

Li + HCl RIOSA cross section calculations on parallel computers

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Summary. Reactive Infinite Order Sudden Approximation calculations have been performed using a computational procedure restructured to run on parallel computers. Computationally intensive sections of the code are analyzed and speedups obtained from a parallel restructuring discussed. The significant speedup obtained on a shared-memory parallel machine has allowed us to perform extensive calculations of the energy dependence of the integral and differential reactive cross sections of the Li + HCl system. A comparison with results of a quasiclassical and an experimental study is also performed.

Key words: Parallel computing – Shared memory – Distributed memory – Cross sections – Reactive Infinite Order Sudden Approximation – Chemical reactions

1. Introduction

The Reactive Infinite Order Sudden Approximation (RIOSA) [1–7] and its variants [8–12] are among the most popular reduced dimensionality approaches to the calculation of reactive scattering properties of atom-diatom systems [13]. Their accuracy has been most often investigated for collinearly dominant systems [14, 15]. However, although not fully tested against 3D accurate results, reduced dimensionality quantum approaches represent a viable alternative to the accurate treatment when extensive calculations of cross sections and rate constants are needed.

Accurate quantum three-dimensional techniques are currently being used for calculating the low energy detailed reactive probabilities and cross sections for atom-diatom systems [16–32]. However, because of the complexity of the numerical procedures and of the related heavy demand of computer resources, an extension to the calculation of higher energy cross sections and rate constants is not straightforward especially for fairly heavy systems. This emphasizes the importance of improving the speed and the accuracy of reduced dimensionality approaches. In fact, once tested against accurate 3D quantum calculations, reduced dimensionality methods can be used for several pure and applied science investigations. Among these, the preliminary test of potential energy surfaces (before undergoing expensive and lengthy accurate 3D quantum calculations)

and the evaluation of rate constants over extended ranges of temperature or initial vibrational energies (for use in modeling complex chemical systems).

Thanks to the growing computational power of non conventional computer architectures, the time needed to perform cross sections or rate constant calculations for elementary reactive atom-diatom processes has been significantly reduced. The study of the impact of modern computer architectures on the design of computational strategies aimed at calculating observables of atom-diatom reactive processes, is, indeed, one of the main aims of our recent investigation. In this paper, the work performed for restructuring our RIOSA code to run on parallel computers is briefly outlined and an application to the Li + HCl reactive system is discussed. The large speedup obtained for the restructured code on parallel computers allows us to perform extended calculations of the reactive cross sections and preliminary quantum investigations of the dynamics on the proposed potential energy surface useful for understanding the causes for the discrepancy between quasiclassical [33] and experimental [34] estimates of the reactive cross section.

The paper is organized as follows: The computational structure of the RIOSA program, parallel restructuring work and speedups are discussed in Sect. 2. Results of the RIOSA investigation of the Li + HCl reaction are reported in Sect. 3. Preliminary work to port the computer program on a distributed memory architecture is illustrated in Sect. 4.

2. Shared memory parallel restructuring

A detailed description of our RIOSA computational procedure is given elsewhere [35–37]. Here, only the basic numerical features and the essential structure of the program useful for understanding the parallel restructuring of the code are briefly outlined. To this purpose, two sections of the code are important. The first (section A) solves the one-dimensional sector eigenvalue equations in the r_λ variable at a fixed value of collision angle γ_λ , total energy E and propagation coordinate R_λ :

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr_\lambda^2} + V(r_\lambda; R_\lambda^i, \gamma_\lambda) - E \right] \phi_{\lambda,v}^i(r_\lambda; R_\lambda^i, \gamma_\lambda) = 0 \quad (1)$$

being R_λ^i the value of R_λ at the midpoint of sector i and r_λ the orthogonal bound coordinate of the λ arrangement channel. The second (section B) integrates numerically from the origin to the asymptotes the equations:

$$\left[\frac{d^2}{dR_\lambda^2} - \mathbf{D}^{E l_\lambda j_\lambda}(\gamma_\lambda) \right] \chi_\lambda(R_\lambda; \gamma_\lambda) = 0 \quad (2)$$

generated by expanding the global RIOSA wavefunction in terms of products of $\chi_{\lambda,v}(R_\lambda; \gamma_\lambda)$ (propagation) and $\phi_{\lambda,v}^i(r_\lambda; R_\lambda^i, \gamma_\lambda)$ local (bound) functions, for both $\lambda = \alpha$ (reactant channel) and $\lambda = \beta$ or β' (product channels). In Eq. (2) $\mathbf{D}^{E l_\lambda j_\lambda}(\gamma_\lambda)$ is the fixed collision angle γ_λ , total energy E , orbital l_λ and rotational j_λ quantum numbers coupling matrix. By forcing the line separating the α and β channels [38, 39] to sit on the ridge, the correspondence between γ_α and γ_β is made unique and the λ labeling of γ unnecessary. The notation can be further simplified by dropping j_λ (because usually set equal to zero).

