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ON THE CONSTRUCTION OF THE R-MATRIX FOR THREE-DIMENSIONAL, REACTIVE ATOM-DIATOM SCATTERING: APPLICATION TO $H+H_2$*†

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Abstract

In an extension of previous work (R. B. Walker, J. C. Light and A. Altenberger-Siczek, J. Chem. Phys. 64, 1166(1976)), equations for the accurate quantum mechanical treatment of three body rearrangement collisions are presented in the R-matrix language. These equations describe how the solutions to Schrodinger's equation in three separate regions of configuration space (each containing one asymptotic atom + diatom arrangement) are matched smoothly to each other. The symmetry of the matching equations is disussed in detail. Within the R-matrix formalism, we may construct unitary S-matrices for arbitrary atom-diatom mass combinations and for small target wavefunction basis expansions. Applications of this method to the three dimensional $H+H_2$ (labelled nuclei) exchange reaction are reported, and comparison is made to prior work.

I. INTRODUCTION

In a recent paper (1) (hereafter called I) we presented a general theoretical approach to the problem of atom-diatom reactive and inelastic scattering, deriving the close coupled equations to be solved for each channel, the coordinate transformations required between channels, and determining the surfaces on which solutions in various channels should be matched. Although the approach given in (I) has been followed, by and large, in implementing the actual computation, we have developed a number of significant improvements in the method. We have applied these methods to the three dimensional reactive scattering of H+HH on the Porter-Karplus surface. In this paper we shall briefly describe our approach to the problem, and some of the improvements in the methods, in particular, accurate techniques for matching which automatically preserve the unitarity of the S matrix.

The coupled equations of (I) are solved by the R-matrix propagation method (2), a fast, stable and accurate technique for integration of coupled linear second order differential equations that we recently developed. The speed of calculation is enhanced by using a "pre-contracted" vibrational basis enabling us to achieve convergence with fewer vibrational states. The vibrational basis is chosen by diagonalizing an appropriate collinear or spherically averaged interaction matrix using a convenient manifold of primitive vibrational functions (such as harmonic oscillators), enabling all integrals to be obtained analytically. Having realistic vibrational states after diagonalization, each carries its own independent rotational manifold. Thus we carry fewer rotations for the higher vibrations, again reducing the number of channels necessary for convergence of the full calculation. Further time-savings come from optimizing the basis at one energy, diagonalizing the full interaction matrix and using this diagonal basis at additional energies (2). Thus all integrals are evaluated only at the first energy.

Other advantages lie in the utilization of the symmetry properties of the R matrix. Since the channel R matrices are symmetric independent of completeness in the basis set, the S matrix for an inelastic problem is always unitary. It has been shown that matching between two channels in the collinear reactive scattering (2) also preserves the symmetry of the R matrix and hence the unitarity of the S matrix. Properties of the operators involved in the matching as opposed to properties of the finite blocks of the matrix representation of the operators are utilized and thus in both the R-matrix propagation and in the subsequent matching procedures, no orthogonalization and no symmetrization of the basis is necessary. Therefore very small basis sets can be used to achieve semiquantitative results (2).

Thus the portion of the problem involving integration of coupled equations corresponding to each chemical channel is well understood, and efficient and accurate techniques for solving this portion of the problem are available. In a general reaction, the solution of the Schroedinger equation in each of the three separate regions of configuration space corresponding to the three separate chemical arrangements ($\lambda = \alpha, \beta, \gamma$) results in three symmetric R matrices, $\underset{\sim}{R}^{\lambda}$, relating wavefunctions and derivatives at $u_\lambda = 0$ to those at $u_\lambda = \infty$, where u_λ is the channel propagation coordinate.

The problems remaining, the resolution of which we present here, are to propagate from the $u_\lambda = 0$ surfaces to the true matching surfaces that we have chosen, to show how the wavefunctions and derivatives are then matched on these surfaces by a least squares procedure, and to demonstrate that the symmetry of the global R matrix, $\underset{\sim}{R}_\gamma$, can be assured in this process even with incomplete basis sets. This assures the unitarity of the global S matrix.

We intend in the following to outline the solution to the matching region (between $u_\lambda = 0$ surfaces and the true matching surfaces) and will leave further details of this to a

future publication. We then discuss the method of matching on the true surface and the method of generating a linear system of equations for the global R matrix (that matrix relating asymptotic functions to asymptotic derivatives). This procedure produces more equations than unknowns and in general forms an over determined set. The method of generalized inverse (or least squares) is then used to solve for the R matrix in a straightforward manner which does not guarantee a symmetric R matrix solution except in the limit of complete sets. We then propose a modified least squares solution to the same set of equations which guarantees in a natural manner (as opposed to ad hoc symmetrization) a symmetric R matrix independent of the size of the basis. In the limit of complete sets both methods converge to the same result.

Based on this result and convergence properties in our collinear reactive scattering studies we assert that the calculations for $H+H_2$ reactive scattering reported here are accurate even for the "small" number of internal states used at large J. We note that for large J the rotational degeneracy makes the number of coupled states large even when the "internal" vibrational and rotational basis is small. We present here some results, mostly J = 0 calculations which are most easily converged and can be compared to prior work (3,4).

II. PROPAGATION ON THE MATCHING REGION

Since the method of solution described in paper I requires solving Schroedinger's equation separately in each of three regions of configuration space, the result is three arrangement channel R matrices, each relating wavefunctions and derivatives at $u_\lambda = 0$ and $u_\lambda = \infty$ for $\lambda = \alpha, \beta, \gamma$. The coordinate system of choice (u, v, χ) transforms smoothly between arrangement channels only for collinear geometries, i.e. the surface in configuration space defined by $u_\alpha = 0$ is tangent to $u_\beta = 0$ only when $\chi_\alpha = 0$ and $\chi_\beta = \pi$ and is tangent to $u_\gamma = 0$ only when $\chi_\alpha = \pi$ and $\chi_\gamma = 0$ (see Fig. 1). In order to match the wavefunctions and derivatives smoothly we defined in paper I appropriate real physical matching surfaces which are tangent to the $u_\lambda = 0$ surfaces for collinear geometries and which define physical boundaries between the regions of space associated with the coordinate system and expansion used in each channel. This is shown schematically in Fig. 1. Since this region between the $u = 0$ surface and the matching surface is small, away from collinear geometries, and a region of high potential for many reactions of interest, it was originally thought that the approximation of "matching" the wavefunctions and derivatives at $u = 0$ instead of the true matching surfaces would be satisfactory (at least for reactions dominated by near collinear transition states). However, this approximation lowers the threshold for reaction and it raises the reactivity across the energy spectrum for the $H+H_2$ reaction. We have tried other approximations to describe the dynamics in this region and have found that a fairly accurate treatment is necessary if we are to obtain the proper threshold and reactivity.

To obtain accurate results, the propagation must be continued from $u = 0$ through the matching region to the true matching surface. Therefore, in this section we discuss a method of propagation through this troublesome region of coordinate space.

During any propagation scheme we single out one coordinate as the "translation" coordinate which describes a continuous set of surfaces of dimension n - 1, one less than the dimension of the physical problem. We then wish to define a matrix problem in one coordinate by integrating the kinetic energy operator plus the potential in a basis on these surfaces, to yield the "interaction" matrix. If the translation coordinate is normal to these surfaces, then the kinetic energy operator separates nicely into one operator that we can associate with translation and another operator which we can associate with dynamics on the surface. This separation is obtained by having one coordinate which follows the progress of the reaction and which is orthogonal to all other coordinates. Such a coordinate system, however, may not be conveniently obtainable for any arbitrary region of space. The region between the $\upsilon = 0$ surface and the matching surface is an example where this is the case. Before now we have always allowed the single propagation coordinate which is orthogonal to all remaining coordinates to define the propagation surfaces. However, in this region of space we are forced first to define the surfaces and then let them define the propagation variable.

