refined and applied to various reactions by several groups.[xxvii-l]

The "flat-spot" problem is avoided by using higher-degree IMLS methods,[li] which can incorporate but do not require either gradients or Hessians. To see this and to better discuss later parts of the proposal, the IMLS method must be briefly described. In this method, the fitted potential is expressed in terms of a linear combination of the basis functions $\{b_i(\mathbf{Z})\}$:

$$V_{\text{fitted}}(\mathbf{Z}) = \sum_{i=1}^{M} a_i(\mathbf{Z})b_i(\mathbf{Z}), \tag{1}$$

where M is the total number of basis functions, $\{b_i(\mathbf{Z})\}$ are polynomials, and $\{a_i(\mathbf{Z})\}$ are determined by minimizing the sum of weighted squared-deviations

$$D[V_{\text{fitted}}(\mathbf{Z})] = \sum_{i=1}^{N} w_i(\mathbf{Z})[V_{\text{fitted}}(\mathbf{Z}^{(i)}) - V(\mathbf{Z}^{(i)})]^2 \tag{2}$$

that is, by the conditions $\partial D/\partial a_i = 0$. Here N is the total number of *ab initio* data points located at $\{\mathbf{Z}^{(1)}, \mathbf{Z}^{(2)}, \ldots, \mathbf{Z}^{(N)}\}$ with energies $\{V(\mathbf{Z}^{(1)}), V(\mathbf{Z}^{(2)}), \ldots, V(\mathbf{Z}^{(N)})\}$, respectively, and $w(\mathbf{Z})$ is a weight function with the property that the data points closer to $\mathbf{Z}$ have larger weights than the more distant ones. This minimization procedure leads to

$$\mathbf{B}^{\text{T}}\mathbf{W}\mathbf{B}\mathbf{a} = \mathbf{B}^{\text{T}}\mathbf{W}\mathbf{V}, \tag{3}$$

where $\mathbf{B}$ is a $N \times M$ matrix,

$$\mathbf{B} = \begin{pmatrix} b_1(\mathbf{Z}^{(1)}) & b_2(\mathbf{Z}^{(1)}) & \mathsf{L} & b_M(\mathbf{Z}^{(1)}) \\ b_1(\mathbf{Z}^{(2)}) & b_2(\mathbf{Z}^{(2)}) & \mathsf{L} & b_M(\mathbf{Z}^{(2)}) \\ \mathsf{M} & \mathsf{M} & \mathsf{O} & \mathsf{M} \\ b_1(\mathbf{Z}^{(N)}) & b_2(\mathbf{Z}^{(N)}) & \mathsf{L} & b_M(\mathbf{Z}^{(N)}) \end{pmatrix} \tag{4}$$

W is a $N \times N$ diagonal matrix,

$$\mathbf{W} = \mathrm{diag}(w_1(\mathbf{Z}), w_2(\mathbf{Z}), \mathrm{K}, w_N(\mathbf{Z})) \tag{5}$$

and V is a column vector,

$$V = (V(\mathbf{Z}^{(1)}), V(\mathbf{Z}^{(2)}), \ldots, V(\mathbf{Z}^{(N)}))^{\mathrm{T}}. \tag{6}$$

Once the coefficient vector a is obtained by solving Eq. (3), the fitted energy at a given point $\mathbf{Z}$ is computed via Eq. (1). Note that because **B** is typically a rectangular matrix (M<<N), a simple inverse does not exist to remove it from both sides of Eq. (3). Equation (3) is most reliably solved by singular value decomposition (SVD) techniques. Trajectories require derivatives of the V_{fitted}, which in turn require the derivatives $\mathbf{a}'$. Taking the derivative of Eq. (3) leads to the expression for $\mathbf{a}'$:

$$\mathbf{B}^{\mathrm{T}}\mathbf{WBa}' = (\mathbf{B}^{\mathrm{T}}\mathbf{WV})' - (\mathbf{B}^{\mathrm{T}}\mathbf{WB})'\mathbf{a}, \tag{7}$$

