

A SINGLE ARRANGEMENT VARIATIONAL METHOD FOR QUANTUM MECHANICAL REACTIVE SCATTERING CALCULATIONS

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ABSTRACT

We present a variational method that reduces the formally three arrangement problem of atom-diatom molecule reactive scattering to a one arrangement problem. The method leads to a large matrix equation $AC = B$. By representing the solution on grid points selected in the physically relevant regions of the potential surface, we reduce A to a smaller, sparse and structured matrix. The sparsity and the structure of A are both exploited in gaining substantial savings in storage, and in obtaining the solutions using either iterative refinement or the Generalized Minimal Residual (GMRes) method. Either approach permits full exploitation of vector or massively parallel computer architectures. The results of applying the method to a few three-dimensional atom-diatom molecule reactions are presented.

1. INTRODUCTION

The atom-diatom molecule reactive scattering problem, $A+BC \rightarrow \text{products}$, is a complicated example of the quantum mechanical three-body problem. Many reactive scattering calculations in the recent past¹ have used three sets of mass-weighted (or mass-scaled) Jacobi coordinates,² one for each atom+diatom combination (or "arrangement"): $A+BC$, $B+AC$ and $C+AB$. The scaling of the Jacobi vectors causes the coordinates for the different arrangements to be at acute angles to each other, causing nonorthogonal overlaps between functions in the different arrangements.³ All these calculations ultimately involve the solution of a large matrix equation of the type $AC = B$ for the unknowns C . Although these calculations are impressive, it has proved to be difficult to extend such treatments to heavier atoms and molecules. The main difficulty is the sheer size of the matrix A , and the fact that

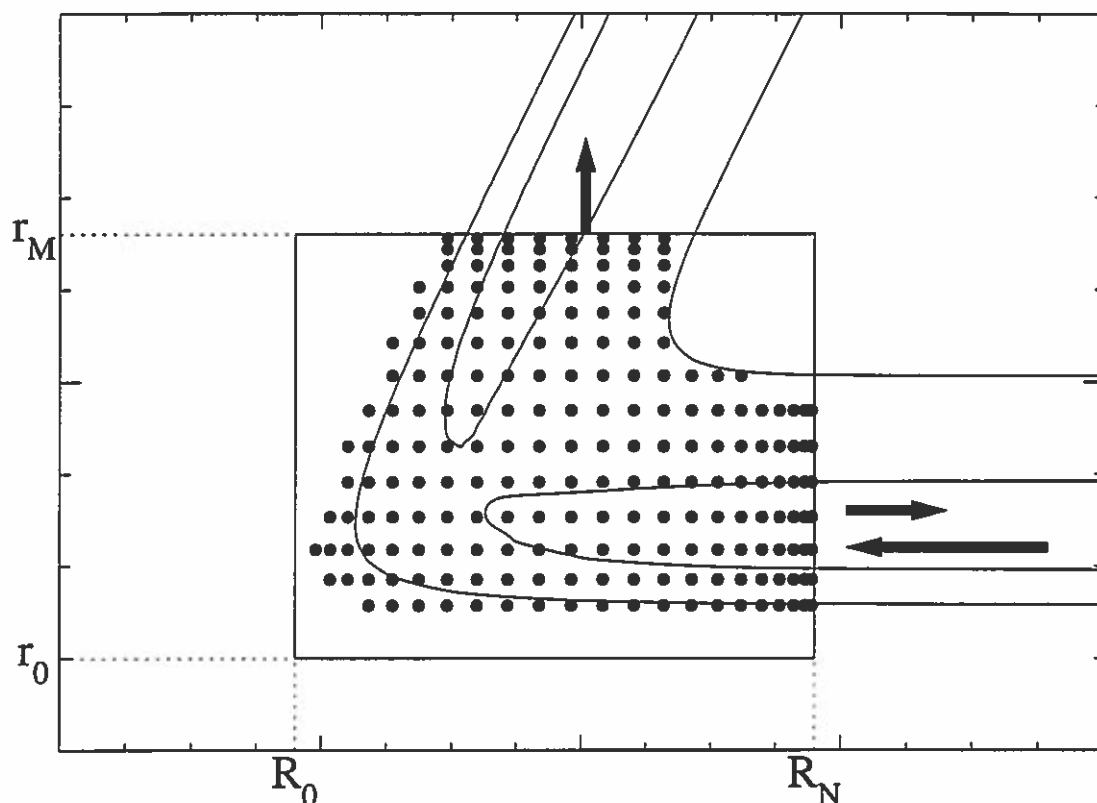


Figure 1. A schematic summary of the essential features of the method. The scattering problem is solved in the rectangular region, and the S-matrix boundary conditions are applied at $R = R_N$ and $r = r_M$ as indicated by arrows. Two contours of the potential as well as the DVR points selected by applying the energy cut-off criteria are shown.