To this end, we define a continuous set of surfaces, beginning with the $\upsilon = 0$ surface, which distorts until the matching surface is reached (see Fig. 1). Then we choose as the translation coordinate, s, just that coordinate which is normal to these surfaces and such that each value of s defines one of these surfaces. With this definition of s, there is an associated metric coefficient $\varkappa$ (a function of all the coordinates) such that $\varkappa ds$ is the metric distance along the normal between surface s and surface s + ds. To describe the dynamics we note that the momentum at a point must be expressible as a sum of two components, one which lies entirely in the surface, $\vec{P}_s$, and another normal to the surface, $\vec{P}_n$. We use this to then express the kinetic energy as

$$T = -\frac{1}{2\mu}\vec{P}\cdot\vec{P} = -\frac{1}{2\mu}\left[\vec{P}_n\cdot\vec{P}_n + \vec{P}_s\cdot\vec{P}_s\right] \qquad (1)$$

We further define a convenient set of curvilinear coordinates on the surface $\{u^\alpha\}$, and the first fundamental form $a_{\alpha\beta}$ on the surface which describes the metric properties of the surface. With $a = \det a_{\alpha\beta}$ and $\sqrt{a}$ equal to the Jacobian on the surface and $a^{\alpha\gamma}a_{\gamma\beta} = \delta^\alpha_\beta$ (sum on γ), the Laplacian on the surface is

$$\nabla_s^2 = \frac{1}{\sqrt{a}} \frac{\partial}{\partial u^\alpha} \sqrt{a}\, a^{\alpha\beta} \frac{\partial}{\partial u^\beta} \qquad [\text{sum on } \alpha,\beta] \tag{2}$$

Then the kinetic energy operator looks like

$$T = -\frac{1}{2\mu} \cdot \frac{1}{\kappa\sqrt{a}} \left[\frac{\partial}{\partial s} \frac{\sqrt{a}}{\kappa} \frac{\partial}{\partial s} + \frac{\partial}{\partial u^\alpha} \kappa\sqrt{a}\, a^{\alpha\beta} \frac{\partial}{\partial u^\beta} \right] \tag{3}$$

where $\kappa\sqrt{a}$ is the total Jacobian (κ as defined earlier), and the $\partial/\partial s$ symbolizes the derivative normal to the s = constant surface.

In order to obtain the coupled equations for propagation in this region we expand the wavefunction in a small sector i ($s_i - h_i/2 \le s \le s_i + h_i/2$) in a basis as

$$\Psi(\{u^\alpha\}, s) = \sum_l \kappa^{1/2} g\, S_l(\{u^\alpha\}; s_i)\, f_l(s) \tag{4}$$

The $\kappa^{1/2} g$ (g will be defined below) factorization is necessary to make the resulting interaction matrix, in the $\{S_l\}$ basis, hermitian, where $\{S_l\}$ form an orthonormal basis on the surface with weighting factor σ_s (σ_s can be a function of any of the coordinates other than s). We do not allow $\{S_l\}$ to have any explicit dependence on s; however, we are free to change the basis from sector to sector with appropriate matching procedures between sectors (1). Thus we have

$$\int_{\substack{\text{surf} \\ s=s_i}} S_l^*(\{u^\alpha\}; s_i)\, S_k(\{u^\alpha\}; s_i)\, \sigma_s\, du^2 \cdots du^n = \delta_{lk} \tag{5}$$

and g in Eq. (4) is defined by the weighting function σ_s; $g^2 = \sigma_s/\sqrt{a}$.

The resulting coupled equations in a sector are

$$\frac{d^2}{ds^2} \underset{\sim}{f} = \underset{\sim}{W} \underset{\sim}{f} \tag{6}$$

$$W_{\ell k} = W^*_{k\ell} = \int_{surf} S_\ell^* \tilde{\omega} S_k \sigma_s du^2 \cdots du^n \tag{7}$$

$$\tilde{\omega} = \mathcal{H} \left\{ -\frac{1}{\sigma_s} \frac{\partial}{\partial u^\alpha} a^{\alpha\beta} \sigma_s \frac{\partial}{\partial u^\beta} + 2\mu[V-E] \right\} \mathcal{H} + V_{eff} \tag{8}$$

where V_{eff} comes from the simplification of the operators in Eq. (3).

This method as described is not exact since $\partial/\partial s$ is the normal derivative to the surface s = constant. Referring to Fig. 3, the arrow shows schematically the normal coordinate curve between surface S_1 and S_2. The lines symbolize constant u^α (one of the internal coordinates). From the figure it can be seen that the derivative along the normal does not necessarily hold all the $\{u^\alpha\}$ constant, therefore $\partial/\partial s \, S(\{u^\alpha\}) \neq 0$. This non-zero derivative has been ignored to obtain Eq. (6). The exact equation is of the form:

$$\frac{d^2}{ds^2} \underset{\sim}{f} + \underset{\sim}{P} \frac{d}{ds} \underset{\sim}{f} = \underset{\sim}{W} \underset{\sim}{f}$$

Although this could be handled exactly, satisfactory results are obtained within the approximation that $\underset{\sim}{P} = 0$.

In this manner we are able to propagate from the u = 0 surface to the true matching surface as required before combining the channel R matrices with matching conditions to generate a global R matrix for the entire interaction region. In the next section we discuss the matching on the matching surfaces.

III. MATCHING AND THE GLOBAL R MATRIX

After propagation to the matching surfaces, the complete channel R matrices relate solution vectors and derivatives on the matching surfaces to an asymptotic surface in each chemical channel

$$\begin{bmatrix} \underset{\sim}{f}_\lambda \\ \underset{\sim}{g}^\infty_\lambda \end{bmatrix} = \begin{bmatrix} \underset{\sim}{R}^\lambda_1 & \underset{\sim}{R}^\lambda_2 \\ \underset{\sim}{R}^\lambda_3 & \underset{\sim}{R}^\lambda_4 \end{bmatrix} \begin{bmatrix} -\underset{\sim}{f}'_\lambda \\ \underset{\sim}{g}^{\infty\prime}_\lambda \end{bmatrix} \tag{9a, 9b}$$

for $\lambda = \alpha, \beta, \gamma$. In Eq. (9), $\underset{\sim}{f}_\lambda$ and $\underset{\sim}{f}'_\lambda$ are translation functions and derivatives defined in Eq. (4) on the matching surfaces and $\underset{\sim}{g}^\infty_\lambda$ and $\underset{\sim}{g}^{\infty\prime}_\lambda$ are asymptotic translation functions and derivatives. We now wish to impose continuity of the wavefunction and its derivative on the matching surfaces between all three channels in order to eliminate the $\underset{\sim}{f}$'s and $\underset{\sim}{f}'$'s and obtain a global R matrix relating the asymptotic $\underset{\sim}{g}^\infty$'s to asymptotic $\underset{\sim}{g}^{\infty\prime}$'s in the three channels. Thus we have (see Fig. 2)

$$\Psi^{JM}_{\alpha^0} = \Psi^{JM}_{\beta^\pi} \quad \text{on } M_{III} \quad (0 \le \chi_\alpha \le \chi^*_\alpha \,;\, \pi \ge \chi_\beta \ge \chi^*_\beta) \tag{10a}$$
$$n_{III} \cdot \nabla \Psi^{JM}_{\alpha^0} = -n_{III} \cdot \nabla \Psi^{JM}_{\beta^\pi}$$

$$\Psi^{JM}_{\alpha^\pi} = \Psi^{JM}_{\gamma^0} \quad \text{on } M_{II} \quad (\pi \ge \chi_\alpha \ge \chi^*_\alpha \,;\, 0 \le \chi_\gamma \le \chi^*_\gamma) \tag{10b}$$
$$n_{II} \cdot \nabla \Psi^{JM}_{\alpha^\pi} = -n_{II} \cdot \nabla \Psi^{JM}_{\gamma^0}$$

where $\Psi^{JM}_{\alpha^0}$ and $\Psi^{JM}_{\beta^\pi}$ are the wavefunctions on M_{III} and n_{III} is the normal to the matching surface M_{III} . The partitioning angles χ^*_λ were defined in paper I (also see Fig. 1) and are $\pi/2$ for a symmetric reaction like $H+H_2$. The normal

derivative to the surface is $n_{III} \cdot \nabla$.