From the computational point of view, the key difference between sections A and B is that Eq. (1) need to be solved once for each value of γ , while the fixed

γ propagation of Eq. (2) has to be repeated for every couple of E and l values. To propagate the solution of Eq. (2) through the sectors, we use an *intrasector* diabatic (*intersector* adiabatic) \mathbf{R} matrix propagation technique [40, 44]. This method has the advantage of reducing the dimension of the expansion basis set while allowing the use of a simple propagator. Once the solution has been propagated-through from the origin to the asymptotic regions of both α and β channels, usual scattering boundary conditions can be applied to derive the fixed γ \mathbf{S} matrix elements $S'_{vv}(E, \gamma)$ (product labels are primed, reactant labels are unprimed). From this the differential:

$$\frac{d\sigma_{vv}(E)}{d\Omega} = \frac{1}{8k_v^2} \sum_{lk} (2l+1)(2k+1)P_l(\cos\theta)P_k(\cos\theta) \times \int_{-1}^1 S'_{vv}(E, \gamma)S_{vv}^{*k}(E, \gamma)d(\cos\gamma) \quad (3)$$

and integral cross sections:

$$\sigma_{vv}(E) = \frac{\pi}{2k_v^2} \sum_l (2l+1) \int_{-1}^1 |S'_{vv}(E, \gamma)|^2 d(\cos\gamma) \quad (4)$$

can be evaluated.

This computational approach shows an obvious potential temporal parallelism. In fact, the expansion of the wavefunction in terms of products of other functions, transforms the calculation mainly into a sequence of matrix manipulations. The spatial potential parallelism of this approach is also apparent. In section A, the calculation of sector one-dimensional eigenfunctions $\phi'_{\lambda, v}(r_\lambda; R_\lambda, \gamma_\lambda)$ can be considered as a convenient *independent computational task* (ICT). In section B, a suitable ICT can be identified in the fixed γ , single E and l propagation of the solution of Eq. (2). The ICT of section B is the most computationally demanding part of the program. For a single energy, single angle and 50 l values run (50 l values are the typical number of partial waves for a low energy scattering calculation of a fairly heavy system) section B accounts for about 80% of the computing time while section A for about 10%. Each process, in fact, performs the propagation of the solution through all sectors from the origin to the asymptotes. For reactions like Li + HCl the number of sectors is, in general, quite large (being of the order of a few hundred). This is due to the fact that, because of the asymmetry and structure of the interaction, the potential extends to quite long range while the width of the sector has to be taken small enough to fulfill the assumptions made to simplify the propagation procedure [40, 41].

Production runs were performed on an IBM 3090/400 VF. On this machine, after maximizing the vector speedup by rearranging indices of some DO loops, restructuring the potential energy routine [42, 43] and adopting the vector version of the library routines [44, 45], the evaluation of a single angle, single energy, 50 l cross section values using an expansion basis set of dimension 15, needed a cpu time of 287 s for a single processor vector calculation. The restructuring for exploiting the spatial parallelism was carried out by making use of the Parallel Fortran (PF) compiler [46] and the MVS/XA [47] operating system. The number of processors to be mapped as MVS/XA tasks can be defined as a running time option and therefore chosen by the user. The compiler can take direct care of the implicit parallelism. As an alternative, the user can insert parallelizing compiler directives defined as extensions of the Fortran language to force explicit parallelism.

For the section B of the program (restructured as a single routine CSL) three processors were used for production runs and an equal number of parallel processes were generated. At the end of each batch of three processes, synchronization was invoked. This gave us the possibility of testing the convergence of the calculated cross section on a small ensemble of partial wave contributions and to prevent the possibility that an occasionally small partial wave contribution to the cross section is interpreted by the program as a reached convergence. At the same time, being the computing time needed to perform the propagation slowly varying with l , negligible load unbalance was introduced.