A tends to be dense. In addition, the nonorthogonal "exchange" matrix elements in A can also lead to linear dependency for very large matrices.

This paper presents one of the many attempts⁴⁻⁶ to reduce the size of A as well as to eliminate the exchange matrix elements from it. In this method,⁶ the scattering problem is solved in a rectangular region defined in terms of mass-weighted Jacobi vectors² for the reactant arrangement (R, r) as shown in Figure 1. The Kohn variational method for the log-derivative matrix⁷⁻⁹ is used to compute the log-derivative matrix at the boundaries ($R_0, R_N; r = r_M$) and ($r_0, r_M; R = R_N$), with the gradients computed *perpendicular to the boundaries*, i.e., with respect to R at $R = R_N$ and with respect to r at $r = r_M$. The reactant vib-rotational states are found at $R = R_N$, as functions of r , while those for the products are evaluated as functions of R , at $r = r_M$. The log derivative matrix is converted to the S matrix by applying the complex incoming and outgoing wave boundary conditions⁸ at $R = R_N$ and $r = r_M$ for the reactants and products respectively, perpendicular to the boundaries. The total reaction probabilities are then found by summing the appropriate column of the reactive block of $|S|^2$. The method is admittedly approximate in nature, since the product channel boundary conditions are applied in the "wrong direction." However, in spite of this, the method yields very accurate results for a wide variety of reactions, as shown below.

2. THE MATRIX EQUATION AND ITS SOLUTION

A detailed discussion of the Kohn variational principle for the log-derivative matrix is presented in Ref. 8. For the purpose of this discussion, it is sufficient to note that the variational functional for the log-derivative Y can be written as

$$Y = Y_0 + \langle \Psi | H - E | \Psi \rangle, \quad (1)$$

where Y_0 is a "guess" for Y (see Ref. 8). The functions $\Psi^m(R, r, \gamma) = (Rr)^{-1}\psi^m(R, r, \gamma)$, where m denotes the initial state of the reactant diatomic, are solutions of

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2} - \frac{\hat{L}^2}{R^2} - \frac{\hat{j}^2}{r^2} \right) \psi^m + V(R, r, \gamma) \psi^m = E \psi^m, \quad (2)$$

where (R, r, γ) are the mass-weighted Jacobi coordinates for the reactant arrangement, \hat{L}^2 and \hat{j}^2 are respectively, the operators for orbital and rotational angular momenta, $V(R, r, \gamma)$ is the Born-Oppenheimer potential for nuclear motion,¹⁰ and E is the scattering energy. The functions $\psi^m(R, r, \gamma)$ are expanded in the rectangular region of Fig. 1 (with $0 \leq \gamma \leq \pi$) as

$$\psi^m(R, r, \gamma) = \sum_{i=1}^N \sum_{k=1}^M \sum_{j,l}^{j_{\max}} u_i(R) v_k(r) Y_{j,l}^{JM}(\gamma) C_{ikjl}^{JM}. \quad (3)$$

The rules of angular momentum coupling² dictate that the values of J and j above determine the allowed values of l . For the applications discussed here, we set $J=0$, and $j=0, 1, \dots, j_{\max}$. We now define a grid in the rectangular region of Fig. 1 by picking a set of points $\{R_n\}$ along R and $\{r_m\}$ along r . The functions u_i and v_k are chosen⁶ to generate a "discrete variable representation" (or DVR)¹¹ of the solution on this grid. These functions satisfy the Kroenecker delta conditions $u_i(R_n) = \delta_{in}$, $v_k(r_m) = \delta_{km}$ etc., on the grid. Substitution of this DVR into the variational functional, followed by extremization of the functional with respect to the expansion coefficients C_{ikjl}^{JM} , results in a system of linear algebraic equations

$$AC = B \quad (4)$$

to be solved for the coefficients C . The order of A is given by NMj_{\max} which tends to be a very large number. We reduce the size of this matrix by rejecting all points (R_n, r_m) that lie in regions where $V(R, r, \gamma_0)$ is higher than a certain cut-off value. The points (R_n, r_m) thus selected are also shown in Fig. 1, along with the contours of the potential.

