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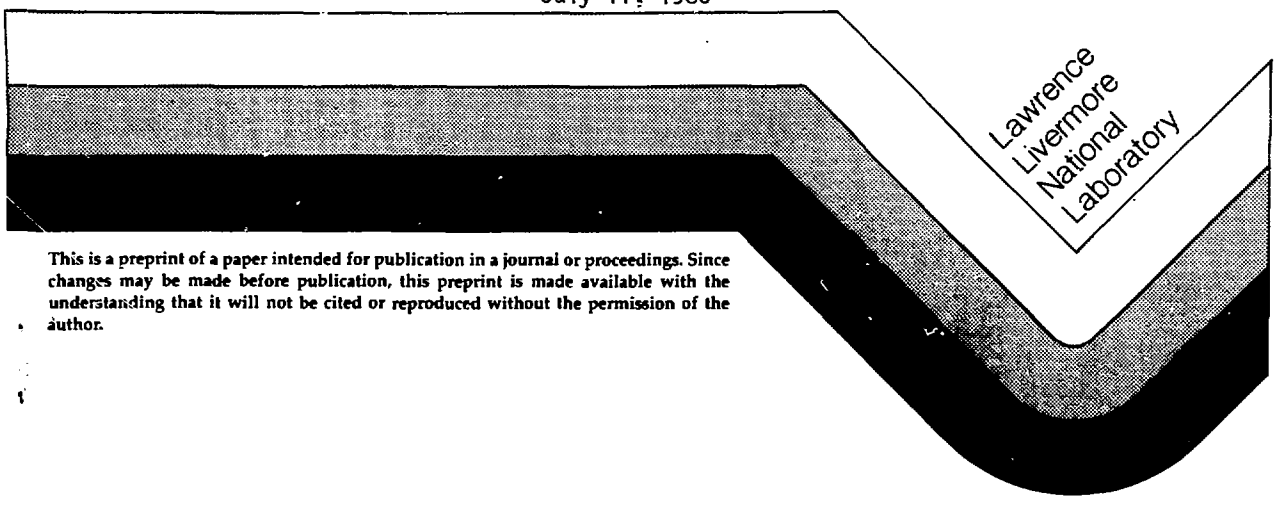

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Reaction Rate Calculations via Transmission Coefficients

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Abstract

The transmission coefficient of a wavepacket traversing a potential barrier can be determined by steady state calculations carried out in imaginary time instead of by real time dynamical calculations. The general argument is verified for the Eckart barrier potential by a comparison of transmission coefficients calculated from real and imaginary time solutions of the Schroedinger equation. The correspondence demonstrated here allows a formulation for the reaction rate that avoids difficulties due to both rare events and explicitly time dependent calculations.

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1. *INTRODUCTION*

The calculation of thermal average reaction rates is a formidable task, requiring, in principle, the solution of a time dependent quantum many body problem involving nuclei and electrons. Such calculations are completely intractable in a practical sense. The theory is simplified by tacitly ignoring all dynamical correlations between the reacting atoms and introducing a Born-Oppenheimer potential surface to describe the motion of the nuclei in the average field of the electrons. This itself entails the solution of an equilibrium quantum many body problem in which the nuclei are held fixed. Assuming the validity of such an adiabatic potential surface (despite the fact that the best known potentials contain the light element hydrogen for which the approximation is least applicable), the rate problem can be formulated in terms of an S matrix linking the reactant and product states. The rate calculation via the S matrix is still an extremely difficult calculation; furthermore all the detailed information about intermediate states is finally thrown away when the thermal averaging is carried out.

The simple reaction rate theory [1] eliminates the need for such time dependent calculations by assuming equilibration along the reaction path. This assumption reduces the time dependent aspect of the rate calculation to a determination, for the given physical situation, of how many reactants attempt to scale the potential barrier per unit time or the flux of such particles. This flux is then related to the reactive flux across the barrier by a Boltzmann factor.

The final step in completing a rate calculation in this model is the determination of the relative probabilities of the system ending up in the reactant or various product channels given that the initial flux was crossing

the phase space surface dividing reactants from products. From these probabilities, the so-called conversion coefficient or transmission coefficient can be calculated.