An appropriate quantity for measuring the performance of a parallel calculation is the overall time needed to end the job (elapsed time). The speedup is then defined as the ratio between the elapsed time measured when running the job on a single processor and that for a run with more than one processor. In our case, the single energy, single angle, 50 l case gave a speedup of 1.5 and 1.9 when running on two and three processors, respectively.

3. RIOSA cross sections

The Li + HCl reaction can be considered as a suitable prototype of non collinearly dominated three different atoms reactive systems. For this reaction, a first potential energy surface [48] was proposed by Shapiro et al. as a result of a DIM [49, 50] investigation of the alkaline atom hydrogen halides systems [48, 51]. This surface has a collinear barrier to reaction of 12 kcal/mol. A collinear quantum investigation [52] of the reactive properties showed this surface to be inappropriate for reproducing the scattering properties of the Li + HCl reaction. Recently, a more accurate *ab initio* calculation of the potential energy values for this reaction was carried out. For the *ab initio* potential energy surface (PES) the geometry of the transition state being highly bent and located late in the exit channel differs significantly from the DIM one. On the contrary, the height of the barrier to reaction is quite similar [53]. This is in clear contrast with the low threshold collision energy found in the scattering experiment [34]. For this reason, the barrier to reaction was lowered and two different potential energy surfaces based on Bond Order (BO) coordinates [54, 55] (BO2 [53] and BO3 [33]) were fitted to the modified *ab initio* values. However, even on the PES having the lower barrier to reaction (BO3) the agreement between calculated and measured scattering properties was not satisfactory. In fact, while more detailed properties such as product energy partitioning and product angular distributions were in substantial agreement with measured data, the absolute value of the cross section was still 4 times smaller than the one derived from the crossed molecular beam measurement. In more recent times, rate constant values for Li reacting with HCl in its ground vibrational state and temperatures in the range 700 K–900 K were measured [56]. Quasiclassical rate constants calculated on the BO3 surface were about 50% smaller than measured ones [33].

Integral cross sections calculated using the RIOSA method are shown in Fig. 1 as a function of collision energy. The figure shows a threshold energy in agreement with experimental findings. As quasiclassical cross sections, RIOSA results show two different energy dependence regimes: a sudden rise at the threshold, a smooth increase at higher collision energies. The ratio between cross section values calculated at 2.9 and 9.2 kcal/mol (the two collision energies at which the most accurate experimental information is available) are in substantial

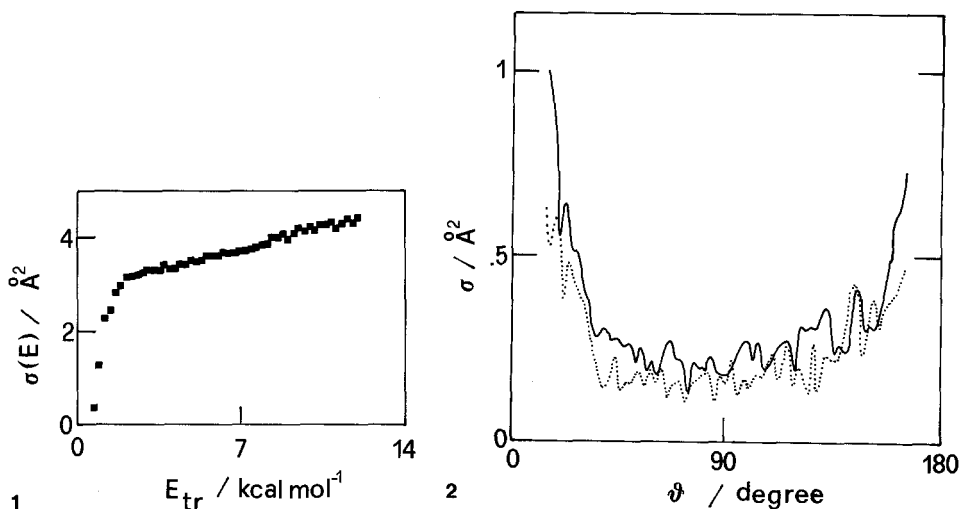


Fig. 1. Differential cross section calculated at $E_{tr} = 9.2$ kcal/mol (solid line) and $E_{tr} = 2.9$ kcal/mol (dotted line) and plotted as a function of scattering angle. Values have been normalized to the maximum of the higher energy curve

