Final Report
DE-FG02-04ER15607

Theoretical Chemical Dynamics Studies of Elementary Combustion Reactions

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Abstract

The objective of this research was to develop and apply methods for more accurate predictions of reaction rates based on high-level quantum chemistry. We have developed and applied efficient, robust methods for fitting global *ab initio* potential energy surfaces (PESs) for both spectroscopy and dynamics calculations and for performing direct dynamics simulations. Our approach addresses the problem that high-level quantum calculations are often too costly in computer time for practical applications resulting in the use of levels of theory that are often inadequate for reactions. A critical objective was to develop practical methods that require the minimum number of electronic structure calculations for acceptable fidelity to the *ab initio* PES. Our method does this by a procedure that determines the optimal configurations at which *ab initio* points are computed, and that ensures that the final fitted PES is uniformly accurate to a prescribed tolerance. Our fitting methods can be done automatically, with little or no human intervention, and with no prior knowledge of the topology of the PES. The methods are based on local fitting schemes using interpolating moving least-squares (IMLS).[1-11] IMLS has advantages over the very effective modified-Shepard methods developed by Collins and others[12-5] in that higher-order polynomials can be used and does not require derivatives but can benefit from them if available.

Completed work

We have developed a general three-atom code for generating a PES to a prescribed accuracy over a specified energy or coordinate range using the IMLS approach interfaced to the electronic structure codes Gaussian, Molpro, or Aces II. The code automatically takes advantage of symmetry, has three options for internal coordinates, and can be run in parallel. We used this code to develop the most accurate ground state PESs currently available for $^1CH_2$ and HCN.[15] They reproduce the experimentally measured equilibrium geometries in both molecules to within 0.001 Å for the two distances and within 0.2° for the bending angle. The calculated vibrational spectra for J=0 have mean unsigned errors relative to experiment of 1.4 cm^{-1} for $^1CH_2$ below 20,000 cm^{-1} and 2.5 cm^{-1} for HCN:HCN 12,000 cm^{-1}.

For $^1CH_2$ this level of accuracy was achieved by a complete basis set (CBS) extrapolation of augmented triple and quadruple zeta level calculations using MRCI wavefunctions, a core-valence correlation correction derived from CCSD(T) calculations with and without frozen cores, and a geometry-scaled Davidson correction where the scaling parameters are set to approximate full-CI calculations at small basis set levels. The CBS extrapolation produced significantly more accurate vibrational frequencies than those derived from the quadruple zeta basis set calculations alone. For $^1CH_2$, full-CI calculations were feasible and tests of the Davidson correction led to a simple scaling of the correction with the bend that reduced error at the small basis level. Application of this scaling to the Davidson correction at the CBS level produced our best result

of a 2.0 cm^{-1} root-mean-square error relative to the 11 known experimental levels. For HCN the most accurate results were obtained by calculations analogous to those for $^1CH_2$. These calculations were feasible because of our efficient and automatic PES fitting scheme that reduced both the number of expensive calculations and the amount of human attention required to produce PESs with negligible fitting error for eigenstate calculations of the vibrational levels. We grew fitted PESs over predefined ranges of energy starting with sparse sets of *ab initio* seed points on a regular grid. Running in parallel on eight processors, a usable PES is quickly generated in an essentially automatic fashion. (On the order of twenty different individually optimized PESs were produced in about a one-month period.) The fitting accuracies of the fitted PESs were confirmed by computing a test set of vibrational levels for $^1CH_2$ using the fitted surface nominally converged to 0.33 cm^{-1} mean unsigned fitting error and using direct *ab initio* electronic structure calculation of the points required by the DVR vibrational eigenstate program. The mean unsigned and maximum differences for these two eigenstate calculations for all 216 levels below 20,000 cm^{-1} are 0.10 cm^{-1} and 0.41 cm^{-1}, respectively. These errors are consistent with the convergence error of the fit and they are small relative to errors produced by deficiencies in the electronic structure calculations.

We have used our automatic PES generating code to construct a global OHCl ($^3A''$) surface at the UB3LYP/aug-cc-pVTZ level of theory.[16] This PES includes all reaction channels and OHCl geometries with energies up to 144 kcal/mol (6.25 eV) above the O+HCl asymptote. We have carried out a comprehensive quasiclassical trajectory study of the O+HCl reactive system for collision energies between 46 kcal/mol and 138 kcal/mol on the fitted PES. Reaction cross sections, opacity functions, and differential cross sections for all open product channels were calculated. This study improves on previous direct dynamics simulations by eliminating many of the drawbacks of that approach, such as trajectory failure due to lack of convergence of the *ab initio* calculations, relatively poor energy conservation during trajectories, and severe limitations on the level of *ab initio* theory that is feasible, and the numbers of trajectories that can be computed. The fitted PES greatly improves energy conservation during trajectory integration and eliminates problems with *ab initio* convergence, which are often encountered during direct dynamics studies.

We develop two approaches for growing IMLS-fitted PESs using classical trajectories.[17] We illustrate both approaches by calculating nitrous acid (HONO) *cis*→*trans* isomerization trajectories under the control of *ab initio* forces from low-level HF/cc-pVDZ electronic structure calculations. As few as 300 *ab initio* energy/gradient calculations are required to converge the isomerization rate constant at a fixed energy to ~10%. Neither approach requires any preliminary electronic structure calculations or initial approximate representation of the PES. Hessians are not required. Both approaches rely on the fitting error estimation properties of IMLS fits. We refer to the first approach as *IMLS-accelerated direct dynamics*, in which the PES is grown "on the fly" with the computation of new *ab initio* data only when a fitting error estimate exceeds a prescribed, tight tolerance. For the isomerization of HONO a speedup over direct dynamics of ~18 was achieved while maintaining a maximum rate of drift in total energy of less than 0.1 kcal/mol·ps. The second approach, called *dynamics-driven IMLS fitting*, uses relatively inexpensive exploratory trajectories to both determine and fit the dynamically accessible configuration space. Once exploratory trajectories no longer find configurations with fitting error estimates higher than the designated accuracy, the IMLS fit is considered to be complete. A converged rate constant for *cis*→*trans* HONO isomerization was computed using between two and three hundred *ab initio* points with energy and gradient data. These method are like the

GROW method[16] of the Collins' group. The IMLS approaches can accommodate basis functions of higher order and *ab initio* derivatives of lower order (i.e., no Hessians required) than the GROW method. Our approaches may be less dynamically biased because they grow the PES based only on the classical trajectories with no prior *ab initio* information whereas a typical GROW application fits an input string of *ab initio* energy/gradient/Hessian calculations to sustain initial trajectories that then grow the PES. The results are quite encouraging. The *dynamics-driven IMLS fitting* method appears particularly promising for both studying dynamical processes and producing fits of the dynamically relevant configuration space in large systems.

Publications

- Y. Guo, L. B. Harding, A. F. Wagner, M. Minkoff, and D. L. Thompson, "Interpolating Moving Least-Squares Methods for Fitting Potential Energy Surfaces: An Application to the H_2CN Unimolecular Reaction," J. Chem. Phys. **126**, 104105(1-9) (2007).
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