which has the same left hand side as Eq. (3). Thus, the SVD decomposition determined for Eq. (3) can be reused to solve Eq. (7) for $\mathbf{a}'$ for each internal coordinate.[xxv]
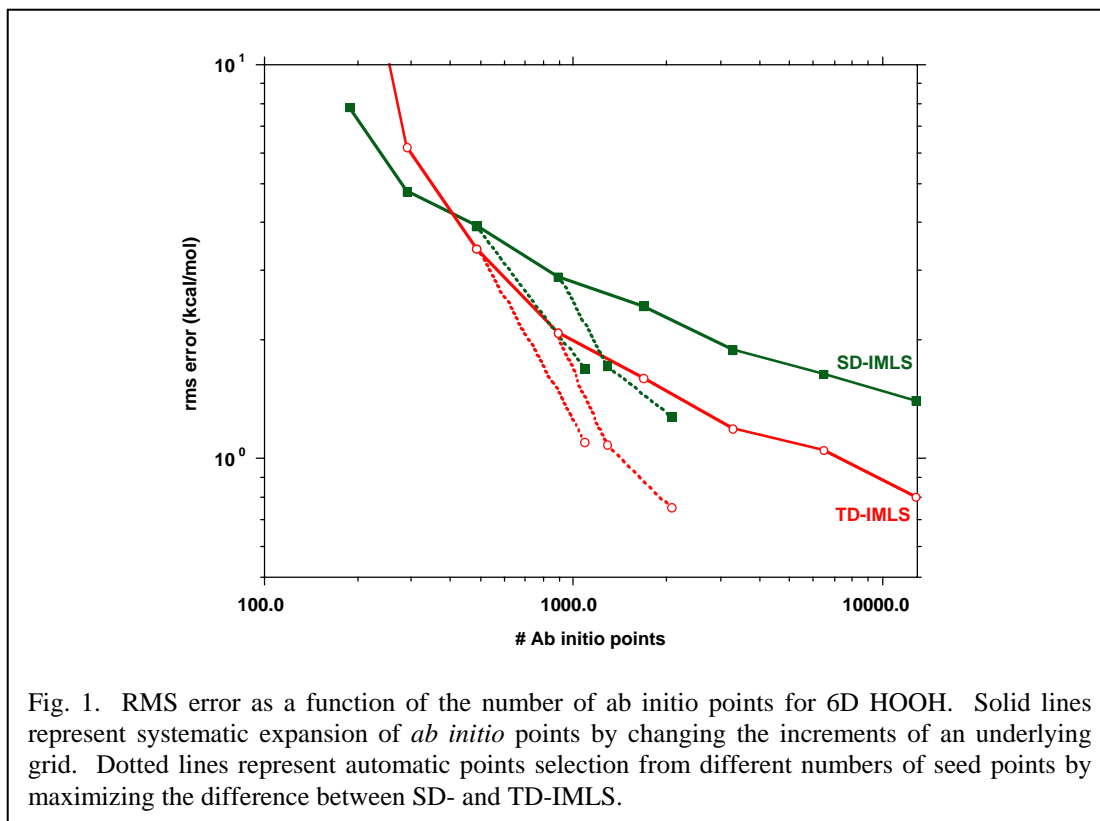
While the description above is fully general, typically each basis set element $b_i(\mathbf{Z})$ is a product of primitive basis sets in each coordinate in $\mathbf{Z}$ or some transformation X of $\mathbf{Z}$. The primitive basis set for each coordinate is typical a power series (e.g, x^0, x^1, x^2,… or 1, e^{-ax}, e^{-2ax},…), implying that the IMLS fit can be characterized by the maximum degree of the power series (e.g., ZD-IMLS or zero-degree IMLS, TD-IMLS or third degree IMLS, etc.). The *un*modified Shepard method is a ZD-IMLS where the basis sets are all unity. Consequently, all the derivative dependence of V_{fitted} comes from the $\mathbf{Z}$ dependence of the weights, which are strongly peaked functions about *ab initio* points. This leads directly to the flat-spot phenomena. For all other degree IMLS fits, the basis carries some of the $\mathbf{Z}$ dependence. Consequently, the flat-spot phenomena disappears and with it the need for gradient or Hessian information.

