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LARGE-SCALE CALCULATIONS OF THE QUANTUM DYNAMICS OF MOLECULAR COLLISIONS AND REACTIONS

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1. INTRODUCTION

Calculation of the accurate quantum dynamics of few-body systems in chemical physics is a challenging class of problems for scientific computation.[1,2] The present paper outlines the use of quantum mechanical scattering theory to describe collisions of diatomic molecules with atoms and with other diatomic molecules. Such systems, containing three or four atoms moving in three dimensions, involve nine or twelve Cartesian coordinates, which reduce to six or nine coordinates after removing the overall motion of the center of mass. The potential function, however, depends on only three or six coordinates, and this allows some dimensions to be treated with less effort. A molecular collision of atom A with diatom BC or of diatom AB with diatom CD is described by the time-independent Schrödinger equation with steady-state scattering boundary conditions.[3] In this paper we consider both nonreactive collisions, in which energy is transferred between collision partners that retain their chemical identity and also reactive collisions, in which both energy and particles are transferred.

The relevant Schrödinger equation is the six-dimensional or nine-dimensional (6-D or 9-D) elliptic partial differential equation (PDE),

$$\left[-\frac{\hbar^2}{2\mu}\left(\nabla_{\mathbf{R}}^2+\nabla_{\mathbf{x}}^2\right)+V_0(\mathbf{x})+V_{\mathrm{int}}(\mathbf{R},\mathbf{x})-E\right]\Psi(\mathbf{R},\mathbf{x})=0. \qquad (1)$$

In this equation, $\hbar$ is Dirac's h, i.e., Planck's h divided by 2π; μ is the collisional reduced mass; $\mathbf{R}$ is a vector from A to the center of mass of BC or from the center of mass of AB to that of CD; $\mathbf{x}$ denotes the other three or six coordinates (assumed to be scaled to the same reduced mass μ as that for $\mathbf{R}$); V_0 is the potential energy of noninteracting collision partners,

$$V_0(\mathbf{x}) = \lim_{R\to\infty} V(\mathbf{R},\mathbf{x}) \tag{2}$$

where V is the full potential energy; V_{int} is the interaction potential, given by

$$V_{\text{int}}(\mathbf{R},\mathbf{x}) = V(\mathbf{R},\mathbf{x}) - V_0(\mathbf{x}); \tag{3}$$

E is the total energy; and Ψ is the scattering wave function.

The steady-state boundary conditions are nonhomogeneous, and their specification involves two steps. First we define the eigenstates ϕ_γ and eigenvalues ε_γ of the noninteracting collision partners, and then we write the boundary conditions in terms of these. For nonreactive collisions, the eigenstates required are solutions of

$$\left(-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{x}}^2 + V_0(\mathbf{x}) - \varepsilon_\gamma\right)\phi_\gamma(\mathbf{x}) = 0 \tag{4}$$

with homogeneous boundary conditions. Then for $R > a$, where a is the distance at which $V_{\text{int}}(\mathbf{R},\mathbf{x})$ becomes negligible, the boundary conditions are

$$\Psi(\mathbf{R},\mathbf{x}) \sim e^{i\mathbf{k}_{\gamma_0}\cdot\mathbf{R}}\phi_{\gamma_0}(\mathbf{x}) + \sum_\gamma f_{\gamma\gamma_0}(\hat{\mathbf{R}})\frac{e^{ik_\gamma R}}{R}\phi_\gamma(\mathbf{x}) \tag{5}$$

where

$$k_\gamma^2 = \frac{2\mu}{\hbar^2}\left(E - \varepsilon_\gamma\right), \tag{6}$$

$f_{\gamma\gamma_0}$ is an unknown scattering amplitude, corresponding to initial state γ_0 and final state γ, and $\hat{\mathbf{R}}$ is the direction of $\mathbf{R}$.

For reactive collisions, e.g., A + BC → AB + C or AC + B, we must enforce boundary conditions for all three arrangements. Let $\alpha = 1$ denote the region of space where A is far from BC, $\alpha = 2$ denote the region where B is far from AC, and $\alpha = 3$ the region where C is far from AB. Let $\mathbf{R}_2$ denote a mass-scaled vector from B to the center of mass of AC and $\mathbf{x}_2$ a mass-scaled vector from C to A; similarly let $\mathbf{R}_3$ denote a mass-scaled vector from C to the center of mass of AB and $\mathbf{x}_3$ a mass-scaled vector from A to B. Then, in addition to eq. (5) we must enforce

$$\Psi(\mathbf{R},\mathbf{x}) \underset{R_\alpha\to\infty}{\sim} \sum_\gamma f^\alpha_{\gamma\gamma_0}(\hat{\mathbf{R}}_\alpha)\frac{e^{ik_\gamma^\alpha R_\alpha}}{R_\alpha}\phi_\gamma^\alpha(\mathbf{x}_\alpha), \quad \alpha = 2,3, \tag{7}$$

where $f^\alpha_{\gamma\gamma_0}$ is an unknown reactive scattering amplitude, and ϕ_γ^α and k_γ^α are defined analogously to eqs. (4) and (6), but in the second and third arrangements.

Typically the wave function of eqs. (1) and (5) is written as a sum of components, each of which has a given total angular momentum J and each of which can be obtained separately. The problem with $J = 0$ is the simplest.

