Advanced software for the calculation of thermochemistry, kinetics, and dynamics

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Abstract. Recent results are presented for the efficient computation of matrix eigenvalue and eigenvector equations, the fitting of discrete sets of energy points using interpolating moving least squares methods, and time-dependent and time-independent calculations of molecular dynamics and cumulative reaction probabilities.

1. Introduction

The Born-Oppenheimer separation of the Schrodinger equation for molecules allows the electronic and nuclear motions to be solved in three steps. 1) The solution of the electronic wave function at a discrete set of molecular conformations; 2) the fitting of this discrete set of energy values in order to construct an analytical approximation to the potential energy surface (PES) at all molecular conformations; 3) the use of this analytical PES to solve for the nuclear motion using either time-dependent or time-independent formulations to compute molecular energy values, chemical reaction rates, and cumulative reaction probabilities. Our SciDAC project involves the development of technology to address all three of these steps.

2. Eigenvalue Bounds

During the development of the Subspace Projected Approximate Matrix (SPAM) diagonalization method [1], it was necessary to compute bounds of approximate eigenvalues and eigenvectors. This work resulted in the development of a general computational procedure to compute rigorous eigenvalue bounds for general subspace eigenvalue methods. This method consists of the recursive application of a combination of the Ritz Bound, the Residual Norm Bound, the Gap Bound, and the Spread Bound. In addition to application within the SPAM method, this method may also be applied to the Davidson method as used in molecular electronic structure calculations, to the Lanczos method as used in the computation of molecular vibrational eigenvalues, and in general it can be applied to any iterative eigenvalue method based on the Ritz subspace approach. Figure 1 shows the general conditions in which this bounds procedure may be applied. Table 1 gives a brief summary of the bounds expressions that are used by the method. More details are available in the published manuscripts [2,3].

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Figure 1. The inner Ritz value $\rho_j$ is isolated from the other Ritz values within the subspace by the Residual Norm bound. The exact gap is $\gamma$; and the computed lower bound to that gap is $\gamma^-$. When the Ritz value is isolated in this manner, the upper and lower bounds to the exact eigenvalue $\lambda_k$ computed by the Gap Theorem are tighter than those from the Residual Norm Bounds.

| Bound Type | Bound Expression |
|------------|------------------|
| Ritz       | $\lambda_j \leq \rho_j$ for $j = 1, \ldots, m$ $\rho_{-j} \leq \lambda_{-j}$ |
| Residual   | $\sqrt{r^T_jM^{-1}r_j} \geq |\lambda_k - \rho_j|$ |
| Gap        | $\frac{r^T_jM^{-1}r_j}{\gamma_j} \geq |\lambda_k - \rho_j|$ |
| Spread     | $\frac{r^T_kM^{-1}r_k}{\sigma^+} \leq |\lambda_k - \rho_k|$ for $k = \pm 1$ |

Table 1. Expressions for the various bounds used in the refinement procedure. The Parlett indexing convention is used for negative indices; $\sigma^+$ is an upper bound to the exact matrix spread; $\gamma$ is a lower bound to the exact gap.

3. Interpolating Moving Least-Squares
In collaboration with Theoretical Chemical Dynamics Studies of Elementary Combustion Reactions (Thompson, Univ. of Missouri) we are developing accurate PESs for ab initio calculations involving large polyatomic molecules and radicals. We are using interpolating moving least-squares methods and singular value decomposition (SVD) to obtain a black-box package for addressing higher dimensional PES including features such as automatic point selection and selection of basis sets. As an example, for the full 6-D HOOH PES, we are able to fit an energy range of 100 kcal/mol to an accuracy of 1 kcal/mol with approximately 1350 points. For further details, see Reference [4].

4. Time-Dependent Dynamics
We have developed a parallel wave packet code for four-atom quantum mechanical simulations, capable of performing very well in massively parallel computing environments. The code can be used to determine ro-vibrational energy levels via iterative diagonalization techniques or to determine reaction probabilities, and ultimately rate constants, for chemical reactions [5].
The code is most efficiently run in a parallel environment of many multiprocessor nodes, each node consisting of two or more processors with a shared memory. The NERSC computing facility at Berkeley is one such massively parallel environment that we have used extensively. The code may also be used with Linux clusters made up of dual-processor nodes.

