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Principal investigator: Donald G. Truhlar
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Considerable progress was achieved on the quantum mechanical treatment of electronically nonadiabatic collisions involving energy transfer and chemical reaction in the collision of an electronically excited atom with a molecule.

In the first step of our work we created a new diabatic representation for the coupled potential energy surfaces. In previous work,¹⁻³ we had developed an eight-configuration valence bond model of the ²A' manifold of NaH₂, and we used the three lowest surfaces for trajectory surface hopping studies of the Na(3p ²P) quenching dynamics. The trajectory surface hopping calculations were in good qualitative agreement with results from molecular beam experiments, thus validating the potential surfaces and their couplings. For more accurate dynamics calculations, though, and in particular for quantum dynamics benchmark calculations which may be used to test approximate theories, it is desirable to have a different representation. On this grant, we developed a two-state diabatic representation designed to realistically reproduce the two lowest adiabatic states of the valence bond model and also to have the following three desirable features: (1) It is more economical to evaluate. (2) It is more portable. (3) All spline fits are replaced by analytic functions. The new representation consists of a set of two coupled diabatic potential energy surfaces plus a coupling surface. It is suitable for dynamics calculations on both the electronic quenching and reaction processes in collisions of Na(3p ²P) with H₂.

The new two-state representation was obtained by a three-step process from a modified eight-state diatomics-in-molecules (DIM) representation of Blais and one of the authors.³ The steps involved were:

- (1) diagonalization of the 8 × 8 DIM Hamiltonian and truncation at the level of 2 adiabatic states;
- (2) numerical transformation of the two adiabatic states and their quantum mechanical momentum coupling, which involves derivative operators, into an equivalent 2 × 2 diabatic representation in which the coupling is a scalar function without momentum operators; and
- (3) analytic representation of the resulting 2 × 2 numerical potential function.

Step (2) was accomplished by the transformation procedure of Baer,⁴ and in step (3) we used an analytic function that dissociates correctly when any atom is removed infinitely far from the other two. Notice that step (1) involves truncation in the adiabatic representation, where each electronic function is a linear combination of eight valence bond functions. The much simpler procedure of truncating the valence bond basis would not yield a qualitatively correct representation.

Accurate fitting of adiabatic potential surfaces for systems with avoided crossings can be very difficult because of the sudden changes in the surfaces as avoided intersections are traversed. These complicated shapes must be fit accurately and in a well correlated fashion (i.e., the sudden change in one surface near an avoided intersection must be well

correlated with that in the other surface and in the coupling) or spurious behavior will be introduced. We have instead used the adiabatic \rightarrow diabatic transformation of Baer to obtain diabatic surfaces and couplings which are easier to fit. We have shown that the results of an eight-state valence bond treatment for the lowest two adiabatic states and their nonadiabatic vector couplings in Na-H₂ collisions may be represented efficiently in terms of a 2×2 scalar potential surface matrix.

The new 2×2 diabatic representation has significant advantages for dynamics calculations over the original 8×8 DIM representation and the 2×2 adiabatic truncation of that representation in that the diabatic representation is more convenient than the adiabatic and in that a 2×2 diabatic representation is more economical than an 8×8 representation.

The fact that we directly fit the 2×2 diabatic representation rather than recomputing it by numerical integration every time we need a value of a potential matrix element U_{ij} means it takes significantly less computer time to evaluate, and this is important both for trajectory surface hopping and also for quantum close coupling calculations of the dynamics. In addition, it is much easier to transform a diabatic representation into an adiabatic one than vice versa because the diabatic-to-adiabatic transformation is a local one whereas the adiabatic-to-diabatic one is nonlocal. Thus the fact that the new representation is originally defined in the diabatic form allows it to be used conveniently in dynamical formulations based on either diabatic or adiabatic representations. We expect that it will provide a useful system for benchmarking dynamical methods since a variety of dynamical methods, both those based on diabatic representations and those based on adiabatic representations, can be applied conveniently with the same set of interactions.

In addition to the specific interest in this particular system, the technique should be of general usefulness for representing other electronic structure calculations based on multiconfiguration wave functions where the number of states can be truncated to a reasonably small number (e.g., 2 or 3) only in the adiabatic representation, but the adiabatic surfaces and nonadiabatic couplings are hard to fit.