Since the wavefunction in each channel is defined in terms of its own appropriate body fixed coordinates, we must match the full wavefunctions (Euler angles for each channel as well as internal body fixed coordinates) and derivatives on the matching surfaces. The wavefunction is expanded as in Eq. (4) with

$$\zeta_{\ell}^{\lambda JM} = D^{J}_{MK}(\Theta_\lambda \phi_\lambda, \nu_\lambda) \beta_j^{\lambda K}(\chi_\lambda) U_n^{\omega_j^{\lambda K}}(v_\lambda) \tag{11}$$

where ℓ symbolizes the collective index njk. J is the total angular momentum and M is its space-fixed z-projection. Both are conserved during the course of the reaction. $D^{J}_{MK}(\Theta_\lambda, \Phi_\lambda, \nu_\lambda)$ are rotation functions of the three Euler angles $\Theta_\lambda, \phi_\lambda, \nu_\lambda$. The rotor function $\beta_j^{\lambda K}(\chi_\lambda)$ is the partitioned rotor defined in paper I such that

$$\int_0^{\chi_\lambda^*} \beta_j^{\lambda K}(\chi_\lambda) \beta_{j'}^{\lambda K}(\chi_\lambda) \sin\chi_\lambda d\chi_\lambda = \epsilon_j^{\lambda K} \delta_{jj'} \tag{12}$$

In Eq. (11), $\omega_j^{\lambda K}$ is defined such that

$$\omega_j^{\lambda K} = \begin{cases} 0 & \epsilon_j^{\lambda K} \geq .5 \\ \pi & \epsilon_j^{\lambda K} < .5 \end{cases} \tag{13}$$

and identifies the vibrational basis appropriate to the localization of ψ_λ^{JK}, i.e. the end of the molecule which is reacting.

Since each channel matches onto both of the other channels and the partitioning of the rotors is not perfect, the matching conditions of Eq. (10) are expressed in sets of equations which are not all linearly independent.

The overlap matrices on the five-dimensional surfaces reduce to the product of two one-dimensional integrals over the vibrational coordinate v and the internal rotational

coordinate χ . The vibrational overlap is obtained analytically and the rotational overlap is evaluated by numerical integration. The matching matrices are denoted $\underset{\approx}{M}^{\lambda}_{K}$, $\underset{\approx}{N}^{\lambda}_{K}$; $\lambda = \alpha, \beta, \gamma$, and $K = 1,3,4$ denotes the function and derivative matching shown below. $\underset{\approx}{M}$ and $\underset{\approx}{N}$ denote cyclic and anti-cyclic ordering, respectively, where, for example, $\underset{\approx}{M}^{\beta}$ relates α-functions to γ-functions and is a matrix of the form $\langle \alpha | m^{\beta} | \gamma \rangle$ where $|\alpha\rangle, |\gamma\rangle$ are internal α and internal γ- functions, respectively. Similarly, $\underset{\approx}{N}^{\beta}$ relates γ to α . (Note: $\underset{\approx}{N}^{\beta}$ does not equal the inverse of $\underset{\approx}{M}^{\beta}$. See Appendix.) All operators in the matching matrices can be derived from Eqs. (10a) and (10b), the orthogonality conditions of Eq. (5) and Euler angle relations between channels. The Euler angle relations describe the rotation between body fixed systems, which for α and β channels are

$$D^{J}_{MK}(\Theta_{\alpha}, \phi_{\alpha}, \nu_{\alpha}) = \sum_{K'} d^{J}_{KK'}(\epsilon_{\gamma})\, D^{J}_{MK'}(\Theta_{\beta}, \phi_{\beta}, \nu_{\beta})$$

The angle ϵ_{γ} is not to be confused with the matrix $\underset{\approx}{\epsilon}^{\gamma}$ defined in Eq. (12). The angle ϵ_{γ} is a function of χ_{α} or χ_{β} alone. Once the $\underset{\approx}{M}^{\lambda}_{K}$ and $\underset{\approx}{N}^{\lambda}_{K}$ matrices ($\lambda = \alpha, \beta, \gamma$; K = 1,3,4) are evaluated we have systems of equations of the following form

$$\begin{bmatrix} \underset{\approx}{\epsilon}^{\alpha}\, \underset{\sim}{f}_{\alpha} \\ \underset{\approx}{\epsilon}^{\alpha}\, \underset{\sim}{f}'_{\alpha} \end{bmatrix} = \begin{bmatrix} \underset{\approx}{N}^{\gamma}_{1} & \underset{\approx}{0} \\ \underset{\approx}{N}^{\gamma}_{3} & \underset{\approx}{N}^{\gamma}_{4} \end{bmatrix} \begin{bmatrix} \underset{\sim}{f}_{\beta} \\ \underset{\sim}{f}'_{\beta} \end{bmatrix} \qquad (14a)\ (14b)$$

$$\begin{bmatrix} (\underset{\approx}{1} - \underset{\approx}{\epsilon}^{\alpha})\, \underset{\sim}{f}_{\alpha} \\ (\underset{\approx}{1} - \underset{\approx}{\epsilon}^{\alpha})\, \underset{\sim}{f}'_{\alpha} \end{bmatrix} = \begin{bmatrix} \underset{\approx}{M}^{\beta}_{1} & \underset{\approx}{0} \\ \underset{\approx}{M}^{\beta}_{3} & \underset{\approx}{M}^{\beta}_{4} \end{bmatrix} \begin{bmatrix} \underset{\sim}{f}_{\gamma} \\ \underset{\sim}{f}'_{\gamma} \end{bmatrix} \qquad (14c)\ (14d)$$

and cyclic in α, β, γ where $\underset{\approx}{\epsilon}^{\alpha}$ (not to be confused with the angle ϵ_{α}) is a

diagonal matrix such that its njk diagonal element is $\epsilon_j^{\alpha k}$ (defined in Eq. (12)).

We note that the cyclic permutation of (14) implies that we have twice as many equations as unknowns ($\underset{\sim}{f}$'s ; $\underset{\sim}{g}$'s). Here we retain all equations, later eliminating the linear dependence by means of the generalized inverse below.

Simply adding (14a) and (14c), and (14b) and (14d) eliminates $\underset{\sim}{\epsilon}^{\alpha}$ from the equations and we have

$$\begin{bmatrix} \underset{\sim}{f}_\alpha \\ \underset{\sim}{f}'_\alpha \end{bmatrix} = \begin{bmatrix} \underset{=}{N}_1^\gamma & \underset{=}{0} \\ \underset{=}{N}_3^\gamma & \underset{=}{N}_4^\alpha \end{bmatrix} \begin{bmatrix} \underset{\sim}{f}_\beta \\ \underset{\sim}{f}'_\beta \end{bmatrix} + \begin{bmatrix} \underset{=}{M}_1^\beta & \underset{=}{0} \\ \underset{=}{M}_3^\beta & \underset{=}{M}_4^\beta \end{bmatrix} \begin{bmatrix} \underset{\sim}{f}_\gamma \\ \underset{\sim}{f}'_\gamma \end{bmatrix} \tag{15a}$$

(15b)

and cyclic. Equations (9b) for each channel can be combined to give

$$\begin{bmatrix} \underset{\sim}{g}_\alpha \\ \underset{\sim}{g}_\beta \\ \underset{\sim}{g}_\gamma \end{bmatrix} = \begin{bmatrix} \underset{=}{R}_4^\alpha & \underset{=}{0} & \underset{=}{0} \\ \underset{=}{0} & \underset{=}{R}_4^\beta & \underset{=}{0} \\ \underset{=}{0} & \underset{=}{0} & \underset{=}{R}_4^\gamma \end{bmatrix} \begin{bmatrix} \underset{\sim}{g}'_\alpha \\ \underset{\sim}{g}'_\beta \\ \underset{\sim}{g}'_\gamma \end{bmatrix} - \begin{bmatrix} \underset{=}{R}_3^\alpha & \underset{=}{0} & \underset{=}{0} \\ \underset{=}{0} & \underset{=}{R}_3^\beta & \underset{=}{0} \\ \underset{=}{0} & \underset{=}{0} & \underset{=}{R}_3^\gamma \end{bmatrix} \begin{bmatrix} \underset{\sim}{f}'_\alpha \\ \underset{\sim}{f}'_\beta \\ \underset{\sim}{f}'_\gamma \end{bmatrix} \tag{16a}$$