In this paper we consider several challenging applications involving the solution of these equations. The first is the treatment of energy transfer in four-body collisions, in particular inelastic diatom-diatom collisions, for which we have solved eqs. (1)–(6) by converting them into coupled ordinary differential equations in R, using an approach that is called the close coupling method.[1,3,4] These coupled equations are then solved by a propagation method. We also mention the application of such propagation methods to three-body collisions. The final challenging problems we discuss are reactive atom-diatom collisions and nonreactive atom-diatom collisions involving multiple electronic states. For these problems we solve equations (1)–(6) or (1)–(7) by converting them to coupled algebraic equations using a variational principle.[5]

The computers used for the present studies are primarily the Cray-2 large-memory vector supercomputer (and its Cray M92 and C90 successors) and the massively parallel, distributed-memory Connection Machine CM-5 from Thinking Machines Corporation. Some calculations were carried out on a heterogeneous combination of the Cray-2 and CM-5 linked by a High Performance Parallel Interface (HiPPI).

2. CALCULATIONS EMPLOYING PROPAGATION METHODS

Consider the collision of two HF molecules with total angular momentum zero. We write

$$\Psi = \frac{1}{R}\sum_{n=1}^{N} f_n(R)\ \varphi_n\left(\hat{\mathbf{R}},\mathbf{x}\right) \tag{8}$$

where each value of n labels a set of quantum numbers, which is called a "channel," R is the magnitude of $\mathbf{R}$, φ_n is a known basis function (formulated to carry zero total angular momentum), and f_n is unknown. By substituting (8) into (1), we can convert the 9–D PDE into N coupled ordinary differential equations (ODEs) of the form

$$\frac{d^2 f_n}{dR^2} + \sum_{n'=1}^{N} C_{nn'}(R)\ f_{n'}(R) = 0, \qquad n = 1,2,\ldots,N, \tag{9}$$

where the coefficient matrix, which is dense, contains the 8–D integrals

$$C_{n'n}(R) = \int d\hat{\mathbf{R}}\ d\mathbf{x}\varphi^*_{n'}\left(\hat{\mathbf{R}},\mathbf{x}\right)\left\{-\frac{\ell^2}{\hbar^2 R^2} + \nabla^2_{\mathbf{x}} - \frac{2\mu}{\hbar^2}\left[V_{\text{int}}(\mathbf{R},\mathbf{x}) + V_0(\mathbf{x}) - E\right]\right\}\varphi_n\left(\hat{\mathbf{R}},\mathbf{x}\right) \tag{10}$$

where l^2 is the quantum mechanical operator for the square of the angular momentum associated with $\hat{\mathbf{R}}$ motion. These equations must be solved subject to regularity boundary conditions at $R = 0$ and scattering boundary conditions at large R. The unknown scattering amplitudes occur in the large-R boundary

conditions. In challenging current applications, $N > 2000$. In future applications one must consider $J > 0$, which leads to much larger N, e.g., $N = O(10^5)$.

This formalism is also applicable to atom-diatom collisions provided we recognize that x is 6-D for the four-body case and 3-D for the three-body case. The expansion (8) is inconvenient for applying reactive scattering boundary conditions, but reactive scattering can be treated by equations similar to (8) by replacing the propagation coordinate R by the hyperspherical radius ρ.[6–11] This allows us to make a connection to the work of Kuppermann[11,12] discussed in an earlier paper at this conference by Messina.[13] One difference of that work[11,12] from the work discussed above and from our own approach[6] to using hyperspherical coordinates for reactive scattering is that Kuppermann's basis functions φ_n depend on ρ, whereas ours do not depend on R or ρ. Faster convergence with respect to basis size can be obtained with basis functions optimized as a function of the propagation coordinate,[14,15] but we will not discuss that aspect further in the present paper.

We consider three sets of calculations using propagation techniques to illustrate the progress that has been made and the challenges that remain. The first example involves a parallel strategy that we employed on global-memory vector computers. The second and third examples involve strategies developed for multi-processor machines with distributed memory.

In all three strategies the two-point boundary value problem for $f_n(R)$ is solved by converting it to an initial value problem which is equivalent to propagating N or $2N$ linearly independent solutions from the small-R region to the large-R region and then taking linear combinations of these solutions to satisfy the boundary conditions. Taking advantage of the regularity boundary condition at $R = 0$ allows one to propagate only N solutions. These solutions are arranged as an $N \times N$ solution matrix. Equivalent information may be propagated in the form of an $N \times N$ global $\mathscr{R}$ matrix as discussed below.

2.1 A Strategy for Vector Machines

Our original strategy for large-scale inelastic scattering problems was designed for vector processors, such as the Control Data Corporation Cyber 205 and various Cray computers, especially the Cray-1, Cray X-MP, and Cray-2. Details of the algorithm and its implementation are presented elsewhere,[14–21] so here we only summarize a few importance aspects.

