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COMMUNICATIONS

Three-dimensional quantum mechanical reactive scattering using symmetrized hyperspherical coordinates^{a)}

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We report here the first three-dimensional (3D) reactive scattering calculations using symmetrized hyperspherical coordinates (SHC). They show that the 3D local hyperspherical surface function basis set leads to a very efficient computational scheme which should permit accurate reactive scattering calculations to be performed for a significantly larger number of systems than has heretofore been possible.

Approximately ten years ago the first accurate differential¹ and integral¹⁻³ cross section calculations for the 3D $H + H_2$ exchange reaction were reported. One of the methods¹ involved matching the solutions of the Schrödinger equation obtained for each of the three arrangement channel regions across half-planes in an internal configuration space separating those regions. The application of this method to less symmetric systems requires an excessive number of channels for satisfactory convergence. There have been no accurate 3D reactive scattering cross section calculations, involving competition among three arrangement channels,⁴ reported since.

At about the same time, a system of SHC was developed.⁵ Their usefulness in performing accurate and approximate 3D reactive scattering calculations was suggested,⁵ and an appropriate computation methodology was outlined.⁶ These coordinates are related to others introduced previously,⁷ and are defined as follows. Let A, B, and C be three atoms, and \mathbf{R}_α and \mathbf{r}_α the mass scaled⁸ vectors from the center of mass of BC to A and from B to C. We now define the hyperradius $\rho = (R_\alpha^2 + r_\alpha^2)^{1/2}$ and the hyperangle $\omega_\alpha = 2 \tan^{-1}(r_\alpha/R_\alpha)$ in the 0 to π range. The factor of 2 in this definition is very important for symmetrizing the coordinates.⁵ The body-fixed SHC are ρ , ω_α , θ_α , ϕ_α , γ_α , and ψ_α , where θ_α , ϕ_α are the space-fixed polar angles of \mathbf{R}_α and γ_α , ψ_α the corresponding angles of \mathbf{r}_α in a body-fixed frame whose polar axis is \mathbf{R}_α .

In these SHC, the 6D Hamiltonian H can be written as the sum of a hyperradial kinetic energy operator $T(\rho)$ and a

hyperangular Hamiltonian $H(\mathbf{w}_\alpha; \rho)$ which operates on the five angles $\mathbf{w}_\alpha \equiv (\omega_\alpha, \theta_\alpha, \phi_\alpha, \gamma_\alpha, \psi_\alpha)$. The eigenfunctions of H , called local hyperspherical surface functions (LHSF), form a complete discrete orthonormal basis set which spans the 5D hyperangular space defined by \mathbf{w}_α , for each value of ρ . They sample all regions of configuration space and, as $\rho \rightarrow \infty$, are related in a simple way to the isolated AB, BC, and CA diatom eigenfunctions. As a result, they constitute a very appropriate basis set for expanding the scattering wave function. Such an expansion leads to a set of coupled ordinary differential equations in the hyperradius, whose numerical solutions, together with a simple asymptotic analysis, furnishes the standard scattering matrix.

The usefulness of these ideas has been extensively tested for a variety of collinear systems, including $H + H_2$ ⁹⁻¹¹ and $I + HI$.^{12,13} They have also been used as a tool for calculating dissociation probabilities,^{14,15} and energy partitioning among the dissociation products¹⁶ in collinear collision-induced dissociation. For collinear exchange reactions, an important feature of the surface function basis set is that it requires fewer asymptotically closed channels than do other approaches.¹⁷⁻¹⁹ The reason for this high convergence efficiency with respect to the number of vibrational states is that, in the strong interaction region, the hyperangle acts as a rapidly changing variable whereas the hyperradius acts as a slow one.²⁰