(16b)

(16c)

Thus we wish to use (15a) and (15b) and (9a) to eliminate $\underset{\sim}{f}'_\alpha$, $\underset{\sim}{f}'_\beta$, $\underset{\sim}{f}'_\gamma$ in favor of $\underset{\sim}{g}'_\alpha$, $\underset{\sim}{g}'_\beta$ and $\underset{\sim}{g}'_\gamma$ from (16) so that we can obtain

$$\begin{bmatrix} \underset{\sim}{g}_\alpha \\ \underset{\sim}{g}_\beta \\ \underset{\sim}{g}_\gamma \end{bmatrix} = \begin{bmatrix} \underset{=}{R}_g^{\alpha\alpha} & \underset{=}{R}_g^{\alpha\beta} & \underset{=}{R}_g^{\alpha\gamma} \\ \underset{=}{R}_g^{\beta\alpha} & \underset{=}{R}_g^{\beta\beta} & \underset{=}{R}_g^{\beta\gamma} \\ \underset{=}{R}_g^{\gamma\alpha} & \underset{=}{R}_g^{\gamma\beta} & \underset{=}{R}_g^{\gamma\gamma} \end{bmatrix} \begin{bmatrix} \underset{\sim}{g}'_\alpha \\ \underset{\sim}{g}'_\beta \\ \underset{\sim}{g}'_\gamma \end{bmatrix} \tag{17a}$$

(17b)

(17c)

where $\underset{=}{R}_g$ is the desired global R matrix for the reactive system from which we can easily obtain the S matrix.

The matching equations (15a) and (15b) together with the R-matrix equations (9a) and (9b) form a set of 12N equations, not all linearly independent. We note that we have 6N unknowns f_λ's and f'_λ's which we wish to eliminate and we have 3N relations (Eq. (17)) which we wish to solve for. (For simplicity in the notation, we take the total number of independent states to be 3N, assuming N in each channel.) With perfect partitioning ($\epsilon_j^{\lambda\kappa}$ 0 or 1, only achievable with complete basis sets) half of the equations (14a)-(14d) would express 0 = 0 which has been folded into Eq. (15). Thus Eqs. (15a) and (15b) form an overdetermined set of 6N equations. By performing a least squares procedure we can solve these equations for the "best" possible solution. We have 6N unknowns $f_\alpha, f_\beta, f_\gamma$ and $f'_\alpha, f'_\beta, f'_\gamma$ which we wish to eliminate using 9N Eqs. (15a), (15b), and (9a). Equations (15a) and (9a) can be directly equated to eliminate $f_\alpha, f_\beta, f_\gamma$ from the equations leaving 6N relations between derivatives $f'_\alpha\ f'_\beta\ f'_\gamma$ on the matching surfaces and asymptotic derivatives $g'_\alpha\ g'_\beta, g'_\gamma$. We obtain a solution of the form:

$$\underset{6N\times 3N}{\underset{\approx}{Z}} \begin{bmatrix} \underset{\sim}{f'_\alpha} \\ \underset{\sim}{f'_\beta} \\ \underset{\sim}{f'_\gamma} \end{bmatrix} = \underset{6N\times 3N}{\underset{\approx}{Q}} \begin{bmatrix} \underset{\approx}{R_2^\alpha} & \underset{\approx}{0} & \underset{\approx}{0} \\ \underset{\approx}{0} & \underset{\approx}{R_2^\beta} & \underset{\approx}{0} \\ \underset{\approx}{0} & \underset{\approx}{0} & \underset{\approx}{R_2^\gamma} \end{bmatrix} \begin{bmatrix} \underset{\sim}{g'_\alpha} \\ \underset{\sim}{g'_\beta} \\ \underset{\sim}{g'_\gamma} \end{bmatrix} \tag{18a, 18b, 18c}$$

where $\underset{\approx}{Z}$ and $\underset{\approx}{Q}$ are known 6N x 3N matrices formed from the channel $\underset{\approx}{R_1^\lambda}$ matrices and the matching matrices. $\underset{\approx}{Z}$ and $\underset{\approx}{Q}$ are derived in the Appendix.

We now define a 3N x 3N matrix $\underset{\approx}{X}$ by

$$\underset{\approx}{Z}\,\underset{\approx}{X} = \underset{\approx}{Q} \tag{19}$$

We could solve this equation directly using a generalized inverse giving

$$\underset{\approx}{X} = \left(\underset{\approx}{Z}^T \underset{\approx}{Z}\right)^{-1} \underset{\approx}{Z}^T \underset{\approx}{Q} \tag{20}$$

Then from Eq. (16) the global R matrix, $\underline{R}_g$, is

$$\underline{R}_g = \underline{R}_4 - \underline{R}_3 \underline{X} \underline{R}_2 \tag{21}$$

with $\underline{R}_g$ defined in (17) and $\underline{R}_2$, $\underline{R}_3$, and $\underline{R}_4$ block diagonal matrices composed of the channel $\underline{R}^{\lambda}_{k}$.

We know that the global R matrix, $\underline{R}_g$, will be symmetric if and only if $\underline{X}$ is symmetric since $\underline{R}_3 = \underline{R}_2^T$ and $\underline{R}_4 = \underline{R}_4^T$. However, it can be shown that $\underline{X}$ defined in Eq. (20) will be symmetric only in the limit of complete sets.

As found in our earlier collinear studies (2), very satisfactory semiquantitative results were obtained with very small basis sets and with large step sizes (which amplifies the non-orthogonality in the basis set transformations from one sector to the next). This feature is not present in other methods of solution to the close-coupled equations. It is a result, in these calculations, of the symmetry preserved by the R-matrix method of solution. It is highly desirable to retain this feature in these 3-dimensional calculations. This requires a method of solution for the global R matrix which preserves its symmetry with finite basis sets. We propose here one such method of solution.

Multiplying Eq. (19) on the righthand side by $\underline{Z}^T$, we have

$$\underline{Z}\,\underline{X}\,\underline{Z}^T = \underline{Q}\,\underline{Z}^T \tag{22}$$

It is clear that $\underline{Q}\,\underline{Z}^T$ should be symmetric to assure that $\underline{X}$ is symmetric and consequently assure the symmetry of $\underline{R}_g$. However, it is shown in the Appendix that $\underline{Q}\,\underline{Z}^T$ is a symmetric matrix product only in the limit of complete sets. However, the symmetry of $\underline{Q}\,\underline{Z}^T$ can be and is preserved in our calculations by evaluating the matrix of the product of operators as opposed to the product of matrices. We show how this is done in the Appendix. We then perform a right as well as a left generalized inverse to Eq. (22) to solve for a symmetric $\underline{X}$.

$$\underline{\underline{X}} = (\underline{\underline{Z}}^T \underline{\underline{Z}})^{-1} \underline{\underline{Z}}^T (\underline{\underline{Q}} \underline{\underline{Z}}^T) \underline{\underline{Z}} (\underline{\underline{Z}}^T \underline{\underline{Z}})^{-1} \qquad (23)$$

Note that this is not an a posteriori symmetrization of the R matrix. Rather a symmetric R matrix results when the appropriate operator products are evaluated in the incomplete basis.

Using $\underline{\underline{X}}$ defined in Eq. (23) and Eq. (21), we build a symmetric global R matrix, and obtain, finally, a unitary S matrix which is superior to the non-unitary S matrix obtained from the direct matrix inversion of Eq. (19). The results presented in the following section are obtained by this procedure and, as expected, the S matrices are unitary.