What distinguishes IMLS from other fitting methods is that it is a *weighted* least-squares method in which the weight depends not only on the *ab initio* points but the distance of each of these points from the point on the PES under the evaluation. This key characteristic confers on IMLS significant advantages that will be discussed below. However, there is the significant disadvantage that it makes $\mathbf{a}$ a function of $\mathbf{Z}$, requiring a separate least-squares solution at every desired value of $\mathbf{Z}$. For example, Eqs. (3) and (7) must be solved at every time step in a trajectory propagation. Thus, IMLS methods must be well optimized to be feasible for practical systems.

Higher degree IMLS methods have been used in combination with modified Shepard methods to evaluate the first and second derivatives at the data points that the modified Shepard method requires.[xxi-xxiii] In the last three years, we have pioneered direct application of higher degree IMLS methods to PES fitting problems with an eye towards large systems. To date, all of our IMLS studies have been carried out on PESs that have

already been fit by others. These include our IMLS fit to a model one-dimensional (1D) Morse oscillator,[xxv] our IMLS fits to a 3D N_2H PES,[xxiv] and our IMLS fits to a 6D HOOH PES.[xxvi] Because the PES is already fit, we used the fit in lieu of *ab initio* electronic structure calculations to develop the IMLS fit, but then monitored the global rms fitting error for all of the PES below an input value (say 100 kcal/mol). Thus, the fitting error implications of the basis, weights, choice of degree, and *ab initio* point selection has been assessed. The qualities of IMLS fits that emerge from our studies are:

• **Broadly applicable**: 1D, 3D, and 6D PESs are fit with basis functions that are straightforward and with weights that are broadly similar and need few if any preliminary calculations to set. Higher degree IMLS generally reduces the fitting error until oscillations in excessively high-degree fits (e.g., degree 8 or 9) degrade the fit quality. Beyond ZD-IMLS, fits are smooth with generally well-behaved derivatives

• **Extensible**: As soon as the number of calculated points available to be fit exceeds the number of basis functions chosen, a global IMLS fit of the PES can be constructed. Such a fit will have a large rms fitting error. Each additional calculated point made available to IMLS refines the fit of the PES. Regular or random selections of *ab initio* points can be used to refine the IMLS fit with equal facility.

• **Capable of automatic PES generation**: Strongly peaked weights means in practice that in the immediate vicinity of an *ab initio* point, an IMLS fit of any degree highly accurately reproduces the *ab initio* value. However, far from *ab initio* points, fits of different degrees differ. The obvious automatic point selection strategy is to calculate

Fig. 1. RMS error as a function of the number of ab initio points for 6D HOOH. Solid lines represent systematic expansion of *ab initio* points by changing the increments of an underlying grid. Dotted lines represent automatic points selection from different numbers of seed points by maximizing the difference between SD- and TD-IMLS.
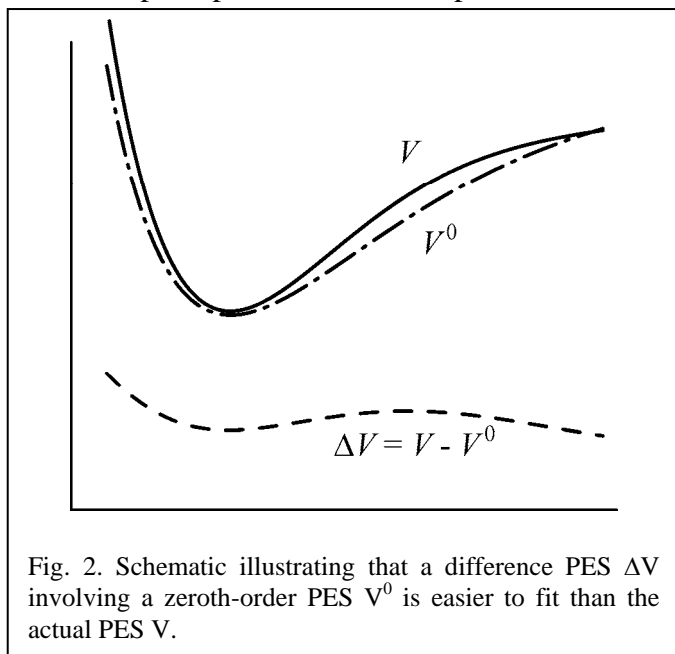
additional *ab initio* values at the points where the difference between IMLS degrees is maximal and to continue with sequential additional selections until everywhere within the desired energy or coordinate range the difference in IMLS fits of different degrees

has dropped below a desired value. Published 1D implementations[xxv] and unpublished 6D implementations of this strategy show its efficacy. The 6D results for HOOH are shown in Fig. 1 and demonstrate substantial reductions in the required number of *ab initio* points with more optimal and automatic methods of selected points for *ab initio* calculations. This key discovery is an underlying basis of our proposed work discussed in Section III to make IMLS a driver for highly parallelized electronic structure calculations.