For 3D reactions, the corresponding LHSF can be expanded in the Wigner rotation functions of ϕ_α , θ_α , ψ_α ²¹ resulting in a set of coupled partial differential eigenfunction equations in the variables ω_α , γ_α . We have employed a finite element method²² to solve these equations numerically for the $H + H_2$ system and total angular momentum $J = 0$. This approach is similar to a previous one²³ which employed a different variety of hyperspherical coordinates.²⁴ We then solved the associated scattering equations, using a logarithmic derivative method,²⁵ over the total energy range 0.5–1.0 eV, for the A_1 , A_2 , and E irreducible representations of the P_3

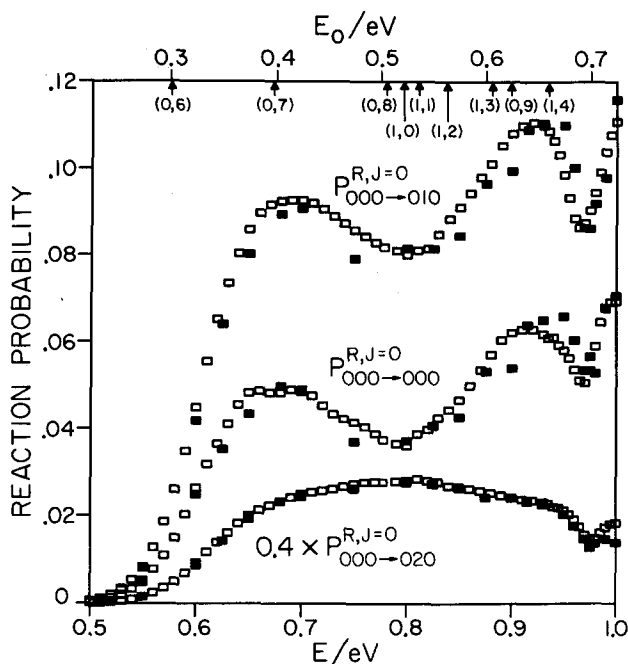


FIG. 1. Distinguishable atom $J = 0$ partial wave reaction probabilities as a function of energy for the $\text{H} + \text{H}_2(v, j, 0) \rightarrow \text{H}_2(v', j', 0)$ reaction on the Porter-Karplus potential energy surface (Ref. 29). The probabilities are denoted by the symbol $P_{v'j' \rightarrow vj}^{R, J=0}$. The lower abscissa is the total energy and the upper abscissa the reagent translational energy. The vertical arrows on the upper abscissa denote the energy at which the corresponding $\text{H}_2(v, j)$ channel opens up. The open symbols represent the present results and the full ones those of a previous calculation (Ref. 1). The $P_{000-020}^{R, J=0}$ results were multiplied by 0.4 prior to plotting.

symmetric group.²⁶ All LHSF were calculated for a grid of $40 \omega_\alpha$ and $50 \gamma_\alpha$ points. Up to 0.9 eV, $10 A_1$, $10 A_2$, and $20 E$ functions were used. Between 0.9 and 1.0 eV, where a Feshbach resonance occurs,²⁷ those numbers were increased to 14 and 28, respectively. In all these calculations, flux was conserved to 1%. With respect to basis set size, transition probabilities greater than 0.01 were converged to 5% and the corresponding phases to 2° over the entire energy range. The corresponding probabilities, within the $v = 0$ manifold, were symmetric to 2% and convergence with respect to the grid coarseness was 3% and 3° for those probabilities and phases. Including the $v = 1$ manifold, the probabilities greater than 0.01 were symmetric to 11% and convergence of those transitions with respect to grid coarseness was 10% and 15° .

From the irreducible representation scattering matrices, distinguishable atom reaction probabilities were calculated, some of which are displayed in Fig. 1, together with the results of previous calculations.¹ For energies below 0.9 eV the two methods agree to within 12% for the probabilities in this figure and 5° for the corresponding phases, which is very encouraging.

Once the LHSF and interaction matrix elements have been obtained, the solution of the scattering equations and the calculation of the scattering matrix is very efficient, taking on an FPS 164-VAX 11/780 system, about 23 s for 10 channels and about 3 min for 20 channels. This efficiency is

due in part to the absence of a matching procedure in the calculation. Instead, a simple asymptotic projection of the surface functions on the isolated diatom states is required. The surface functions themselves already span all three arrangement channels, and are energy independent.