IV. RESULTS FOR $H+H_2$

In this section we present some preliminary results for the $H+H_2$ reactive scattering. Although quantum reactive scattering calculations for this system have been reported by Schatz et al (3) (SK) and by Elkowitz and Wyatt (4), we consider this system here for several reasons. First, because of the low masses and high symmetry, it is the most economical realistic system on which to do accurate calculations. Second, we desired to compare our results with published results using independent mathematical techniques, algorithms, and computer codes. Finally accurate calculations have been reported only in the low ($\lesssim .7$ eV) range, well below the energy range ($\sim .97$ eV) at which a resonance has been reported (5). We have, therefore, determined accurately the energy and depth of this resonance. In addition the convergence of the results with respect to basis, i.e. vibrational and rotational functions, and with respect to step size has been determined.

We consider first the low energy convergence properties. In the following we denote a basis by n_1, n_2, n_3 ... where n_i is the maximum rotational angular momentum of free rotor states used in the i^{th} vibrational state of the diatomic. The vibra-

tional states themselves are determined by diagonalizing the collinear Hamiltonian in a harmonic oscillator basis consisting of 6 to 8 functions. From 3 to 6 of the resulting eigenfunctions were used as the contracted vibrational basis. The total number of coupled equations, remaining after total angular momentum, J; parity, P; and the even and odd rotational manifolds have been separated ranged up to 44 in our calculations. When the solutions of the coupled equations are joined to yield the S matrix for a given J, S^J, up to 120 states are coupled in the reactive scattering problem, for some values of J and parity.

We first did a series of calculations for J = 0 varying the step size and basis size. A sample of the convergence of these calculations is shown in Fig. 4 which shows the probability of reaction from $(0,0,0)_o$ to $(0,j,\ell)_o$ [We denote the states by (i,j,ℓ) where i is the vibrational state, j the rotational state, ℓ the orbital angular momentum, and p = 0 (1) refers to even (odd) parity. When indices rather than numbers appear, we imply averaging over initial state and summing over final state.]. From these (and other calculations not shown) we determined that 60 steps (from u = 0 to $u = u_{FINAL} = 8.4\ a_o$) and a four vibration, 11,9,7,3 basis was sufficient for about 2% accuracy in the reactive transition probabilities. For J = 0, both the 13,11,9,5,3,3 and 11,9,7,3 results agree with the published SK result to within 2%.

The reactive cross sections were determined at E = .65 eV. Shown in Figs. 5 and 6 are the contributions to the reactive cross sections from each value of J for $\sigma^R_{(00\ell)_o \to (0j\ell)_o}$ and $\sigma^R_{(01\ell)_{0,1} \to (0j\ell)_{0,1}}$. As can easily be seen, the cross sections converge easily by J = 10, and the contribution to the reactive scattering peaks for values of $J \approx 3$. The computed cross sections at E = .65 eV agree satisfactorily with those of Schatz et al as shown in Table I. At this energy increasing the basis size reduces the cross section. Thus we believe that our cross sections are an upper bound to the true cross sections and are accurate to 5%.

Table I

Cross Sections (a_o^2)	This work	SK
$\sigma^R_{(00\ell)_0 \rightarrow (0j\ell)_0}$	.843	.933
$\sigma^R_{(01\ell)_{0,1} \rightarrow (0j\ell)_{0,1}}$	.527	.648

The basis sets used in our calculations at this energy were

J	0	1 + 2	3 + 4	5 - 12
$n_0, n_1, \ldots$	11 9 7 3	9 7 5 3	7 5 5 3	7,5,3

and 60 steps were taken in the integration. Note on the graphs the points off the line are for different basis sets: 7, 5, 3 for both J = 0 and J = 4. As can easily be seen, the difference appears small. These results confirm the adequacy of both our calculations and those of Schatz et al in this energy regime, and provide an important validation of both methods and programs.

We note also that at this energy the negative parity scattering contributes very little to the reactive cross sections ($<$ 5% of the total). This is an orientation effect since the collinear configuration can only occur when the projection of the rotational angular momentum on the body fixed axis, K, is zero. Since the K = 0 manifold is of even parity, this parity dominates the reactive scattering at low energy. At higher energy the contribution of odd parity scattering is more important.

Of more interest is the behavior of the system in the vicinity of the resonance at 0.97 eV. In this energy range both the ground and first excited vibrational states of the reactants and products are energetically open and convergence with respect to both vibra-

tional and rotational basis sets is more difficult to obtain. As noted for collinear scattering (2) the behavior at the resonance is significantly more sensitive to basis set size than in other energy regions. In Fig. 7 the J = 0, even parity reaction probability $(0,0,0)_o \rightarrow (0, j, \ell)_o$ is shown from E = 0.7 to 1.12 eV for calculations with three different basis sets, 7,5,3; 7,5,3,1; and 13,11,7,5,1. As can easily be seen, the position of the resonance is very sensitive to the vibrational basis (4 vibrational states are required) and the depth of the resonance is sensitive to the number of rotational states as well. It appears that the resonance, when fully converged with respect to rotational states (the 13,11,7,5,1 is converged) is less deep than indicated in Ref. 5. The dip in the reaction probability to the ground vibrational state at .97 eV is accompanied by an increase in the reaction probability to the first excited vibrational state (also shown on Fig. 7). The total reaction probability, therefore, is almost constant across the resonance region, i.e. the probability missing in n = 0 goes into n = 1.

For J = 1, shown in Fig. 8, it can be seen that the position of the resonance is essentially unchanged, but the depth is slightly reduced. The basis used was 11,7,3,3,1. Up to J = 3 preliminary results indicate a slight shift in the position of the resonance. It seems likely that the total cross section from (00ℓ) to $(0j\ell)$ will show, at most, a small (< 15%) dip across the resonance energy range.

Finally, in Fig. 9 we show for J = 0 the probability of a particular transition $(000)_o \rightarrow (011)_o$. This varies somewhat more across the resonance. Also shown on the graph are the results of SK up to E = .7 eV. Except for the last (E = .7 eV) point the agreement is excellent indicating their smaller basis was adequate in that energy range.

In conclusion we have presented accurate but not complete results for the 3-D $H+H_2$ reactive scattering in the energy range up to 1.12 eV. At the low energies ($\leq$ .7 eV) they

confirm earlier work (3) and, in the resonance region (~ .97 eV) indicate that the resonance is not as deep as earlier work indicated (5).

APPENDIX

The full derivation of the global R matrix from the matching equations and the arrangement channel R matrices is lengthy and involves specific properties of the matching matrices. It is not presented in detail in this paper. However, we outline the steps of the derivation.

The relevant equations for the derivation of Eq. (18) are (9a), (15a), and (15b). These 9N equations are relations among the $9N$ quantities f_λ, f'_λ, g'_λ ($\lambda = \alpha, \beta, \gamma$). The equations relating g_λ to g'_λ and the boundary conditions determine the S matrix. Thus the $6N$ f_λ, f'_λ's must eventually be eliminated from the equations. To this end we first use (9a), (15a), and (15b) to eliminate the f_λ's, leaving the 6N Eqs. (18). Thus substituting (9a) into (15a) yields the 3N relations between f'_λ and g'_λ shown below in Eq. (24a)

$$f_\lambda = \underline{\underline{R}}_2^\lambda g'_\lambda - \underline{\underline{R}}_1^\lambda f'_\lambda \tag{9a}$$

$$f_\alpha = \underline{\underline{N}}_1^\gamma f_\beta + \underline{\underline{M}}_1^\beta f_\gamma \tag{15a}$$

$$(\underline{\underline{R}}_2^\alpha g'_\alpha - \underline{\underline{R}}_1^\alpha f'_\alpha) = \underline{\underline{N}}_1^\gamma (\underline{\underline{R}}_2^\beta g'_\beta - \underline{\underline{R}}_1^\beta f'_\beta) + \underline{\underline{M}}_1^\beta (\underline{\underline{R}}_2^\gamma g'_\gamma - \underline{\underline{R}}_1^\gamma f'_\gamma) \tag{24a}$$

and cyclic. Rearranging we get the first 3N equations of Eqs. (18), shown explicitly in Eq. (25a) below:

$$\begin{bmatrix} -\underline{\underline{1}} & \underline{\underline{N}}_1^\gamma & \underline{\underline{M}}_1^\beta \\ \underline{\underline{M}}_1^\gamma & -\underline{\underline{1}} & \underline{\underline{N}}_1^\alpha \\ \underline{\underline{N}}_1^\beta & \underline{\underline{M}}_1^\alpha & -\underline{\underline{1}} \end{bmatrix} \begin{bmatrix} \underline{\underline{R}}_1^\alpha & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{R}}_1^\beta & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{R}}_1^\gamma \end{bmatrix} \begin{bmatrix} f'_\alpha \\ f'_\beta \\ f'_\gamma \end{bmatrix} = \begin{bmatrix} -\underline{\underline{1}} & \underline{\underline{N}}_1^\gamma & \underline{\underline{M}}_1^\beta \\ \underline{\underline{M}}_1^\gamma & -\underline{\underline{1}} & \underline{\underline{N}}_1^\alpha \\ \underline{\underline{N}}_1^\beta & \underline{\underline{M}}_1^\alpha & -\underline{\underline{1}} \end{bmatrix} \begin{bmatrix} \underline{\underline{R}}_2^\alpha & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{R}}_2^\beta & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{R}}_2^\gamma \end{bmatrix} \begin{bmatrix} g'_\alpha \\ g'_\beta \\ g'_\gamma \end{bmatrix} \tag{25a}$$

where the M's and N's are matching matrices over the appropriate matching surfaces defined earlier (Eq. (14)). Although this equation is of the form

$$\underset{\sim}{q}_1 \underset{\sim}{R}_1 \underset{\sim}{f}' = \underset{\sim}{q}_1 \underset{\sim}{R}_2 \underset{\sim}{g}' \tag{26a}$$

we note that $\underset{\sim}{q}_1$ has no inverse and, therefore,

$$\underset{\sim}{f}' \neq \underset{\sim}{R}_1^{-1} \underset{\sim}{R}_2 \underset{\sim}{g}'$$

Similarly, substituting (9a) into (15b) yields another 3N relations between $\underset{\sim}{f}_\lambda'$ and $\underset{\sim}{g}_\lambda'$ shown below in Eq. (24b)

$$\underset{\sim}{f}_\alpha' = \underset{=}{N}_3^\gamma \underset{\sim}{f}_\delta + \underset{=}{N}_4^\gamma \underset{\sim}{f}_\beta' + \underset{=}{M}_3^\beta \underset{\sim}{f}_\gamma + \underset{=}{M}_4^\beta \underset{\sim}{f}_\gamma' \tag{15b}$$

$$\underset{\sim}{f}_\alpha' = \underset{=}{N}_3^\gamma [\underset{=}{R}_2^\beta \underset{\sim}{g}_\beta' - \underset{=}{R}_1^\beta \underset{\sim}{f}_\beta'] + \underset{=}{N}_4^\gamma \underset{\sim}{f}_\beta' + \underset{=}{M}_3^\beta [\underset{=}{R}_2^\gamma \underset{\sim}{g}_\delta' - \underset{=}{R}_1^\gamma \underset{\sim}{f}_\delta'] + \underset{=}{M}_4^\beta \underset{\sim}{f}_\gamma' \tag{24b}$$

and cyclic. Rearranging (24b) we get the second 3N equations of Eqs. (18)

$$\begin{bmatrix} \underset{=}{1} & \underset{=}{N}_3^\gamma \underset{=}{R}_1^\beta - \underset{=}{N}_4^\gamma & \underset{=}{M}_3^\beta \underset{=}{R}_1^\gamma - \underset{=}{M}_4^\beta \\ \underset{=}{M}_3^\gamma \underset{=}{R}_1^\alpha - \underset{=}{M}_4^\gamma & \underset{=}{1} & \underset{=}{N}_3^\alpha \underset{=}{R}_1^\gamma - \underset{=}{N}_4^\alpha \\ \underset{=}{N}_3^\beta \underset{=}{R}_1^\alpha - \underset{=}{N}_4^\beta & \underset{=}{M}_3^\alpha \underset{=}{R}_1^\beta - \underset{=}{M}_4^\alpha & \underset{=}{1} \end{bmatrix} \begin{bmatrix} \underset{\sim}{f}_\alpha' \\ \underset{\sim}{f}_\beta' \\ \underset{\sim}{f}_\gamma' \end{bmatrix} = \begin{bmatrix} \underset{=}{0} & \underset{=}{N}_3^\gamma & \underset{=}{M}_3^\beta \\ \underset{=}{M}_3^\gamma & \underset{=}{0} & \underset{=}{N}_3^\alpha \\ \underset{=}{N}_3^\beta & \underset{=}{M}_3^\alpha & \underset{=}{0} \end{bmatrix} \begin{bmatrix} \underset{=}{R}_2^\alpha & \underset{=}{0} & \underset{=}{0} \\ \underset{=}{0} & \underset{=}{R}_2^\beta & \underset{=}{0} \\ \underset{=}{0} & \underset{=}{0} & \underset{=}{R}_2^\gamma \end{bmatrix} \begin{bmatrix} \underset{\sim}{g}_\alpha' \\ \underset{\sim}{g}_\beta' \\ \underset{\sim}{g}_\gamma' \end{bmatrix} \tag{25b}$$

which is of the form

$$[\underset{=}{q}_3 \underset{=}{R}_1 - \underset{=}{q}_4] \underset{\sim}{f}' = \underset{=}{q}_3 \underset{=}{R}_2 \underset{\sim}{g}' \tag{26b}$$

Combining the two sets of equations (24a) and (24b), we have the 6N Eqs. (18)

$$\underset{=}{Z} \underset{\sim}{f}' = \underset{=}{Q} \underset{=}{R}_2 \underset{\sim}{g}' \tag{18}$$

with

$$\underset{=}{Z} = \begin{bmatrix} \underset{=}{q}_1 \underset{=}{R}_1 \\ \underset{=}{q}_3 \underset{=}{R}_1 - \underset{=}{q}_4 \end{bmatrix} \tag{27a}$$

$$\underset{=}{Q} = \begin{bmatrix} \underset{=}{q}_1 \\ \underset{=}{q}_3 \end{bmatrix} \tag{27b}$$

and

$$\underline{Q}_K = \begin{bmatrix} \underline{A}_K & \underline{N}_K^{\gamma} & \underline{M}_K^{\beta} \\ \underline{M}_K^{\gamma} & \underline{A}_K & \underline{N}_K^{\alpha} \\ \underline{N}_K^{\beta} & \underline{M}_K^{\alpha} & \underline{A}_K \end{bmatrix} \qquad K = 1,3,4 \tag{28}$$

with $\underline{A}_K = -\frac{1}{2}$, $K = 1,4$; $\underline{A}_K = \underline{0}$, $K = 3$.