The strategy for solving eq. (9) is to convert the equations to an initial value problem, as in the invariant imbedding[22] method. In particular, we use the $\mathscr{R}$ matrix propagation algorithm.[14,15] In $\mathscr{R}$ matrix propagation, the R axis is divided into sectors, and each step consists of finding the local $\mathscr{R}$ matrix (a matrix relating the reciprocal of the logarithmic derivative of the wave function components at the right of a sector to those at its left) and using this to update the global $\mathscr{R}$ matrix[23] (which relates the logarithmic derivative components at the right side of a sector to their values at the left of the first sector, assuming propagation proceeds left to right). Step sizes may be determined adaptively

with little extra effort.[16,19,20] This method is intrinsically stable,[14] and it allows large steps, especially at large R, but the computational effort per step is high, involving the diagonalization of an $N \times N$ matrix and several other matrix operations.[17,20] Nevertheless the code typically spends 90–98% of its time on these highly vectorizable matrix operations, and the method provides an efficient way to solve large-scale problems on vector supercomputers. Memory management can be flexible, and when memory is scarce, one can operate with storage of only two $N \times N$ matrices in central memory.[24]

Because HF has a permanent dipole moment, the interaction potential for HF collisions with HF has a very long range, decaying only as R^{-3}, and many propagation steps, e.g., 300–600, are required to reach the asymptotic region. (Even more steps would be required if it weren't for the valuable feature of $\mathscr{R}$ matrix propagation that one can take very large steps at large R.) It is essential therefore to evaluate the C matrix efficiently. First of all, each element is an 8-D integral. Second, the matrix is dense; since C is symmetric, the number of unique elements is $N(N + 1)/2$, and these must be evaluated. Third, C must be evaluated at every step. In one approach,[17] the 8-D integrals are computed by a combination of 3-D analytic integration and 5-D numerical quadrature. The 3-D angular integrals were carried out by expanding the interaction potential in terms of orthogonal angular basis functions and then analytically evaluating the integrals involving these expansion functions and the channel basis functions. The determination of the expansion coefficients requires a 3-D numerical quadrature which is independent of N, and the analytic angular integrals involve vector coupling coefficients which are nontrivial to evaluate but independent of v_n and $v_{n'}$, where v_n and j_n denote the vibrational and rotational quantum numbers of a particular monomer in channel n. The two quadratures over the monomer vibrational coordinates are carried out by N^{QV}-point quadrature, which are programmed as an inner vectorized loop of length $(N^{QV})^2$. The outer loops were arranged to avoid unnecessary repetitions, and we used an optimized quadrature scheme[25] to minimize N^{QV}. In particular, we precalculated and stored separate quadrature weights for each combination of monomer vibrational and rotational quantum numbers (thus the weights depend on four indices: v_n, j_n, $v_{n'}$, and $j_{n'}$). The extra storage required for these weights is negligible compared to the computer time savings they afford.

The second approach[19] to the quadratures also involves a preparatory step. In this approach, we refit the interaction potential to a sum of separable products. This allows the $C_{nn'}(R)$ matrix for any R to be constructed from a relatively small number of R-independent matrix elements. This approach makes the cost of the quadrature step almost negligible, but it may require more storage than the first approach, depending on N and the number of separable products. Using the second approach we have solved eq. (9) with N as large as 2472.

Because dense matrix diagonalizations do not usually parallelize well when distributed across processors on a distributed-memory multiprocessor, we explored other strategies for parallelization on such machines.

2.2 Parallelization in the Physical Domain

Each propagation step involves the same arithmetic operations on different data. Therefore one possible approach to parallelization is to assign the sectors, each spanned by a single propagation step, to individual processors. In this strategy one performs many steps simultaneously, obtaining a local $\mathscr{R}$ matrix for each sector or each set of contiguous sectors on a single processor and then combining these into a global $\mathscr{R}$ matrix, in a process corresponding to the reverse of successive bisections. There are several penalties for using this approach. The first disadvantage results from the nature of the boundary conditions. The initial sector has homogeneous boundary conditions at small R, and this causes certain submatrices to start out as zero. As long as the steps are performed in order, these zeros remain zero, and they may be propagated analytically.[16] However, if steps are performed out of order, replacing the global initial value problem by a sequence of boundary value problems across the individual sectors, one must calculate the general solution rather than this simpler particular solution, and this raises the operation count about 35%.

A second disadvantage of parallelization across the physical domain is the inefficiency in treating problems where the number of sectors is less than the number of processors. A third disadvantage occurs when the local $\mathscr{R}$ matrices are combined; this step leads to a load balancing problem. Fourth, to run efficiently this algorithm would require a large memory on each node, especially if I/O is slow.

The strategy presented next does not have these disadvantages.

2.3 A Strategy Based on Parallel Matrix Multiplications

The essence of the next strategy we employed is to use a very simple propagation algorithm consisting of a limited number of primitive matrix operations that can be parallelized across the processors. The algorithm we chose is the de Vogelaere algorithm,[26] for which the effort consists almost entirely of matrix multiplications and QR factorizations,[27] with the latter needed for stability.[28] In practice we found it was more efficient actually to carry out the QR application on the transpose (T) of the solution matrix. In particular the stabilization transformation we used involved the explicit formation of Q and its application to four matrices. We then spread each matrix operation over all the processors. In reducing this idea to practice, the implementation we have used to date is to create the C matrices on the Cray-2, then move them via the HiPPI to the CM-5, where the propagation steps are performed. The prototype problem we considered corresponds to vibrational-rotational excitation of H_2 by He.