- *Compact*: Our 1D, 3D, and 6D IMLS studies all show accurate fits can be produced with few points. This is essentially due to the fact that the weights convey a non-linear flexibility to an otherwise linear least-squares fit. How few points are required depends on the degree, *ab initio* point selection, on what is being fit, and how "accuracy" is measured. While space does not permit a full discussion of these aspects, a terse summary of our results is that, over a 100 kcal/mol range in PES values, ten or so *ab initio* points are needed for 1D applications, a few hundred for 3D, and a few thousand for 6D (see Fig. 1). Several key discoveries, all illustrated for 6D HOOH, are:

  IMLS can be applied to not only a PES but to the difference of a PES from a zeroth order reference PES. This is inspired by the dual method of Nguyen *et al.*[lii] in which the difference between an expensive high-level and an inexpensive lower-level *ab initio* calculation is interpolated using the modified Shepard method. However, instead of using low level *ab initio* calculations for our zeroth-order PES, we will exploit practical, semi-empirical methods we have developed over several decades for constructing PESs for complex reactions involving large molecules. These methods are incorporated them into our trajectory code GenDyn[liii] (which we will soon post on our SciDAC webpage along with a manual for its use). With these methods and with relatively small numbers of *ab initio* calculations to characterize equilibria or saddle points, we can design a zeroth-order potential V^0 that is a good approximation to V (e.g., matching at the critical points), making the difference $\Delta V = V - V^0$ less variable and much easier to fit than V itself with far fewer *ab initio* points. This is qualitatively illustrated in Fig. 2. Introducing V^0 adds negligible computational time to the overall cost of computing an interpolated surface but the reduction in *ab initio* points is substantial. In our 6D SD-IMLS HOOH study,[xxvi] the rms fitting errors are reduced 50% by fitting the difference rather than the original

Fig. 2. Schematic illustrating that a difference PES ΔV involving a zeroth-order PES V^0 is easier to fit than the actual PES V.

PES. This reduced the number of *ab initio* calculations needed to arrive at a given accuracy by approximately a factor of five. In general, the method works better for the IMLS than for the modified Shepard.

This difference approach can incorporate into the zeroth-order function both *ab initio* and experimental information. For regions we do not wish to fit, e.g. regions where an empirically corrected zeroth-order potential is already accurate enough, ΔV_{fitted} can be damped to zero so that the total potential becomes equal to the zeroth-order PES. This difference approach can also be incorporated into the modified Shepard method. We found for HOOH that for the same number of *ab initio* points, the modified Shepard was slightly more accurate but includes vector gradient and matrix Hessian information at substantial cost (at least an order of magnitude more CPU time than calculating only the energy). The combination of this difference approach with automated optimal selection of data points for *ab initio* calculation promises to produce highly compact PESs for MD or Monte Carlo applications.

If the figure of merit in an IMLS fit is the accuracy of dynamical observables, for example, dissociation rates, then the number of *ab initio* calculations required can be much lower than that needed for PES accuracy directly. In unpublished studies on HOOH dissociation rates as calculated by trajectories, converged dissociation rates where produced with only a few hundred *ab initio* point with a mixed degree IMLS fit (up to fourth degree in some coordinates).[liv] In this case, the rms fitting error to the PES directly is ~4 kcal/mol (which is in fact roughly consistent with Fig. 1). Iterative trajectory calculations similar to the modified Shepard studies of others could lead to dynamically useful IMLS fits with few *ab initio* calculations and no calculations of gradients or Hessians.