The essential point we wish to make here is that this conversion coefficient, which accounts for multiple crossings of the dividing surface and tunneling, need not be obtained from a dynamic calculation. It should be obtainable from a steady state quantum Monte Carlo calculation. Not only are such calculations easier than time dependent calculations, they can readily be extended to multidimensional situations.

The physical reason steady state calculations should suffice is simply that at long times the relative probabilities in the various channels are time independent. After the reaction is over, the products and reactants are far removed from the potential barrier and can be considered as "free" particles. With increasing time, their wave functions spread and become more plane wave like as the particle moves down a channel; however, the net probability in a given channel remains invariant.

The method proposed here is analogous to the well established classical picture of reaction rates. In that picture, a particle confined to the top of the barrier, selected from an equilibrium distribution, is released and monitored to determine where it ends up. Starting such particles at the top of the barrier overcomes the difficulty of looking for rare events. An average over many initial releases determines the conversion coefficient.

Alternatively, one could have dynamically followed a particle at the top of the barrier with an initial velocity selected from a thermal distribution and calculated a velocity-velocity autocorrelation function by averaging over many different initial velocities. The time integral of the autocorrelation

function directly measures the conversion factor since it is proportional to the probability of ending up in a given channel. Calculations of such time dependent flux-flux autocorrelation functions quantum mechanically in many dimensional systems have not been possible. Recently such flux autocorrelation functions have, however, been calculated numerically in "imaginary time" since that involves only an equilibrium calculation [2]. To obtain the real time autocorrelation function, one is then faced with an uncertain extrapolation from imaginary to real time behavior, i.e., numerical analytic continuation. The present work shows that such analytic continuation is unnecessary. The equivalence of a real time dynamic calculation with a steady state calculation of the flux is demonstrated in a one dimensional example.

2. FORMALISM

The formal equivalence of these different approaches is easily demonstrated from the definition of the transmission coefficient as the temporal integral of the probability flux into the product space normalized by the total probability. It is from the direct calculation of the probability flux according to the above definition that we obtain the transmission coefficient. The connection between such a real time calculation of the probability flux and the corresponding imaginary time one will be made by noting that at long times the behavior in both cases is dominated by small energy splittings. The connection is made quantitative by accounting for the non-conservation of probability in imaginary time calculations by scaling the steady state calculation by a factor corresponding to the weight of the

outgoing final state present in the initial wavepacket.

To define the transmission coefficient, consider a simple wavepacket initially located on the transition surface and having an initial velocity v along the reaction coordinate. The transition surface is defined here as passing through the saddle point, and otherwise being everywhere normal to equipotentials. In the case of multiple product channels, we assume the product space can be divided into parts associated with each product separately. This should cause no practical difficulty. The transmission coefficient is calculated directly by integrating the Schroedinger equation of motion

$$(2.1) \qquad i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi$$

until there is no longer any change in the division of probability between the reactant and product channels. The probability density $\rho = \psi^* \psi$ obeys the continuity equation

$$(2.2) \qquad \frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J} = 0 \quad ,$$

where the probability current density J is given by

$$(2.3) \qquad \vec{J} = \frac{\hbar}{2im} \left(\psi^* \nabla \psi - \psi \nabla \psi^*\right) \quad .$$

If we call f the amount of probability in the product space (p.s.), it follows that

$$(2.4) \qquad \frac{df}{dt} = \int_{p.s.} \frac{\partial p}{\partial t}\, dV = -\int_{p.s.} \nabla \cdot J dV = -\int_{n} J\, dA \equiv F(t) \quad ,$$

where the first two forms are integrated over the entire product space volume V. Green's theorem allows the volume integral to be transformed into a surface integral over the transition surface A. We define the flux F(t) as the probability per unit time flowing across the transition surface into the product space, noting that f changes because of this probability flow. The transmission coefficient τ is defined as the normalized increase of probability in the product space in the long time limit, i.e.

$$(2.5) \qquad \tau = f(t)-f(0) = \int_{0}^{t} F(t')dt' \quad .$$

A wavepacket with initial flux F(0) then contributes τ F(0) to the reactive flux $\mathscr{F}$. The rate k equals the thermal average reactive flux $\langle \mathscr{F} \rangle$ times a Boltzmann factor $\exp(-V_0/kT)$, where V_0 is the barrier height. The equivalence between the flux autocorrelation function expression for the rate and the transmission coefficient expression used in the present work is shown by writing the reactive flux as

$$(2.6) \qquad \langle \mathscr{F} \rangle = \langle \tau F(0) \rangle = \int_{0}^{t} dt' \langle F(t')F(0) \rangle \quad ,$$

where we have interchanged the temporal and ensemble averaging, which is permitted at equilibrium. Thus, the thermal average of the net reactive flux, taken as the initial flux times a transmission coefficient, can be rewritten as the temporal integral of a thermally averaged flux-flux autocorrelation function.