We simplified our code as much as possible to keep overhead down, and we were able to solve the prototype problem with $N = 509$ on 512 processors of the CM-5 with only 6% overhead. In addition we obtained good speeds on the matrix multiplications and QR stabilization transformations. Figure 1 illustrates the speedups for matrix multiplication as a function of matrix size for one processor on a Cray-2 or C90, for 16 processors on a C90, and for 32, 128, 256,

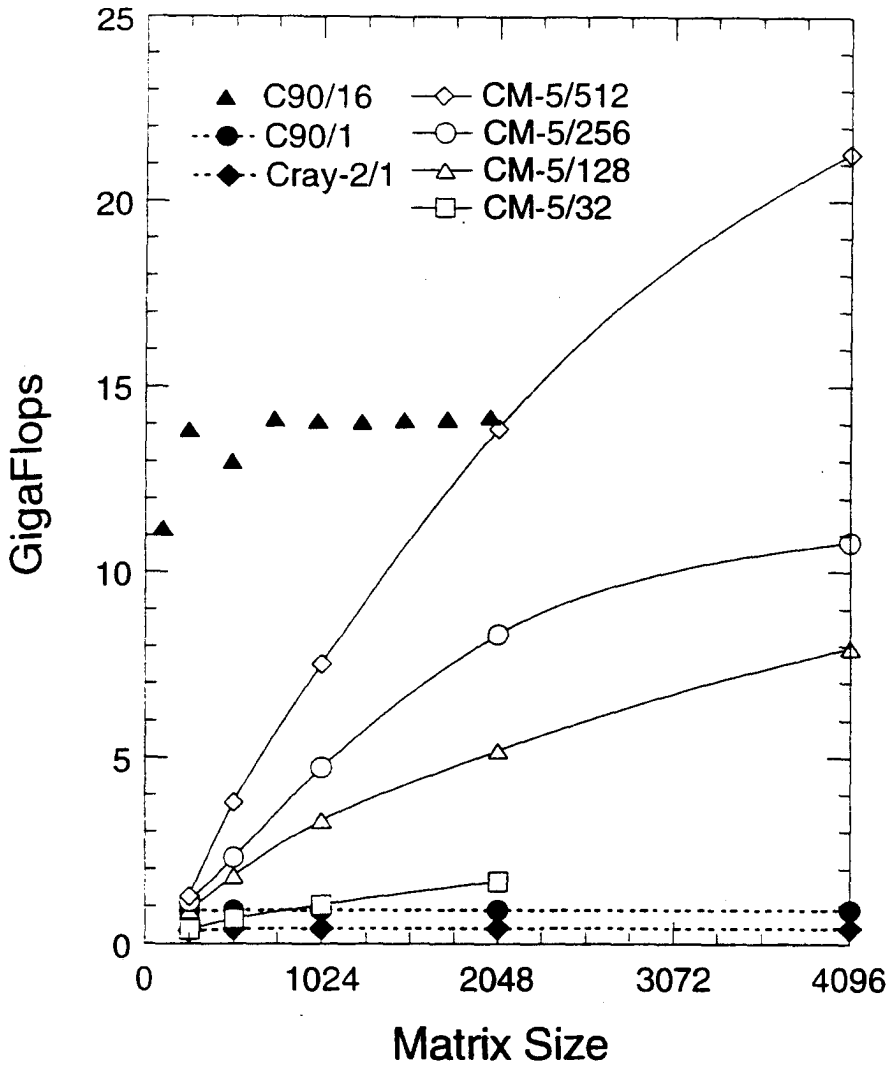

Figure 1. Speeds (billions of floating point operations per second) as functions of matrix size for matrix multiplications required in de Vogelaere algorithm on various computers with various numbers of processors, indicated by the value after /. On the Cray machines, the matrices were stored with leading dimension $2^N + 1$ to avoid bank conflicts. The C90/16 speeds are for a dedicated machine and are taken from Ref. 74, and the other Cray speeds are based on CPU times obtained by the authors in time-share batch mode; in both cases the LAPACK BLAS routine SGEMM is used. The CM-5 speeds are based on elapsed times obtained by the authors using the CMSSL library routine GEN_MATRIX_MULT.