Scalable: These advantageous attributes are the result in part of the fact that IMLS weights vary with the point at which the fit evaluation is being made. However, as previously mentioned, the disadvantage is that every evaluation of the fit requires its own weighted least-squares fit. Analysis of Eq. (3) and our timing studies show that the time-to-solution goes as the square in the number of IMLS basis functions and goes linearly with the *effective* number of *ab initio* points. An effective *ab initio* point is one whose weight is large enough to significantly influence the accuracy of the fit. Typically weights can vary by tens of orders of magnitude depending on how remote an *ab initio* point is from the evaluation point. Thus, scalability to large systems requires:

Optimal point selection: Automatic point selection and reference potentials, as described above, focuses on this. While IMLS does not require gradients, it can incorporate them and the impact that would have on optimal point selection is unknown. Every reduction in the number of *ab initio* points translates to a linear reduction in the time-to-solution.

Screening on the basis of weights: Our preliminary results suggest that a few tens of percent of all the *ab initio* points required for a globally accurate fit are on the average *effective* for any specific evaluation. The time-to-solution is directly reduced by this percentage.

Optimization of the basis: Simple basis set optimization can focus on cross term basis functions that increasingly dominate an IMLS fit of higher degrees. Many or most cross terms are of little importance because they involve coordinates that are

only weakly coupled. In HOOH, eliminating a third of the cross terms in a TD-IMLS fit causes the global rms fitting error to increase by a few percent. Eliminating two thirds causes a 20% increase. Deeper optimization of basis sets that involve changes in coordinates or non-linear functions of coordinates, e.g., $\cos(ax)$ or e^{-ax}, we have yet to systematically explore. Reduction in the number of basis functions reduces by the square the time-to-solution.

Further progress in IMLS fitting methods require a focus on broadly applicable strategies like those above that will ultimately address time-to-solution and scalability to large systems. However, even an expensive IMLS fit will be cheaper to evaluate than an *ab initio* calculation. In the worst of circumstances, less compact fitting methods that require a denser amount of *ab initio* information but are relatively less expensive to evaluate can use an accurate IMLS fit to supplement *ab initio* calculations. This is exactly the spirit of the approach used by Ishida and Schatz,[xxiii] who used IMLS to generate gradients and Hessians for modified Shepard fits.

Based on our experience with higher-order IMLS methods to date, we have constructed a general higher degree IMLS code. This code requires the user to define the weights and direct-product basis functions according to a particular protocol. The user then provides the *ab initio* points and the code will return the IMLS fit. Screening of *ab initio* points by the size of weights is an option. The SVD solution method is used and undetermined IMLS fits by too sparse a list of *ab initio* points is monitored.

C. Chemical Dynamics Studies

Most of our efforts during the grant period were devoted to the development of efficient PES fitting methods; however, we did carry out a few studies of chemical dynamics. The main focus of those studies was to explore the fundamental nature of classical dynamics, and we did this primarily through studies of state-specific processes: tunneling and *cis-trans* isomerization in HOOH and bond rupture in HOOH and HONO. State specificity in rates provides a critical test of the classical approximation.

Hydrogen peroxide provides an excellent test case since it displays mode-selective tunneling splittings because of strong intramolecular couplings. Depending on the mode excited, the excitation promotes, suppresses, or does not affect the tunneling rate. We performed semiclassical tunneling calculations[lv] using the highly accurate Kuhn *et al.*[lvi] PES for which there are quantum results for comparisons.[lvii] Our semiclassical results for the ground- and excited-states generally agree with the experimental[lviii] and quantum results. One of the conclusions of the study is that the quasiclassical approximation of assigning initial conditions by normal-mode sampling begins to break down with increasing anharmonicity.