The equivalence between real and imaginary time calculations of the transmission coefficient is established by first noting that at long times the probability in each channel becomes time independent. Then it is shown that the ultimate steady state division of probability between the channels depends, in both real and imaginary time, on the energy splitting of the lowest energy states.

In practice, the system can be considered to be confined to a "box" of side L and the steady state result is reached when the wavepackets are well removed from the potential barrier, but have not reached the boundaries of the box. The use of wavepackets in a finite size "box" should be acceptable provided the box is large compared to the scale size of the potential barrier. It can be shown that the total flux is independent of L since the flux is proportional to the energy splitting, which varies as 1/L as the box gets larger, while the number of contributing states is proportional to the density of states $L/2\pi$, so the product is independent of L. The final asymptotic steady state can be considered to consist of plane waves $\exp(\pm i\, k\, x)/\sqrt{L}$ of wavenumber $k = 2\pi n/L$. The long time division of probability will be shown to depend on the energy splitting between these lowest energy plane wave states. This situation is entirely analogous to the transfer of probability between two states coupled through a potential energy barrier [3]; the rate of transfer is proportional to the energy splitting

between the states and the amount transferred depends on an overlap integral. The main difference is that in the double potential well an equilibrium distribution is established while here a steady state is reached.

The flux across the potential barrier in a box can be written in terms of energy differences by expressing ψ as a linear combination of eigenstates u_ℓ

$$(2.7) \qquad \psi = \sum_\ell A_\ell \, U_\ell(r) \exp(-iE_\ell t/\hbar) \quad ,$$

with expansion coefficients A_ℓ. We use the definition of the flux F(t) given in Eq. (2.4), and substitute $H\psi$ for $i\hbar \, d\psi/dt$ to find

$$(2.8) \qquad F(t) = \int_{p.s.} \frac{\partial}{\partial t} (\psi^*\psi) dV = \frac{1}{i\hbar} \int_{p.s.} (\psi^* H\psi - \psi H\psi^*) dV \quad ,$$

with H the Hamiltonian operator of Eq. (2.1). Thus, the eigenfunction expansion yields

$$(2.9) \qquad F(t) = \sum_{\ell,m} A_\ell^* A_m \left[\int_{p.s.} U_\ell^* U_m dV\right] \left(\frac{E_m - E_\ell}{i\hbar}\right) \exp(-[E_m - E_\ell]t/\hbar) \quad .$$

This expresses the flux as a sum of terms, each of which is proportional to an overlap integral over the product space, and to an energy difference. At long times, the different cosine and sine terms representing the exponential of imaginary argument dephase from each other and F(t) vanishes. Thus, the total

probability, given by the time integral of F(t) in the product space, becomes time independent.

$$(2.10) \qquad \int_0^t F(t')dt' = \sum_{\ell,m} A_\ell^* A_m \left[\int_{p.s.} U_\ell^* U_m dV\right] \exp\left(-i[E_m - E_\ell]t/\hbar\right) - 1) \quad .$$

At long times, the dominant contribution to the sum comes from the state with the smallest energy splitting (the longest dephasing time).

The crucial point is that in the imaginary time solution of the Schroedinger equation, the same eigenstates are involved as for the real time solution. The main difference is that the sinusoidal real time dependence of exp (-i Et/$\hbar$) is replaced by the decaying exponential exp (- Et/$\hbar$) in imaginary time. Again only the lowest energy states contribute at long times, all higher energy states decay faster. As a consequence of this decay, rather than cancellation a change in normalization of the wavefunction must be taken into account by projecting the final surviving state onto the initial wavepacket. That is, since only the lowest energy state survives to long times, the normalization is relative to the weight of the final state in the initial wavepacket.