The resulting matrix A , thanks to the Kroenecker delta properties of the DVR, is a very sparse, structured matrix. The largest matrix elements are concentrated along the diagonal, the great majority of the nonzero elements are concentrated in blocks along the diagonal, and the remaining nonzero elements, which become successively smaller as one moves away from the diagonal, occur in "stripes" parallel to the diagonal. This suggests substantial savings in memory for storing A , and also that the problem of Eq. (4) is ideally suited for solution by the several iterative methods available today,¹²⁻¹⁴ which do not require the full matrix to be stored in memory. In our applications of the method, we have used two iterative methods to solve Eq.(4), both designed to take full advantage of the structured sparsity of A , as described below.

2.1 Iterative Refinement

We write matrix A as $A = P+Q$, where P contains the diagonal blocks of A , and Q contains the off-diagonal "stripes." This can be solved iteratively as

$$PC_n = B - QC_{n-1}, \quad (5)$$

where C_0 , the first "guess" is obtained by setting $Q = 0$. The advantages of this approach are the following. Firstly, the blocks that make up P can be stored as separate, smaller matrices, and the stripes in Q can be stored as vectors, resulting in tremendous savings in memory. Secondly, the iterative scheme of Eq.(5) involves only one LU decomposition, followed by a series of matrix-vector multiplications. Both steps, especially the latter, are highly suitable for achieving high speeds on vector and parallel computers.

2.2 The Generalized Minimal Residual (GMRes) Method

This is an implementation of the Generalized Minimal Residual (GMRes) method of Saad and Schultz.¹³ When applied to a linear algebraic problem $Ac = b$, the GMRes algorithm begins with an initial solution vector c_0 , and generates the corresponding residual vector $r_0 = b - Ac_0$. At each iteration n , a correction z_n is determined in the Krylov subspace spanned by the vectors $\{r_0, Ar_0, \dots, A^{n-1}r_0\}$ so as to minimize the Euclidean norm of the residual $r_n = b - Ac_n$, where $c_n = c_0 + z_n$. The residual r_n is a non-increasing function of n , and in fact, the solution is guaranteed to converge within N iterations, where N is the order of A .

One way to accelerate the convergence is to "precondition" the system of equations so that the initial vector c_0 contains a substantial amount of information regarding the physical nature of the problem.¹⁴ For the systems considered here, we choose the preconditioned system of equations to be

$$(P^{-1}A)C = P^{-1}B, \quad (6)$$

where, as noted above, P is relatively easy to invert because of its block-diagonal structure. The faster convergence in this case is expected from the fact that as P tends to A , Eq.(6) converges in a single iteration. In actual applications, rather than explicitly use $P^{-1}A$, one generates the preconditioned Krylov subspace by a sequence of operations of the type $s = Ar$, $t = P^{-1}s$. Once again, the vector or parallel architectures of the computing platforms can be fully exploited for the matrix-vector multiplications involved at each step.¹⁵

3. APPLICATIONS

We present the results of applying the method described above to three simple reactions with $J = 0$, viz., the $D+H_2$, $H+D_2$ and the $F+H_2$ reactions. The total reaction probabilities can be seen to be accurate over a wide range of scattering energies, even in the case of the $F+H_2$ reaction, which has a sharp (mass-weighted) angle between the reactant and product arrangements. An extension of the present method to calculate state-to-state reaction probabilities has already been implemented.¹⁶ As expected from the preceding discussion, the convergence of the GMRes method is considerably aided and accelerated by preconditioning the linear system of equations.