Fig. 2. Integral cross section plotted as a function of the collision energy

agreement with measurements. However, the absolute value of the calculated cross section is much smaller (about 10 times) than the measured one being even smaller than the quasiclassical result. Therefore, RIOSA results while being able to confirm the negligible role played by tunneling effects at threshold and to give an appropriate translational energy dependence of the cross section calculated on the BO3 potential energy surface, are unable to provide a quantitative estimate of its absolute value. However, as evidenced in previous investigations [57], this is not uncommon in RIOSA studies and is currently under investigation. It is also worth noticing, at this point, that the differential cross section calculated at $E_{tr} = 9.2$ kcal/mol (solid line of Fig. 2) and 2.9 kcal/mol (dotted line of Fig. 2) are in the same kind of agreement with the experiment as quasiclassical results (a clear forward distribution increasing with the collision energy). This suggests that it may be useful to spend part of the time gained by parallelizing the code to further improve the RIOSA method.

4. Distributed memory parallel restructuring

Parallel restructuring for distributed memory architectures is being carried out on a Meiko Computing Surface. While a detailed report of the work done for designing a parallel computational strategy for the RIOSA code will be given elsewhere [58], here preliminary results will be discussed. Main features of the Computing Surface machine used for restructuring the RIOSA code are: The machine has an extensible network of computing elements. Each computing element is endowed with a 25 MHz transputer processor T800, a 4 Mbyte local memory and 4 full duplex links. The computing speed of the processor is 6 Mips and 1.5 Mflops. Communications to the System Supervisor and the management of the network are taken by intelligent interfaces.

A task farm model of cooperation consisting of a master program running on one processor and controlling a set of identical worker processors all executing the fixed angle, single energy and single l propagation was adopted to structure the program for a distributed memory environment. In practice, after completing section A of the program on the computing element running the master process, copies of the eigenvalues and of the energy-independent part of the coupling matrix elements are forwarded to the worker nodes. After receiving this information each worker node starts running section B of the code. As a result of the restructuring work, a fixed collision angle, single energy and single l cross section calculated by propagating over 300 sectors took an average time of 25 s (on a single node).

Further restructuring work was then carried out along two directions: reduce communications and improve the load balance. Communication times were improved by separating input constants (to be transferred to worker processors only once for each collision angle) from those specifying the initial conditions of individual propagation runs. Because of the large quantity of data to be transferred only once for each collision angle, (these are the values of the coupling matrix elements of all the propagation sectors) this saved about 25% of the computer time. The load balance was improved by following the same criterion adopted for trajectory calculations [59]. After issuing at the beginning the first batch of calculations to all processors, subsequent parallel processes were activated every time a worker processor ends the running process. This implied a restructuring of the procedure devoted to the check of the convergence of the calculated cross section with l . The speedup achieved for section B was quite close to the number of available worker processors (1.93, 3.81, and 6.68 for 2, 4, and 7 processors, respectively) indicating a high scalability of the application.

5. Conclusions

The aim of our study was to investigate whether the implementing of approximate 3D quantum reactive scattering codes on a parallel machine was a suitable way for reducing the computer time to the point of routinely using these computational procedures for the theoretical investigation of three different atom systems. Our efforts have been focussed on the RIOSA computational procedure. To achieve a large speedup, use was made of both vector and multiprocessor features of the shared memory architecture of an IBM 3090/400 VF. Being the quantum program based on matrix manipulations, vectorization led to a significant speedup thanks also to the fact that the potential energy surface was functionally represented as a polynomial of exponentials and that the wavefunctions were given as vectors of thousand elements. The speedup gained on a shared memory few processor machine has allowed us to carry out an extensive calculation of the reactive cross section of the $\text{Li} + \text{HCl}$ reaction to test some dynamical assumptions made in the past to simplify scattering calculations. Parallelism also proved to be efficient at coarse grain level by leading to high speedup when running in parallel the propagation section for different l values. Additional effort was paid for implementing the program on a distributed memory machine (a Meiko Computing Surface). To maximize the speedup the same parallel strategy chosen for restructuring the quasiclassical trajectory program (i.e. the distribution to the worker nodes of the computationally

independent section of the program as parallel computational tasks) was adopted. By properly reducing communication times and balancing the computing load, a speedup close to the number of available processors was obtained.

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