3. NUMERICAL EXAMPLE-THE ECKART BARRIER

As a simple test of the ideas expressed here, we have carried out both real time and imaginary time calculations of the transmission coefficient for

a one dimensional Eckart barrier potential

$$(3.1) \qquad V(x) = V_0 \left[\mathrm{sech}^2(x/a) + e \tanh(x/a)\right] \ .$$

Here a is the width of the barrier, V_0 its height, and e is a parameter that determines the degree of asymmetry in the barrier. Both real and imaginary time solutions of the Schroedinger equation were found numerically using a split operator Fast Fourier Transform method [4] of demonstrated accuracy.

The initial wavepacket for the real time calculations consisted of a minimum uncertainty (Gaussian) wavepacket of form $\exp(-(x/\sqrt{2}s)^2)$ $\exp(imvx/\hbar)$. The width of the wavepacket was chosen so that the momentum distribution was thermal, i.e., $2s^2 = h^2/mkT$, and the initial velocity across the barrier was v. The long time fraction of probability on the product side was found from the real time solution of the Schroedinger equation with these initial conditions by using the definition of f given in Eq. (2.4). Since, by symmetry, $f(-v) = 1-f(v)$ for the symmetric barrier ($e = 0$), we report the net transmission coefficient $f(v) - f(-v) = 2f(v) - 1$ in the results for the symmetric barrier below. The corresponding initial wavepacket for imaginary time calculations is of the form $\exp(-(x/\sqrt{2}s)^2)$ $\exp(-mvx/\hbar)$, i.e., with v changed to iv, which has an initial probability gradient proportional to v.

A comparison of the real and imaginary time determinations of the transmission coefficient for a symmetric barrier is given in Fig. 1 for a set of initial velocities, and at a temperature of $kT/V_0 = 0.01$. In accordance with the formal discussion, the velocity axis for the imaginary time calculation has to be scaled or renormalized by the number of plane wave

states (Fourier components) present in the initial state relative to the single final state. In a box of side L, the plane wave states have wavenumbers separated by $2\pi/L$. Our initial Gaussian wavepacket of half-width s has k-space rms half-width $1/(\sqrt{2}\,s)$. The scaling factor is thus $2(1/\sqrt{2}s)/(2\pi/L)$ or $L/(\sqrt{2}cs)$ which equals 14.405 in the present case. This scaling was tested for several values of the parameters.

For an asymmetric barrier, account has to be taken of the fact that in the imaginary time calculation probability decays faster at long times on one side of the barrier than on the other because of the different plateau energies on the two sides. The long time probability is given by $P_L \exp(-E_L t)$ to the left and by $P_R \exp(-E_R t)$ to the right. Hence an additional renormalization of the right side probability relative to the left of $\exp[T(E_R-E_L)]$ must be applied at time T. It is also necessary to account for the fact that the initial wavefunction is slightly displaced from the saddle point. The very small shift in the saddle position due to the asymmetric term in the potential is numerically unimportant in the present case. However, the velocity dependent shift due to the form of the imaginary time initial wavepacket is significant. Unimportant for the symmetric barrier, this shift enters now because of the asymmetry in probability decay rates. The wavepacket can be considered as having started at some earlier (later) time or equivalently as starting with enhanced (decreased) probability for displacement of the initial wavepacket to the right (left). The enhanced probability is easily calculated from the fractional increase in initial probability of the displaced Gaussian $s\,mv/\hbar\sqrt{\pi}$ and applied as a multiplicative factor for the right side probability. In the present example, this adjustment is much smaller than the factor correcting for the different

plateau energies. The overall adjustment amounts to multiplying the final right side probability by a factor of 30-100 in the cases shown in Fig. 2. These corrections are in addition to the velocity renormalization of $L/(\sqrt{2\pi s})$ which still is necessary. Results for an asymmetric barrier with $e = 0.001$ are shown in Fig. (2). Again, there is a clear correspondence between real and imaginary time results.

From the correspondence demonstrated here between real time and imaginary time determinations of the transmission coefficient, we conclude that it is possible to calculate rates without recourse to time dependent computations. The correspondence found here should be extendable to higher dimensionality. In this case, one can still pick a minimum uncertainty wavepacket along the reaction coordinate, and sample the transverse coordinates from a thermal distribution. As a practical matter, such many dimensional calculations will be feasible only with a quantum Monte Carlo technique [5].