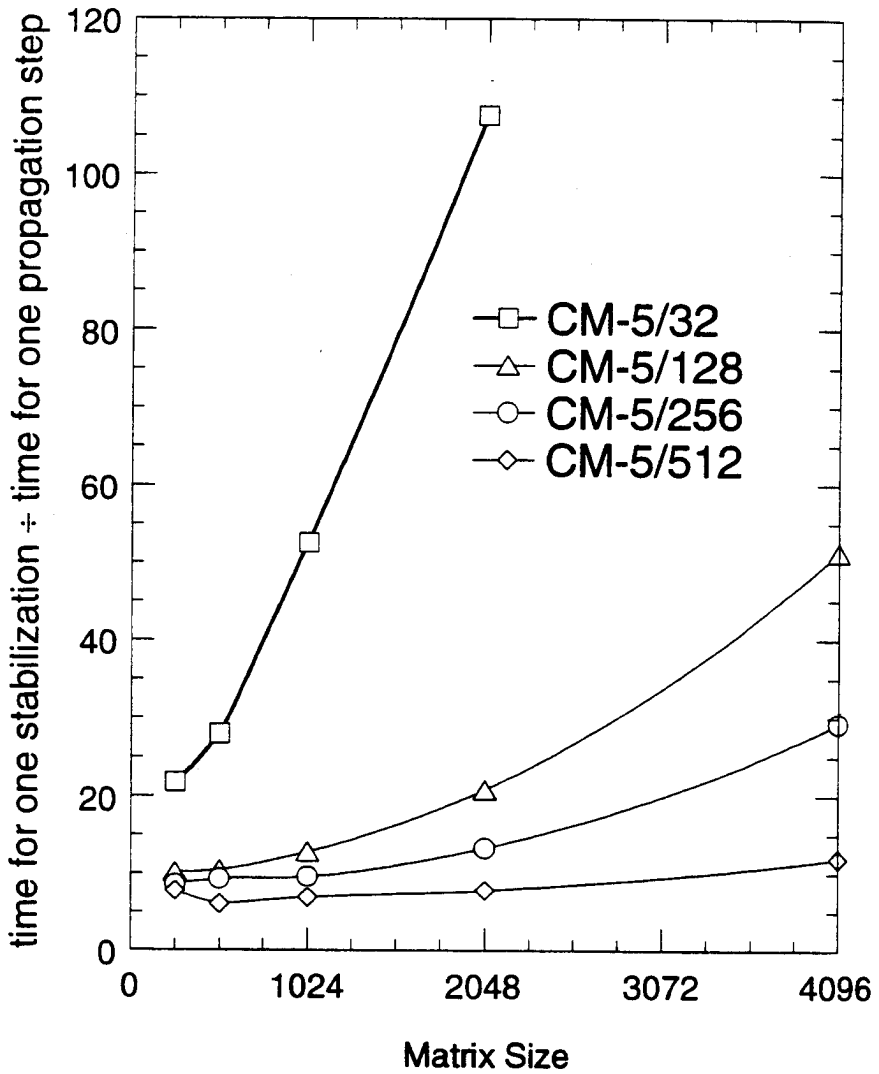

Figure 2. Ratio of time required for a single stabilization transformation to that required for a single propagation step on various partitions of the CM-5 as a function of matrix order.

or 512 nodes of the CM-5. Figure 2 shows the time required on the CM-5 for a stabilization transformation divided by the time for a propagation step, which consists of two matrix multiplies. We found, for the H_2-He problem, that a stabilization needs to be performed on only about 1% of the steps. Thus, when the ratio in Fig. 2 is less than about 100, the efficient matrix multiplications dominate the computer time. Since, as stated above, 94% of the effort in our prototype problem goes into the propagation steps and stabilization transformations, and since the ratio in Fig. 2 is much less than 100 for 512 processors, the excellent speeds on matrix multiplication translate into good performance on the whole algorithm for 512 processors. However, the number of steps required by the de Vogelaere algorithm is large.

Disclaimer. These results are based upon a beta version of the TMC software and, consequently, are not necessarily representative of the performance of the full version of the software.

3. CALCULATIONS EMPLOYING ALGEBRAIC VARIATIONAL METHODS

The description of chemical reactions requires the theory of quantum mechanical rearrangement scattering.[3] For rearrangement collisions we restrict our consideration to three-body systems. For reactive collisions we replace eq. (8) by

$$\Psi = \sum_{\alpha=1}^{3} \sum_{n_\alpha=1}^{N_\alpha} f_{n_\alpha}(R_\alpha)\phi_{n_\alpha}(\hat{\mathbf{R}}_\alpha, x_\alpha) \tag{11}$$

where $\mathbf{R}_1 = \mathbf{R}$, $\mathbf{x}_1 = \mathbf{x}$, and α is the arrangement quantum number explained below eq. (6). Note that $\mathbf{x}_1$ consists of the BC vibrational coordinate r_1, the BC rotational coordinates $\hat{\mathbf{r}}_1$, and the A-BC angular orbital coordinates $\hat{\mathbf{R}}_1$, with similar definitions for the B-AC and C-AB arrangements. Note also that even if f_{n_α} form an orthogonal set, the basis functions in different arrangements would be nonorthogonal. Furthermore, as explained below eq. (6), we must simultaneously impose collisional boundary conditions in three different coordinate systems. The approach we have found most suitable for attacking such problems is the algebraic variational approach,[5] especially the outgoing wave variational principle[29–38] (OWVP), with basis functions motivated[32,38] by the integral-equation-based generalized[39,40] Newton[41,42] variational principle.

In applying the OWVP, we first partition the interaction potential (3) as

$$V_{\text{int}}(\mathbf{R},\mathbf{x}) = V_1^{\text{D}}(\mathbf{R}_1,\mathbf{x}_1) + V_1^{\text{C}}(\mathbf{R}_1,\mathbf{x}_1) \tag{12a}$$

$$= V_2^{\text{D}}(\mathbf{R}_2,\mathbf{x}_2) + V_2^{\text{C}}(\mathbf{R}_2,\mathbf{x}_2) \tag{12b}$$

$$= V_3^{\text{D}}(\mathbf{R}_3,\mathbf{x}_3) + V_3^{\text{C}}(\mathbf{R}_3,\mathbf{x}_3) \tag{12c}$$

where V_α^{D} is called a distortion potential, and V_α^{C} is a coupling potential. A critical element in this partition is that V_α^{D} does not couple basis functions in different arrangements, but V_α^{C} does. We then write

$$\Psi = \psi_{\text{incoming}}(\mathbf{R}_1, \mathbf{x}_1) + \sum_{\beta} A_\beta \Gamma_\beta \left(\mathbf{R}_{\alpha_\beta}, \mathbf{x}_{\alpha_\beta} \right) \tag{13}$$

where ψ_{incoming} is a solution to

$$\left[-\frac{\hbar^2}{2\mu} \left(\nabla_{\mathbf{R}}^2 + \nabla_{\mathbf{x}}^2 \right) + V_0(\mathbf{x}) + V_1^{\text{D}}(\mathbf{R}, \mathbf{x}) - E \right] \psi_{\text{incoming}}(\mathbf{R}, \mathbf{x}) = 0, \tag{14}$$

A_β is a complex coefficient, and each Γ_β is taken as one of three types[36,37] of 6-D basis function in a given arrangement α_β:

- gaussian, centered at $R_\beta^G \neq 0$, in radial translational coordinate R_{α_β}, times an asymptotic vibrational function for r_{α_β} times a 4-D rotational-orbital function $Z_{j\Omega}^{JM_JP}\left(\hat{\mathbf{r}}_{\alpha_\beta}, \hat{\mathbf{R}}_{\alpha_\beta} \right)$;
- 2-D gaussian in R_{α_β} and r_{α_β} times $Z_{j\Omega}^{JM_JP}\left(\hat{\mathbf{r}}_{\alpha_\beta}, \hat{\mathbf{R}}_{\alpha_\beta} \right)$;
- coupled-channel 6-D Green's function obtained by solving a problem with up to ~50–100 rotationally coupled channels in a single arrangement with a localized inhomogeneity.