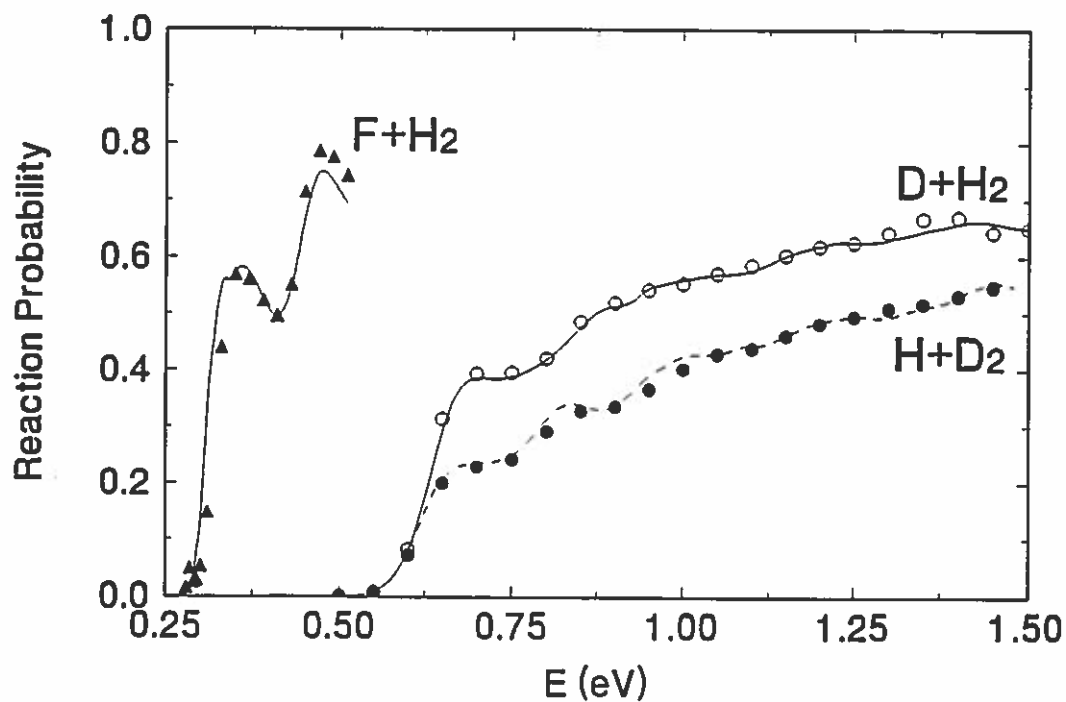


Figure 2. The total reaction probability from the ground state of the reactant molecule for three reactions with $J = 0$. The lines represent the results of the present method, and the symbols the exact results from literature.

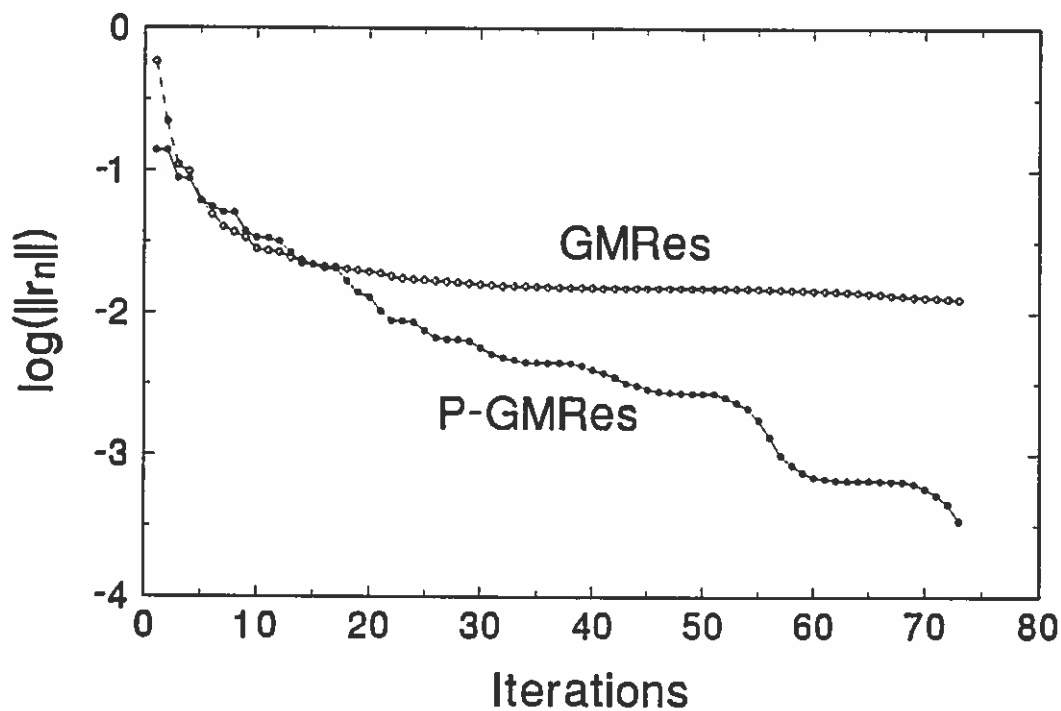


Figure 3. The norm of the residual vector for the $F+H_2$ reaction at $E = 0.37$ eV plotted against the number of iterations for GMRes without preconditioning, and with preconditioning (P-GMRes).