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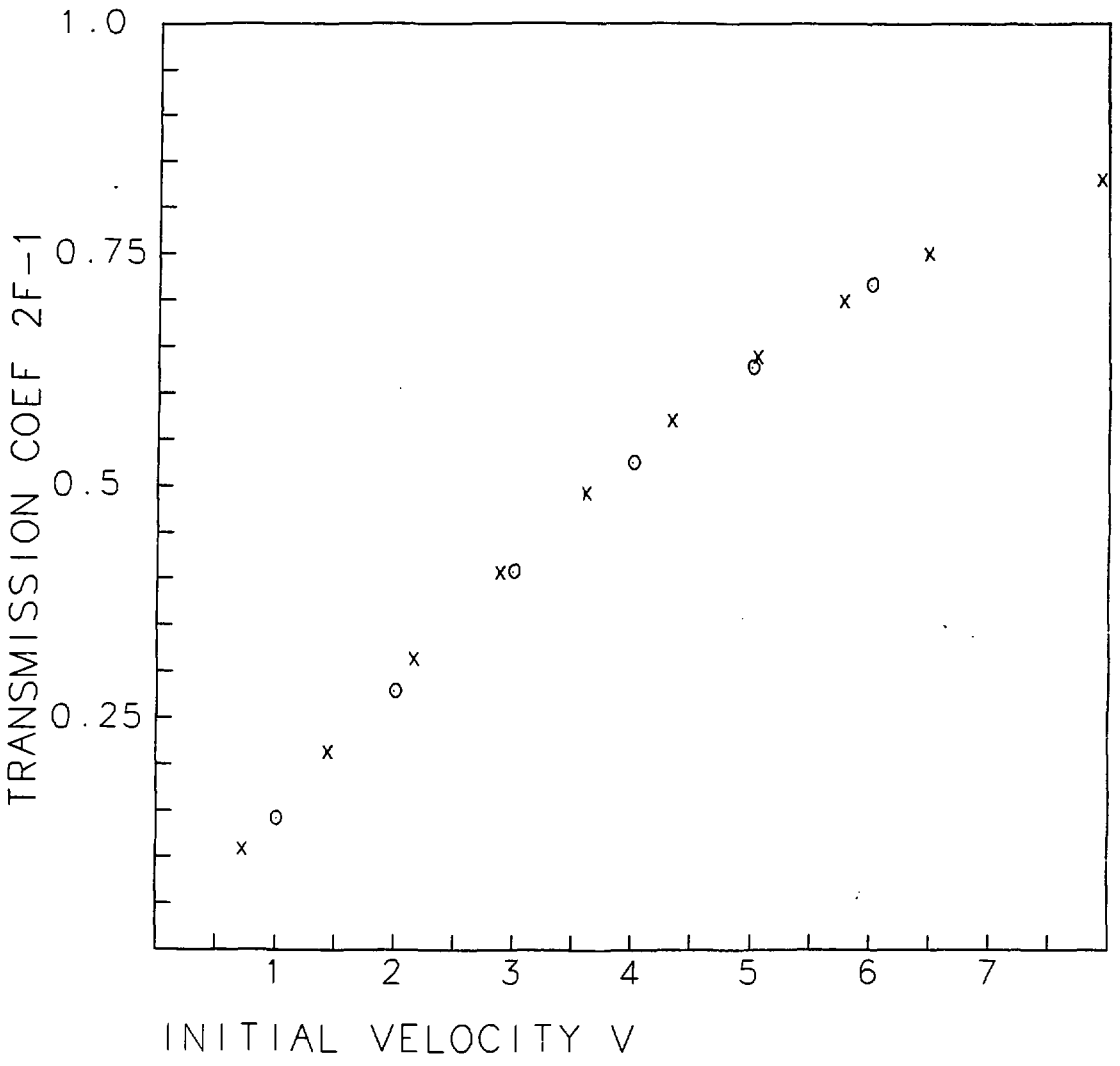
Figure captions

Fig. 1: Comparison of the real time and imaginary time calculations of the transmission coefficient 2f-1 as a function of the initial wavepacket velocity along the reaction coordinate for a symmetric Eckart potential barrier. The (o) real time calculations; (x) imaginary time calculations. The velocity is given in units of $\hbar/ma$.