The third type of basis function is called a dynamically adapted basis function.[32,38] For reactive scattering one could have all three types of basis function in all three arrangements, leading to a large number of different kinds of integrals.[36] Some economy of coding is achieved by restricting the $\mathbf{x}_\alpha$ dependencies of the forms of the type-1 basis functions and of the inhomogeneities in the type-3 basis functions to be the same.

The computational steps for the OWVP are as follows:

- Compute the radial parts of ψ_{incoming} and the coupled-channel radial Green's functions directly on quadrature grids (for the next step) by high-order finite differences[33,35] (typically a 13-point approximation to d^2/dR_α^2).
- Compute 6-D quadratures over V_{int}, ψ_{incoming}, and basis functions; three dimensions are treated analytically in a body-fixed coordinate frame,[36,43] and three are treated by numerical integration.
- Solve a dense, complex, non-Hermitean linear algebraic system for the coefficients of basis functions and for the complex scattering matrix (which is a matrix of fixed-J scattering amplitudes). Both direct methods involving partitioned matrices[44] and also preconditioned iterative methods[45] have been employed.

For atom-diatom reactive collisions, the state of the art involves treating all J at a given energy with stable convergence of the phases of the scattering matrix elements as required to calculate differential cross sections[46–48] or on a fine energy grid as required to study quantized transition state spectra[49,50] or to calculate thermally averaged rate constants.[51] For atom-diatom collisions involving multiple electronic states,[37,52–54] even low-E, low-J calculations are currently challenging problems. Increasing E or J or the number of electronic

states increases the number of channels and hence the number of basis functions required for convergence. The order N of the final dense system of equations is equal to the number of basis functions; the largest calculation we have completed to date has $N = 17413$.[37]

Selected recent applications we have carried out using the algebraic variational method include the following studies:

For the $D + H_2 \rightarrow HD + H$ reaction, we calculated[51] thermally averaged rate constants as a function of temperature and found excellent agreement (< 9%) with a fit[55] to the available experimental values for T = 200–800 K. The comparison is shown in Figure 3. The curve representing experimental results is the three-parameter fit from Ref. 55 to their own and literature[56–58] data. Over the whole region shown, theory agrees with experiment within the 20% reliability of the fit. The theoretical values are based on a potential energy function[59] fit to *ab initio* electronic structure calculations from several sets[59–62] of calculations. This comparison shows that converged quantum dynamics calculations can compete with experimental methods for the accurate determination of chemical kinetics rate coefficients when the potential energy surface is well known. This example suggests two challenges to Teraflop computing: (i) obtaining chemically accurate potential energy surfaces for more complicated systems, and (ii) extending converged quantal kinetics schemes to more complicated systems. At the present time we can calculate converged quantum dynamical rate constants for more complicated atom-diatom systems, but the potential energy surface is not known to chemical accuracy for any system except $H + H_2$ and its isotopomeric analogs.

Converged quantum dynamics calculations have also been compared successfully to experiment for differential cross sections. Recent papers presented such comparisons for the $F + H_2 \rightarrow HF + H$[47] and $H + D_2 \rightarrow HD + D$[48] reactions. The former study is particularly noteworthy in that the experimental results[63] showed strong evidence of participation by quantum mechanical resonance states, but the differential cross sections for the various v' states of HF, where v is the vibrational quantum number and primes denote final-state values, were unreproducible by theory until converged quantum dynamics was combined with a new potential energy function.[47] The latter study was particularly interesting in that it yielded qualitatively different differential cross sections from quasiclassical trajectory calculations[64] for the state-to-state differential cross sections for reaction into various final rotational states. This comparison provides a striking indication of the necessity to solve reactive scattering dynamical problems at the quantum mechanical rather than the classical mechanical level.

A third application area to which we have applied algebraic variational methods is the study of quantized transition states. Transition state theory[65,66] (also called activated complex theory) has provided the dominant quantitative and qualitative framework for understanding chemical kinetics dating back to the 1930s, and quantization of transition states has been considered essential dating back to the seminal work of Wigner[67] and Eyring[66]; consideration of the quantized nature of transition states has been especially indispensable for the

