First Principles
Study of Elementary Chemical Reaction Dynamics

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The atom-diatom reactive scattering problem has been extensively studied since 1976 when the full three-dimensional quantum calculation was reported for the prototype \( \text{H} + \text{H}_2 \) reaction on an empirical potential energy surface. Since then, one of the grand challenges in theoretical and computational molecular reaction dynamics has been the first principles calculation of four-atom reactions and beyond.

Variational algebraic methods and hyperspherical coordinate methods that have been successful in atom-diatom reactive scattering problems proved difficult to extend to four-atom reactions and beyond. In particular, in going from the three-atom reaction to the four-atom reaction, the dimensionality of the problem, which is given by \( 3N-6 \), where \( N \) is the number of atoms, doubles from three to six. The size of the Hamiltonian matrix to be inverted, which grows exponentially with the number of basis functions or the dimensionality, then becomes prohibitively large on today’s computers.

We have successfully combined quantum chemistry with quantum dynamics to solve some four-atom reactions accurately in full-dimensional space. This is a major advance in the study of chemical reaction dynamics, since the accurate solution of the three-atom system.

We have used the initial state time-dependent wavepacket propagation (TDWP) approach to the four-atom reactive scattering problem. In the time-independent (TI) methods, an S-matrix connects the reactant states with the product states, and scales as \( M^3 \), where \( M \) is the total number of basis functions. The TDWP approach allows us to solve for one column of the S-matrix at a time, and therefore scales \( < M^2 \). Moreover, by a Fourier transformation, a single wavepacket propagation provides the scattering information for all energies in the initial wavepacket. Formally, however, the TI and TDWP methods are equivalent, but there are major computational advantages in the TDWP method.

Even by using the TDWP method, the computation for solving a 6-dimensional time-dependent Schrödinger equation for a four-atom reaction is still extremely intensive both in memory and CPU time. We need to use approximately 1 billion basis functions in order to calculate state-to-state S-matrix elements for the simplest four-atom \( \text{H}_2 + \text{OH} \) reaction. This means it takes about 8 GB memory to store the wavefunction we want to solve. Thus the total memory required for such a calculation can easily exceed 10 GB. Propagation of such a large wave packet is extremely time consuming. On a Compaq Alpha 833 MHz processor, it takes about 50 minutes to propagate one step, and typically it requires 500 steps to converge one calculation. And even more challenging, to obtain state-to-state differential cross section, we need to carry out 40-50 such calculations. Thus it takes about 800 days to calculate state-to-state differential cross section on a
single Alpha processor.

Substantial effort has been put to speed up the computation by parallelizing our programme on shared memory computers. We achieved a speed-up of 3.8 on the 4-processor Compaq ES40. We also used the GS320 in SVU for a sustained time period. Somehow, we only managed to get a speed-up of 4 by using 8 processors in the GS320 machine, and we will need to get more time on the machine to optimize our program.

Now we are studying the H + CH₄ reaction by using a 7-dimensional model, and we are going to attempt some heavier four-atom reactions, such as HO + CO. The memory and CPU time required to study such systems are considerably larger than what we have used for the H₂ + OH system. Thus we need the continued support of SVU for a large shared memory computer to start these calculations. In addition, we are also working hard to exploit the possibility of parallelizing our program on distributed memory computer systems.

We truly appreciate the support of SVU in providing state-of-the-art resources for this cutting edge research.