Fig. 2: Comparison of real time and imaginary time calculations of f for an asymmetric Eckart barrier.



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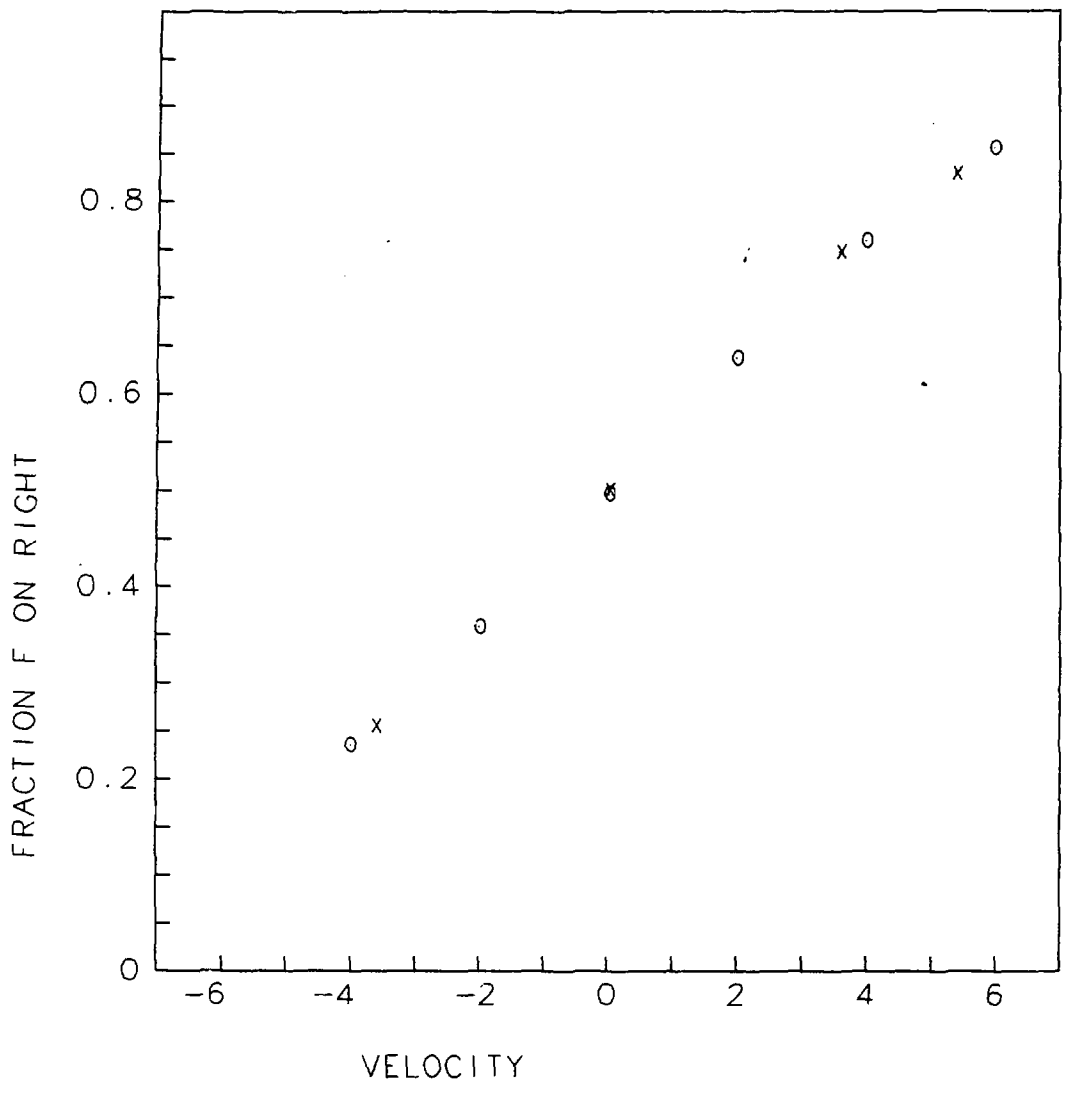

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