The work just described was published in the following reference:

“A New Diabatic Representation of the Coupled Potential Energy Surfaces for $\text{Na}(3p \ ^2P) + \text{H}_2 \rightarrow \text{Na}(3s \ ^2S) + \text{H}_2$ or $\text{NaH} + \text{H}$,” P. Halvick and D. G. Truhlar, *Journal of Chemical Physics* **96**, 2895-2909 (1992).

The second step of this project required the development of new dynamical methods. We developed a formalism for treating reactions with very general basis functions including electronically excited states. Our formalism is based on the generalized Newton,⁵ scattered wave,⁶⁻⁸ and outgoing wave^{7,9} variational principles that we have used previously for reactive collisions on a single potential energy surface, and it incorporates three new features.

- (i) The basis functions include electronic degrees of freedom, as required to treat reactions involving electronic excitation and two or more coupled potential energy surfaces.

- (ii) The primitive electronic basis is assumed to be diabatic, and we do not assume that it diagonalizes the electronic Hamiltonian even asymptotically.
- (iii) Contracted basis functions for vibrational-rotational-orbital degrees of freedom are included in a very general way, similar to previous prescriptions for locally adiabatic functions¹⁰ in various quantum scattering algorithms.

We also allow for contracted translational basis functions as treated previously.¹¹⁻¹³

This formalism is presented in more detail in:

“Linear Algebraic Formulation of Reactive Scattering with General Basis Functions,” G. J. Tawa, S. L. Mielke, D. G. Truhlar, and D. W. Schwenke, in *Advances in Molecular Vibrations and Collision Dynamics: Quantum Reactive Scattering*, Vol. 2B, edited by J. M. Bowman (JAI Press, Greenwich, Connecticut, 1993), in press.

References

- ¹D. G. Truhlar, J. W. Duff, N. C. Blais, J. C. Tully, and B. C. Garrett, *J. Chem. Phys.* **77**, 764 (1982).
- ²N. C. Blais, D. G. Truhlar, and B. C. Garrett, *J. Chem. Phys.* **78**, 2956 (1983).
- ³N. C. Blais and D. G. Truhlar, *J. Chem. Phys.* **79**, 1334 (1983).
- ⁴M. Baer, *Mol. Phys.* **40**, 1011 (1980).
- ⁵R. G. Newton, *Scattering Theory of Particles and Waves* (McGraw-Hill, New York, 1966), Section 11.3.
- ⁶L. Schlessinger, *Phys. Rev.* **167**, 1411 (1968), **171**, 1523 (1968); S. C. Pieper, J. Wright, and L. Schlessinger, *Phys. Rev. D* **3**, 1419 (1971)
- ⁷Y. Sun, D. J. Kouri, D. G. Truhlar, and D. W. Schwenke, *Phys. Rev. A* **41**, 4857 (1990).
- ⁸Y. Sun, D. J. Kouri, and D. G. Truhlar, *Nucl. Phys. A* **508**, 41c (1990).
- ⁹D. W. Schwenke, S. L. Mielke, and D. G. Truhlar, *Theor. Chim. Acta* **79**, 241 (1991).
- ¹⁰J. C. Light and R. B. Walker, *J. Chem. Phys.* **65**, 4272 (1976); A. Kuppermann, G. C. Schatz, and M. Baer, *J. Chem. Phys.* **65**, 4596 (1976); N. A. Mullaney and D. G. Truhlar, *Chem. Phys.* **39**, 91 (1979); N. M. Harvey and D. G. Truhlar, *Chem. Phys. Lett.* **74**, 252 (1980); A. Kuppermann, J. A. Kaye, and J. P. Dwyer, *Chem. Phys. Lett.*

- 74, 257 (1980); R. T Pack and G. A. Parker, *J. Chem. Phys.* **87**, 3888 (1987); J. Z. H. Zhang and W. H. Miller, *Chem. Phys. Lett.* **173**, 489 (1990).
- ¹¹D. W. Schwenke, K. Haug, M. Zhao, D. G. Truhlar, Y. Sun, J. Z. H. Zhang, and D. J. Kouri, *J. Phys. Chem.* **92**, 3202 (1988).
- ¹²J. Abdallah, Jr. and D. G. Truhlar, *J. Chem. Phys.* **61**, 30 (1974); G. Staszewska and D. G. Truhlar, *J. Chem. Phys.* **86**, 1646 (1987).
- ¹³M. Zhao, D. G. Truhlar, D. W. Schwenke, C.-h. Yu, and D. J. Kouri, *J. Phys. Chem.* **94**, 7062 (1990).