Our finite element code for calculating the LHSF is accurate and efficient. The A_1 and A_2 functions (including the evaluation of all the interaction potential matrix elements needed for the scattering part of the calculation) required an average of only 17 s each, and the E functions utilized 34 s each. However, they were calculated at 140 values of ρ , which made their evaluation dominate the calculation, for the relatively small number of channels discussed here. A variational approach promises to be significantly faster. Recently, such a method has been developed for the $e + \text{H}$ system, which takes only about 0.3 s per surface function even for $J > 0$.²⁸ It is currently being adapted to triatomic systems and preliminary results indicate that it will speed up the calculation of the LHSF by one to two orders of magnitude.

In conclusion, the LHSF approach to 3D reactive scattering has been successfully tested and gives strong indications that it will become a powerful tool for studying the quantum dynamics of chemical reactions, which other accurate methods have so far not permitted.

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NOTES

Reflexive pair production probability study for equal spheres in a saturated random distribution in three dimensions

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Nearest neighbor distributions studies¹⁻¹¹ are of interest in physics, chemistry, metallurgy, biology, and astronomy. The purpose of this study is to determine the probability of forming reflexive pairs for nearest neighbors in three-dimensional space. The space is assumed to be filled with uniform nonpenetrating spheres which have been arranged sequentially by random means in such a way that they saturate the volume they are free to occupy, i.e., there are no interstitial spaces large enough to accommodate an extra sphere. A reflexive pair is defined as a pair of neighbors that share the property that each member of the pair is also the other member's nearest neighbor. Specifically the study investigated the relation between the coordination number as determined for reflexive pair members vs nonreflexive pair numbers.

The random distribution of the spheres was simulated by a program adapted from previous work^{12,13} simulating space saturation. The previous study determined that a saturation density of 0.709 centers per unit volume is obtained when spheres are placed randomly one after the other in three-dimensional space so that each sphere is not allowed to penetrate any previously placed sphere until no more spheres can be accommodated. This also implies that none of the spheres are touching.

The probability of reflexive pair formation for random points (i.e., volumeless spheres) in n dimensions is given by¹⁴⁻¹⁶ as

$$P = \frac{4n}{n+1} + \frac{2}{(n-1)\pi^{1/2}} \left(\frac{3^{1/2}}{2}\right)^{n-1} \frac{\Gamma\{n-2\}}{\Gamma\{(n-1)/2\}}.$$

For $n = 3$ this yields $16/27 = 0.5926$. The probability of reflexive pair formation is not known for cases of random distributions of entities other than points. When the entities possess a volume themselves it becomes too difficult to calculate the pair formation probabilities.

This study does a random computer simulation of 103 cases of random distributions of equal spheres. Each distribution is carried to the point of saturation, i.e., approximately 0.709 sphere centers per unit volume. The distributions were done for a basic volume of a $5 \times 5 \times 5$ unit diameters cube where boundary corrections were done by standard replication simulation of basic cubes in a cubic array in three dimensions. Saturation is ensured by inspecting the distribution for interstitial spaces large enough to accommodate an additional sphere. Such a space was then filled by generating random coordinates for the center of an extra sphere within the space. The process was continued until no more voids were found. The average saturation density found was 0.704 ± 0.007 for the 103 cases. This value agrees well with the previous work just cited. The distribution is then checked for reflexive pair density. The reflexive pair membership probability for any given sphere was found to be 0.517 ± 0.004 for the 4679 pair members identified in a total of 9059 spheres studied. In addition, averages were found for three separate distances. These were the nearest first neighbor distances of reflexive pairs, all pairs, and nonreflexive pairs. These values are, respectively, 1.015, 1.030, and 1.044 sphere diameters.

A determination of coordination number for a smaller sample of reflexive pair members vs nonreflexive pair members gave results similar to the results indicated in Fig.