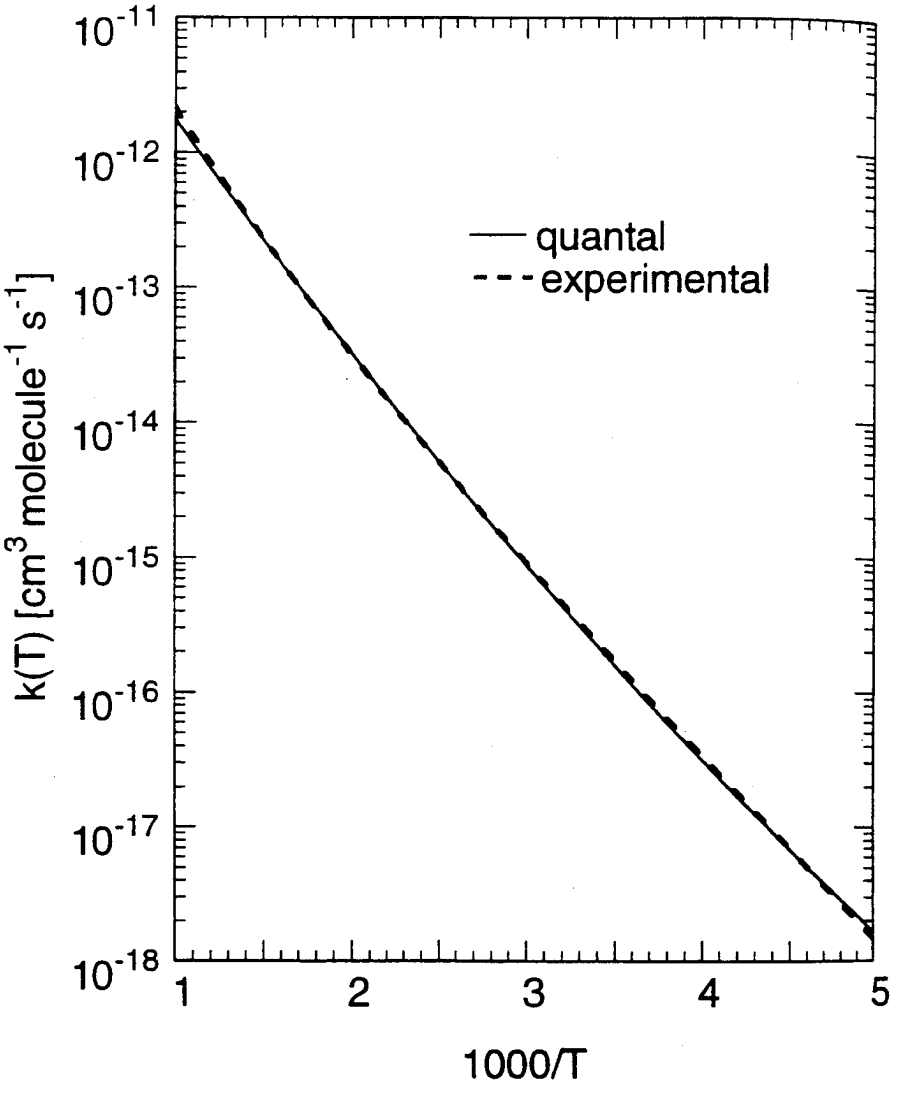

Figure 3. Rate constants vs. 1000/temperature (in degrees Kelvin) for the reaction D + H_2 → HD + H. The solid curve represents the values calculated by quantum mechanical theory, and the dashed curve is experiment.

interpretation of kinetic isotope effects.[68] However, the observation of the "spectrum" of the transition state has proved experimentally elusive. Now this spectrum has been observed in accurate quantum dynamics calculations on the $H + H_2$ and $O + H_2$ reactions.[49,50,69]

Figure 4 shows the spectrum of the $O + H_2$ reaction. The top half of this figure shows the cumulative reactive probability $N(E)$ for this reaction, for $J = 0$, with the potential energy function taken from the work of Johnson, Winter, and Schatz.[70,71] This quantity is defined by

$$N(E) = h\rho^R(E)k(E) \tag{15}$$

where h is Planck's constant, $\rho^R(E)$ is the density of states of the reactant (a nondynamical quantity), and $k(E)$ is the converged microcanonical-ensemble quantum mechanical rate coefficient (for the assumed potential energy function). A rate coefficient for a microcanonical ensemble involves an equally weighted sum of all state-to-state reaction probabilities, including all excited states energetically accessible at a given total energy, and that is why it has never been measured experimentally. But, by including the contributions from all states, which is possible in a computational study, one brings out the quantized structure of the dynamical bottleneck to reaction. This is shown in the bottom half of Fig. 4, which is the energy derivative of the top half. Each peak in the lower half of the figure corresponds to a rise in the cumulative reaction probability as the system accesses a new quantized state of the activated complex.

The peaks observed in the transition state spectrum have all been assigned quantum numbers and individual transmission coefficients.[50] In transition state theory, the transmission coefficient of each state of the activated complex is assumed to be unity; and by comparison of thermally averaged rate constants to experiment one can hope at best to determine the average transmission coefficient for all the activated-complex states and hence the average breakdown of the transition state assumption to the extent that this value deviates from unity. The accurate quantum mechanical calculations provide a new level of detail in understanding the validity of the transition state assumption in that we can now see that some quantized dynamical bottleneck states correspond to the unit-transmission-coefficient assumption better than others. For example, the first two peaks in Fig. 4 correspond to activated-complex states that have transmission coefficients of 0.96 and 0.9, respectively, but the third peak, at 0.97 eV, corresponds to a transmission coefficient of only 0.6. The third peak in Fig. 4 is interesting in another way as well. The first two peaks correspond to the ground state and a bend-excited state of the activated complex, but the third state (at 0.97 eV) has the bound stretching motion of the activated complex excited. The energy of this third peak corresponds very closely to the threshold energy for the reaction of H_2 ($v = 1$) with O. This indicates that vibrationally excited reactants principally access the stretch-excited states of the activated complex. We see then that the excited states of the activated complex are *state-specific* doorways between reactants and products, confirming the validity of ideas advanced earlier in approximate theory, in particular in state-specific variational transition state theory.[72] The converged quantum dynamics calculations also identified dynamical bottlenecks