The purpose of a second study was to investigate the accuracy of the quasiclassical approximation in simple bond-fission reactions, more specifically the effects of aphysical flow of ZPE on reaction rates. We chose HOOH and HONO, two somewhat similar molecules, for this study.[lix] We calculated dissociation rates for the O-N bond in *trans*-HONO and the O-O bond in HOOH for selected O-H excitations. The computed rates are quite different for the two systems despite the similar molecular structures and bond dissociation energies. The quasiclassical trajectory method seems to

work reasonably well for HONO. For the ν_{OH}=5 state where the energy is about 100 cm^{-1} below the reaction threshold, the computed dissociation rate is quite small, indicating that aphysical flow of ZPE is not a serious problem here. The rate for the ν_{OH}=5 state is also about an order of magnitude smaller than that for the ν_{OH}=6 state, thus the error introduced by the ZPE flow should not have significant effect on the calculated rates for the ν_{OH}=6 and 7 states. Both calculated lifetimes for the ν_{OH}=6 and 7 states are well above the experimental lower limits derived from spectral linewidths, suggesting that line broadening due to dissociation is not a dominant contributor to the observed linewidths. We have also performed calculations for the same energies classically distributed among the modes, and the computed rates are much slower than that for the local-mode sampling, showing that IVR is not fast enough for the system to be statistical. These results are consistent with the conclusions of Reiche $et\ al.$[lx] based on their spectral analysis that the IVR is the major source of the linewidths and the state mixing is not complete on the time scale of the reaction. On the other hand, the quasiclassical trajectory approximation breaks down for HOOH near the threshold region because of the aphysical flow of the ZPE.   For the $5\nu_{OH}$ state where the energy is about 800 cm^{-1} below the threshold, the computed dissociation rate is not negligible. For the $5\nu_{OH}+\nu_{OO}$ state where the energy is about 200 cm^{-1} above the threshold, the calculated rate is far larger than the higher limit estimated from the observed linewidths. Nevertheless, the method seems to work better for higher energy states.

  The reason that the quasiclassical trajectory approach works for HONO and not for HOOH near the threshold region is because of differences in their intramolecular couplings, which is manifested in the dissociation rates. The couplings are relatively weak in HONO and the calculated rates are non-statistical while the couplings are strong in HOOH, except the coupling between the two OH modes is relatively weak, and the rates are statistical. One way to check for aphysical behavior of the ZPE is to compute rates near the reaction threshold. However, even if the computed rates for low-energy states are not accurate due to aphysical energy flow, the rates for high-energy states may still be valid, as shown by our calculations of HOOH.

  As a part of our efforts to find better ways of representing PESs, we have explored the feasibility of using the empirical valence-bond (EVB)[lxi] method for "linking" existing analytical PESs as "components" in the construction of PESs for larger systems.   We began with the EVB formalism of Chang and Miller.[lxii] We applied it to the cis-$trans$ isomerization of HONO and computed the rates in the low-energy tunneling regime using our semiclassical approach.[lxiii] The EVB approach is conceptually straightforward to use for constructing global PESs and readily implemented if only up to quadratic terms are used in the exchange potential, which if properly formulated exactly reproduces a harmonic force field about a transition state. Thus, it is a straightforward way to use an $ab\ initio$ TS in a global PES, which is especially important in treating tunneling. We found that the using only quadratic terms in the exchange potential causes it to not converge or decay sufficiently rapid away from the TS region. We corrected this problem by introducing a damping function along the reaction coordinate. However, we found that we also had to adjust (aphysically) some of the force constants at the TS in order to obtain good behavior in the PES. Our conclusion is that the EVB approach may be useful in some applications, but does not provide a

general, reliable method for constructing PESs. Methods such IMLS, however, do hold the promise of being completely general and thus our focus was on that approach.

III. Concluding Remarks

Over the past two or three decades there have been significant progress in understanding the details of reaction dynamics. Molecular dynamics studies have played a crucial role in this, providing results that, coupled with those from the wide range of experimental techniques that have probed ever deeper into the details of chemical reactions, have lead to a highly refined understanding of reactions involving a few atoms. The challenge now is to develop better theoretical computational methods that can be used to complement the experimental studies of reactions involving many atoms. Quantum chemistry methods have reached a point where it is now feasible to accurately predict the energies of relatively large molecules, including their chemical reactions. Also, we have seen an enormous increase in the availability and capabilities of high-performance computers. The goal of this project was to develop methods that take advantage of this. Specifically, our aim was to develop the theoretical methods and computational software for automatic *ab initio* predictions of the rates (and other attributes) of chemical reactions of large, complex molecules and radicals. The results obtained in this project demonstrate the promise of the IMLS.

The research was carried out in a collaborative effort between the groups at Argonne National Laboratory and the University of Missouri.

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