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REFERENCES

1. Recent reviews are (a) D.E. Manolopoulos and D.C. Clary, *Annu. Rep. C (R. Soc. Chem.)* **86**, 95 (1989); (b) W.H. Miller, *Annu. Rev. Phys. Chem.* **41**, 245 (1990).
2. For example, see J.Z.H. Zhang, D.J. Kouri, K. Haug, D.W. Schwenke, Y. Shima and D.G. Truhlar, *J. Chem. Phys.* **88**, 2492 (1988).
3. W.H. Miller, *J. Chem. Phys.* **50**, 407 (1969).
4. D. Neuhauser and M. Baer, *J. Chem. Phys.* **92**, 3419 (1990); D. Neuhauser and M. Baer, *J. Phys. Chem.* **94**, 185 (1990); D. Neuhauser, M. Baer and D.J. Kouri, *J. Chem. Phys.* **93**, 2499 (1990); D. Neuhauser, *J. Chem. Phys.* **93**, 7836 (1990); M. Baer, D. Neuhauser and Y. Oreg, *J. Chem. Phys. Faraday Trans.* **86**, 1721 (1990); I. Last, D. Neuhauser and M. Baer *J. Chem. Phys.* **96**, 2017 (1992).
5. T. Seideman and W.H. Miller, *J. Chem. Phys.* **96**, 4412 (1992); **97**, 2499 (1992); S.M. Auerbach and W.H. Miller, *J. Chem. Phys.* **98**, 6917 (1993); P. Saalfrank and W.H. Miller, *J. Chem. Phys.* **98**, 9040 (1993); W.H. Miller, *Acc. Chem. Res.* **26**, 174 (1993); W.H. Thompson and W.H. Miller, *Chem. Phys. Lett.* **206**, 123 (1993).
6. X. Wu, B. Ramachandran and R.E. Wyatt, *Chem. Phys. Lett.* **214**, 118 (1993).
7. D.E. Manolopoulos and R.E. Wyatt, *Chem. Phys. Lett.* **152**, 23 (1988); **159**, 123 (1989).
8. D.E. Manolopoulos, M. D'Mello and R.E. Wyatt, *J. Chem. Phys.* **91**, 6096 (1990).
9. D.E. Manolopoulos, M. D'Mello and R.E. Wyatt, *J. Chem. Phys.* **93**, 403 (1990); M. D'Mello, D.E. Manolopoulos and R.E. Wyatt, *Chem. Phys. Lett.* **168**, 113 (1990); *J. Chem. Phys.* **94**, 5985 (1991).
10. See for example, K.D. Lawley (Editor), *Potential Energy Surfaces*, Wiley, New York, 1980; D.G. Truhlar (Editor), *Potential Energy Surfaces and Dynamics Calculations*, Plenum, New York, 1981; J.N. Murrell, S. Carter, S.C. Farantos, P. Huxley, and A. Varandas, *Molecular Potential Energy Functions*, Wiley, New York, 1984.
11. J.V. Lill, G.A. Parker and J.C. Light, *Chem. Phys. Lett.* **89**, 483 (1983); J.C. Light, I.P. Hamilton and J.V. Lill, *J. Chem. Phys.* **82**, 1400 (1985); Z. Bacic and J.C. Light, *ibid.*, **85**, 4594 (1986); **86**, 3065 (1987); R.M. Whitnell and J.C. Light, *ibid.*, **90**, 1774 (1989); S.E. Choi and J.C. Light, *ibid.*, **92**, 2129 (1990).
12. For example, see C. Duneczky, R.E. Wyatt, D. Chatfield, K. Haug, D.W. Schwenke, D.G. Truhlar, Y. Sun and D.J. Kouri, *Comput. Phys. Commun.* **53**, 357 (1989).
13. Y. Saad and M.H. Schultz, *SIAM J. Sci. Stat. Comput.* **7**, 856 (1986).
14. D.E. Manolopoulos, R.E. Wyatt and D.C. Clary, *J. Chem. Soc. Faraday Trans.* **86**, 1641 (1990).
15. J.M. Ortega and R.G. Voigt, *SIAM Rev.* **27**, 149 (1985); J.M. Ortega, *Introduction to Parallel and Vector Solution of Linear Systems*, Plenum, New York, 1988.
16. B. Ramachandran, X. Wu and R.E. Wyatt, manuscript in preparation.