As shown in the body of the paper $\underline{Q}\underline{Z}^T$ must be symmetric if the global R matrix is to be symmetric. We have explicitly,

$$\underline{Q}\underline{Z}^T = \begin{bmatrix} \underline{Q}_1 \underline{R}_1 \underline{Q}_1^T & \underline{Q}_1 \underline{R}_1 \underline{Q}_3^T - \underline{Q}_1 \underline{Q}_4^T \\ \underline{Q}_3 \underline{R}_1 \underline{Q}_1^T & \underline{Q}_3 \underline{R}_1 \underline{Q}_3^T - \underline{Q}_3 \underline{Q}_4^T \end{bmatrix} \tag{29a}$$

Since $\underline{R}_1 = \underline{R}_1^T$, it is easily seen that $\underline{Q}\underline{Z}^T$ will be symmetric if and only if

$$\begin{aligned} \underline{Q}_1 \underline{Q}_4^T &= \underline{0} \\ \underline{Q}_3 \underline{Q}_4^T &= \underline{Q}_4 \underline{Q}_3^T \end{aligned} \tag{29b}$$

We now show that the conditions (29b) are satisfied for complete sets and that $\underline{Q}_3 \underline{Q}_4^T$ when computed as a matrix of the operator product in a finite basis is symmetric. Three elements of the 3x3 matrix product $\underline{Q}_i \underline{Q}_j^T$ are sufficient to study the symmetry properties.

$$\begin{aligned} (\underline{Q}_i \underline{Q}_j^T)^{\alpha\alpha} &= \underline{A}_i \underline{A}_j + \underline{N}_i^{\gamma} \underline{N}_j^{\gamma T} + \underline{M}_i^{\beta} \underline{M}_j^{\beta T} \\ (\underline{Q}_i \underline{Q}_j^T)^{\alpha\beta} &= \underline{A}_i \underline{M}_j^{\gamma T} + \underline{N}_i^{\gamma} \underline{A}_j + \underline{M}_i^{\beta} \underline{N}_j^{\alpha T} \\ (\underline{Q}_i \underline{Q}_j^T)^{\beta\alpha} &= \underline{M}_i^{\gamma} \underline{A}_j + \underline{A}_i \underline{N}_j^{\gamma T} + \underline{N}_i^{\alpha} \underline{M}_j^{\beta T} \end{aligned} \tag{30a}$$

All other elements can be generated by cyclic permutation of the indices, α, β, γ . For convenience we define four additional matrices:

$$(P^{ij})^{\alpha\alpha 1} \equiv N_i^{\gamma} N_j^{\gamma T} \qquad (P^{ij})^{\alpha\alpha 2} \equiv M_i^{\beta} M_j^{\beta T}$$

$$(P^{ij})^{\alpha\beta} \equiv M_i^{\beta} N_j^{\alpha T} \qquad (P^{ij})^{\beta\alpha} \equiv N_i^{\alpha} M_j^{\beta T} \tag{30b}$$

To proceed, we write the product terms out explicitly. Then we show that the symmetry properties follow from elimination of intermediate complete sets (that is, using the closure property of complete, orthonormal sets). The form of the matching matrices is explicitly shown below

$$(N_i^{\gamma})_{njK,n'j'K'} = \int dV_\alpha \, U_n^{\alpha}(V_\alpha) \, n_i^{\gamma}(V_\alpha) U_{n'}^{\beta}(V_\beta) \int_0^{\chi_\alpha^*} d\chi_\alpha \sin\chi_\alpha \, S_j^{\alpha K}(\chi_\alpha) d^{J}_{KK'}(\epsilon_\gamma) S_{j'}^{\beta K'}(\chi_\beta) \tag{31a}$$

$$(M_i^{\gamma})_{njK,n'j'K'} = \int dV_\alpha \, U_n^{\beta}(V_\beta) \, m_i^{\gamma}(V_\alpha) U_{n'}^{\alpha}(V_\alpha) \int_0^{\chi_\alpha^*} d\chi_\alpha \sin\chi_\alpha \, S_j^{\beta K}(\chi_\beta) d^{J}_{K'K}(\epsilon_\gamma) S_{j'}^{\alpha K'}(\chi_\alpha) \tag{31b}$$

where $V_\beta \equiv V_\beta(V_\alpha)$, $\chi_\beta = \chi_\beta(\chi_\alpha)$, and $\epsilon_\gamma \equiv \epsilon_\gamma(\chi_\alpha)$ and m_i^{γ} , n_i^{γ} are functions of V_α . Consider now $(P_{ij}^{\alpha\alpha 1})$ defined in eq. (30b):

$$(P^{ij})^{\alpha\alpha 1}_{njK,n'j'K'} = \sum_{n''} \iint dV_\alpha dV_\alpha' \, U_n^{\alpha}(V_\alpha) n_i^{\gamma}(V_\alpha) U_{n''}^{\beta}(V_\beta) U_{n''}^{\beta}(V_\beta') \, n_j^{\gamma}(V_\alpha') \, U_{n'}^{\alpha}(V_\alpha') \tag{32a}$$
$$\otimes \sum_{j''K''} \int_0^{\chi_\alpha^*} \int_0^{\chi_\alpha^*} d\chi_\alpha d\chi_\alpha' \sin\chi_\alpha \sin\chi_\alpha' \, S_j^{\alpha K}(\chi_\alpha) d^{J}_{KK''}(\epsilon_\gamma) S_{j''}^{\beta K''}(\chi_\beta) S_{j''}^{\beta K''}(\chi_\beta') d^{J}_{K'K''}(\epsilon_\delta') S_{j'}^{\alpha K'}(\chi_\alpha')$$

Summing the n' sum, integrating over V_α' and using the closure property of the set $\{U_{n''}^{\beta}(V_\beta)\}$:

$$\sum_{n''} U^{\beta}_{n''}(v_\beta) U^{\beta}_{n''}(v'_\beta) = \delta(v_\beta - v'_\beta) \tag{33a}$$

the matrix element in (32a) reduces to

$$(\rho^{ij})^{\alpha\alpha'}_{n_j K, n'_{j'} K'} = \int dv_\alpha U^{\alpha}_{n}(v_\alpha) n^{\gamma}_{i}(v_\alpha) n^{\gamma}_{j}(v_\alpha) U^{\alpha}_{n'}(v_\alpha) \tag{32b}$$
$$\otimes \sum_{K'' j''} \int_0^{\chi^*_\alpha} \int_0^{\chi^*_\alpha} d\chi_\alpha d\chi'_\alpha \sin\chi_\alpha \sin\chi'_\alpha S^{\alpha K}_{j}(\chi_\alpha) d^{J}_{KK''}(\epsilon_\delta) S^{\beta K''}_{j''}(\chi_\beta) S^{\beta K'}_{j''}(\chi'_\beta) d^{J}_{K'K''}(\epsilon_\delta) S^{\alpha K'}_{j'}(\chi'_\alpha)$$

Summing the j' sum, integrating over χ'_α and using the closure property of the set $\{ S^{\beta K}_{j''}(\chi_\beta) \}$ for each value of K":

$$\sum_{j''} \sin^{1/2}(\chi_\beta) S^{\beta K''}_{j''}(\chi_\beta) S^{\beta K''}_{j''}(\chi'_\beta) \sin^{1/2}\chi'_\beta = \delta(\chi_\beta - \chi'_\beta) \tag{33b}$$

the matrix element in (32b) reduces to

$$(\rho^{ij})^{\alpha\alpha'}_{n_j K, n'_{j'} K'} = \int dv_\alpha U^{\alpha}_{n}(v_\alpha) n^{\gamma}_{i}(v_\alpha) n^{\gamma}_{j}(v_\alpha) U^{\alpha}_{n'}(v_\alpha) \tag{32c}$$
$$\otimes \sum_{K''} \int_0^{\chi^*_\alpha} d\chi_\alpha \sin\chi_\alpha S^{\alpha K}_{j}(\chi_\alpha) d^{J}_{KK''}(\epsilon_\delta) d^{J}_{K'K''}(\epsilon_\delta) S^{\alpha K'}_{j'}(\chi_\alpha)$$

Summing the final sum, K", and using the unitarity of the d^J-rotation matrices:

$$\sum_{K''} d^{J}_{KK''}(\epsilon_\delta) d^{J}_{K'K''}(\epsilon_\delta) = \delta_{KK'} \tag{33c}$$

the matrix element further reduces to

$$(\rho^{ij})^{\alpha\alpha'}_{n_j K, n'_{j'} K'} = \delta_{KK'} \int dv_\alpha U^{\alpha}_{n}(v_\alpha) n^{\gamma}_{i}(v_\alpha) n^{\gamma}_{j}(v_\alpha) U^{\alpha}_{n'}(v_\alpha) \tag{32d}$$
$$\otimes \int_0^{\chi^*_\alpha} d\chi_\alpha \sin\chi_\alpha S^{\alpha K}_{j}(\chi_\alpha) S^{\alpha K}_{j'}(\chi_\alpha)$$

Usgin Eq. (12) the matrix element is reduced to its final form:

$$(P^{ij})^{\alpha\alpha 1}_{n_jK,n'_{j'}K'} = \delta_{jj'}\,\delta_{KK'}\,\epsilon_j^{\alpha K} \otimes \int dv_\alpha\, \upsilon_n^\alpha(v_\alpha)\, n_i^\sigma(v_\alpha)\, n_j^\sigma(v_\alpha)\, \upsilon_{n'}^\alpha(v_\alpha) \tag{32e}$$

We note that

$$(P^{ij})^{\alpha\alpha 1}_{n_jK,n'_{j'}K'} = (P^{ij})^{\alpha\alpha 1}_{n'_{j'}K',n_jK} = (P^{ji})^{\alpha\alpha 1}_{n_jK,n'_{j'}K'} \tag{34}$$

and thus $(P^{ij})^{\alpha\alpha 1}$ is a symmetric matrix when evaluated in complete basis sets or when evaluated as a matrix of the product of the operators.