Discretization of spatial grids and/or the introduction of a finite number of basis functions for some degrees of freedom transforms the relevant partial differential equation (Schrödinger equation) into a matrix-vector differential equation. The numerical solution of this equation involves repeated actions of a Hamiltonian matrix on a wave packet vector. The use of special finite-difference (FD) approximations we have previously developed [6] allows us to devise a domain-decomposition of the wave packet over nodes that involves relatively small amounts of communication.

A key feature of our parallelization is the combined use of OpenMP [7] and MPI [8] parallel tools. OpenMP allows for efficient parallelization within a node and MPI is used for internode communications. One processor per node is associated with performing the MPI communication, whereas the other processors are involved in a task farm to carry out the computational work required. See Ref. [5] for a more thorough description of the techniques employed.

Our parallel four-atom quantum wave packet code was developed and thoroughly tested on up to 1024 processors for a realistic problem, the combustion-important OH + CO reaction [5]. Figure 2 below illustrates the results we have achieved at the NERSC facility. The approach is seen to scale very well up to 512 processors, working at up to 20% of the theoretical peak performance rate. The speed-up leveled off between 512 and 1024 processors, and the highest total floating point rate achieved was 0.16 TFLOPS with 768 processors.

The very encouraging performance achieved with our code suggests that a variety of challenging four-atom problems may be addressed with it. The basic ideas and techniques employed in the parallelization scheme are not limited to four-atom problems and so could be extended to larger polyatomic problems. 

Figure 2. Speed-up achieved with a large wave packet propagation problem (see main text). The speed-up is the ratio of wall clock times associated with one- and n-processor runs. The solid curve is the theoretical ideal limit and the symbols are our results. Thus, for example, we see the 512-processor run is almost at the theoretical limit i.e. is about 500 times faster than a one-processor run.

5. Cumulative Reaction Probability
Following approaches developed by Miller and coworkers, we are using iterative eigenvalue methods and iterative solutions of linear equations for solving large-scale time-independent cumulative reaction probability (CRP) calculations. In this approach, the probability operator is evaluated at each
eigenvalue iteration and this, in turn, requires the solution of two linear algebraic systems to apply the Green’s functions in the operator. Instead of developing specialized software that is specific to this problem, we use the PETSc software toolkit, which is a component of the SciDAC TOPS ISIC to obtain a GMRES solution of the linear systems.

There are two focuses in our recent work. First, we have replaced the Lanczos solver previously used in our code with an interface to a wide-range of state-of-the-art eigenvalue solvers available to PETSc thru SLEPc (Scaleable Library for Eigenvalue Problem Computations). This allows us to effectively deal with conditioning issues such as “ghost” eigenvalues. Performance results on up to seven degree of freedom problems are illustrated in Figure 3. Secondly, we are collaborating with the PETSc group on developing efficient linear-solve methods. While the matrices involved are presently treated as sparse matrices, the matrix structure evolves from a mix of the basis set and the Discrete Variable Representation (DVR) and can be exploited to reduce memory requirements. Since the key computational kernel of our CRP software is the matrix-vector calculation in GMRES, we are collaborating with the TOPS group as well on the use of tensor product representations of the Hamiltonian. In doing so one can achieve more than 50% of peak processor performance in such matrix-vector products. Figure 4 illustrates the performance of several standard matrix-vector routines and customized software we are developing for an automated approach. This approach has broad utility and may apply to other problems.

In related work we have studied the role of effective preconditioning for the solution of these linear systems. Truncated banded preconditioners are useful for small problems and we have also used diagonal preconditioning for larger problems in parallel applications. Related results by our collaborators in W. Poirier's group (Texas Tech University) using optimal separable basis preconditioners for DVR methods in Cartesian coordinates is quite encouraging. These methods have been developed for use in CRP problems in a parallel environment.

**Figure 3.** Performance of the CRP solution for one eigenvalue with diagonal scaling and parallel calculations using PETSc.

**Figure 4.** Matrix-vector product performance in tensor form applied to the solution of Eckert’s problem (we extend it to higher dimensions with directions orthogonal to the reaction path). The dimensions in the figure use 9 DVR variables in the orthogonal direction and 53 variables in the reaction path direction.
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