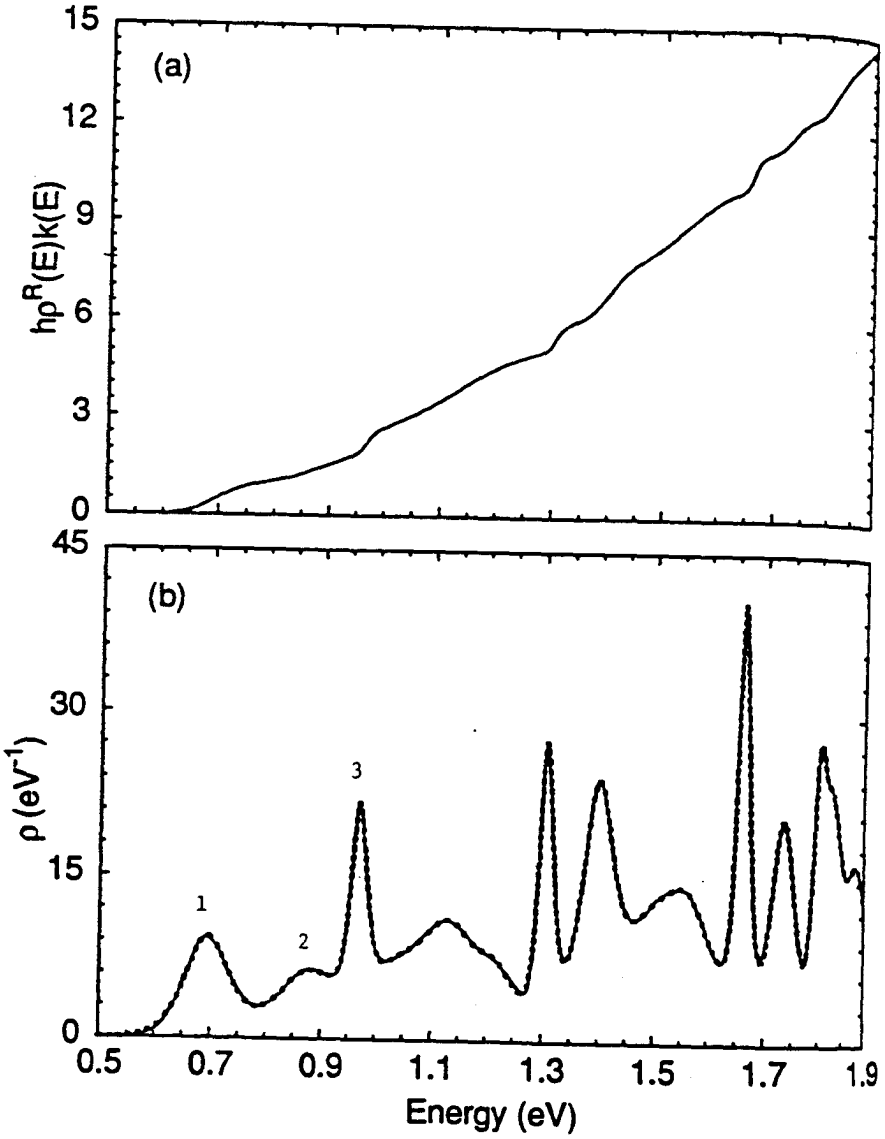

Figure 4. (a) Cumulative reaction probability for the $O + H_2 \rightarrow OH + H$ reaction. (b) Derivative of part (a).

to state-specific reactivity that do not affect the overall rate coefficient; these were called supernumerary transition states of the second kind.[50] This discussion has identified a new role for accurate quantum dynamics calculations—namely, by providing a detailed picture of chemical reactivity at the ultimate level of resolution allowed by quantum mechanics, such calculations can provide insight into the conceptual framework by which we understand phenomena in quantum mechanical systems. The use of large-scale calculations to provide conceptual insight—as well as hard numbers—will be a major challenge for Teraflop computing.

We will close this section with an introduction to a new area which will benefit greatly from Teraflop computing, namely the quantum mechanical treatment of chemical reactions of electronically excited reagents—or "quantum photochemistry."

In 1938, Wigner said,[73] "It seems that one can divide the chemistry of reactions into three groups," the first group being those which exchange translational, rotational, and vibrational energy but do not change electronic state or chemical formula, and the second being those which involve no change in electronic quantum numbers but which may involve a change in constitution. Wigner continued, "The remaining third class deals with reactions which involve a jump in the electronic structure.... It is clearly the most general type and probably the most difficult of all."[73] The accurate quantum mechanical treatment of the dynamics of such systems will be a challenge for Teraflop computers. Meanwhile we have made a start. Our initial efforts in this field have involved the development of a formalism general enough to handle the problem,[36] and a series of calculations[37,52-54] on nonreactive collisions of Na($3p$) with H_2 at energies above the conical intersection of the ground and first excited electronic state surfaces. These calculations enabled us to discover a new phenomenon, namely the enhancement of molecular energy transfer by the intermediate participation of metastable states associated with the conical intersection region. The metastable states in the vicinity of the conical intersection were assigned quantum numbers, and their lifetimes and decay probabilities into various final states were mapped out.[53,54] We anticipate that additional new phenomena are likely to be uncovered as the calculations are extended to higher energies where chemical reaction becomes possible.

4. SUMMARY

This paper discusses our recent experience with large-scale quantum mechanical calculations for molecular collisions, and it identifies several challenges for Teraflop computation.

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