Similarly, $(P^{ij})^{\alpha\alpha 2}$ can be reduced:

$$(P^{ij})^{\alpha\alpha 2}_{n_jK,n'_{j'}K'} = \delta_{jj'}\,\delta_{KK'}\,[1-\epsilon_j^{\alpha K}] \otimes \int dv_\alpha\, \upsilon_n^\alpha(v_\alpha)\, m_i^\beta(v_\alpha)\, m_j^\beta(v_\alpha)\, \upsilon_{n'}^\alpha(v_\alpha) \tag{35}$$

where $(P^{ij})^{\alpha\alpha 2}$ is again a symmetric matrix.

Consider next $(P^{ij})^{\alpha\beta}$ and consider only the rotational integral:

$$(P^{ij})^{\alpha\beta}_{n_jK,n'_{j'}K'} \propto \sum_{j''K''} \int_0^{\chi_0^*} d\chi_\delta \int_{\chi_\delta^*}^{\pi} d\chi'_\delta \sin\chi_\delta \sin\chi'_\delta\, S_j^{\alpha K}(\chi_\alpha)\, d^j_{KK'}(\epsilon_\beta)\, S_{j''}^{\delta K''}(\chi_\delta)\, S_{j''}^{\delta K''}(\chi'_\delta)\, d^j_{K''K'}(\epsilon_{\alpha'})\, S_{j'}^{\beta K'}(\chi_{\beta'}) \tag{36a}$$

$$= 0$$

Summing the j" sum and integrating of χ'_δ reduced the integral to zero since the ranges of integration do not overlap. Similarly:

$$(P^{ij})^{\beta\alpha} = 0 \tag{36b}$$

Thus, we have, from (30a), using (32e), (35), and (34a) and (34b)

$$
\begin{aligned}
(q_i q_j^T)^{\alpha\alpha} &= \underline{A}_i \underline{A}_j + (\underline{P}^{ij})^{\alpha\alpha 1} + (\underline{P}^{ij})^{\alpha\alpha 2} \\
(q_i q_j^T)^{\alpha\beta} &= \underline{A}_i \underline{M}_j^{\delta T} + \underline{N}_i^{\delta} \underline{A}_j \\
(q_i q_j^T)^{\beta\alpha} &= \underline{M}_i^{\delta} \underline{A}_j + \underline{A}_i \underline{N}_j^{\delta T}
\end{aligned}
\tag{37}
$$

with $\underline{A}_i$, $\underline{A}_j$ diagonal matrices defined in Eq. (28).

At this point we state without derivation properties of the n_i^λ and m_i^λ functions involved in the matching matrices, from which it can easily be shown that conditions (29b) are satisfied

$$
\begin{aligned}
n_1^\lambda &= -(n_4^\lambda)^{-1} & m_1^\lambda &= -(m_4^\lambda)^{-1} \\
n_1^\lambda &= -m_4^\lambda & n_3^\lambda &= m_3^\lambda
\end{aligned}
\tag{38}
$$

From the matrix elements which are explicitly shown in Eqs. (31a) and (31b), and from the relations expressed in (38a), it follows that

$$\underline{N}_4^{\lambda T} = -\underline{M}_1^\lambda \tag{39a}$$

$$\underline{M}_4^{\lambda T} = -\underline{N}_1^\lambda \tag{39b}$$

$$\underline{N}_3^{\lambda T} = \underline{M}_3^\lambda \tag{39c}$$

From Eqs. (37), (32e), and (35)

$$
\begin{aligned}
(q_i q_4^T)^{\alpha\kappa}_{n_j K, n' j' K'} &= \delta_{jj'} \delta_{KK'} \left[1 + \int dV_a U_n^\alpha(V_a) \left\{ \epsilon_j^{\alpha K} n_i^\delta n_4^\delta + (1-\epsilon_j^{\alpha K}) m_i^\delta m_4^\delta \right\} U_{n'}^\alpha(V_a) \right. \qquad (40a) \\
&= 0
\end{aligned}
$$

since $n_1^\gamma n_4^\gamma = m_1^\gamma m_4^\gamma = -1$, and

$$(q_1 q_4^T)^{\alpha\beta} = \underline{\underline{N}}_4^{\gamma T} + \underline{\underline{M}}_1^\gamma = \underline{\underline{0}} \tag{40b}$$

$$(q_1 q_4^T)^{\beta\alpha} = \underline{\underline{M}}_4^{\gamma T} + \underline{\underline{N}}_1^\gamma = \underline{\underline{0}} \tag{40c}$$

Thus $(q_1 q_4^T) = 0$ and it is only left to show that $q_3 q_4^T$ is symmetric. Since $(q_i q_j^T)^{\alpha\alpha}$ is symmetric for all i and j, we need only show $(q_3 q_4^T)^{\alpha\beta} = (q_3 q_4^T)^{\beta\alpha T}$. With $\underline{\underline{A}}_3 = 0$, Eq. (37) reduces to

$$(q_3 q_4^T)^{\alpha\beta} = \underline{\underline{N}}_3^\gamma \tag{41a}$$

$$(q_3 q_4^T)^{\beta\alpha} = \underline{\underline{M}}_3^\gamma \tag{41b}$$

From (39c) it is quickly established that $q_3 q_4^T$ is symmetric.

For the purposes of calculation, $q_3 q_4^T$ in Eq. (29a) is evaluated such that

$$(q_3 q_4^T)^{\alpha\alpha}_{ijk,n'j'k'} = \delta_{jj'}\delta_{kk'} \int dV_\alpha \upsilon_n^\alpha(V_\alpha)\{\epsilon_j^{\alpha k} n_3^\gamma n_4^\gamma + (1-\epsilon_j^{\alpha k}) m_3^\gamma m_4^\gamma\} \upsilon_{n'}^\alpha(V_\alpha) \tag{42a}$$

$$(q_3 q_4^T)^{\alpha\beta} = \underline{\underline{N}}_3^\gamma \tag{42b}$$

$$(q_3 q_4^T)^{\beta\alpha} = \underline{\underline{M}}_3^\gamma \tag{42c}$$

All other elements are obtained by cyclic permutation of the indices. $q_1 q_4^T$ is simply set to zero.

In calculations presented in this paper the global R matrix is constructed via the prescription in Eq. (21) with $\underset{\sim}{X}$ defined by Eq. (23) and with $\underset{\sim}{Q}\underset{\sim}{Z}^{T}$ constructed symmetrically as above. The R matrix so constructed is symmetric and consequently the S-matrix is unitary.

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FIGURE CAPTIONS

Fig. 1 Representation of non-collinear matching surfaces in relation to the $u = 0$ surface and intermediate s = constant surface.

Fig. 2 Schematic representation of the three arrangement channel tubes and the matching surfaces.

Fig. 3 Schematic representation of the coordinate system in the matching region and the directions of the derivatives with respect to the propagation coordinates and the internal coordinates.

Fig. 4 Probability of reaction, $P(0,0,0)_o \rightarrow (0, j, \ell)_o$ vs. E. $J = 0$. (·) Basis 11,9,7,3, 60 steps; (Δ) Basis 13,11,9,5,3,3, 73 steps; (o) 7,5,3, 50 steps; x SK.

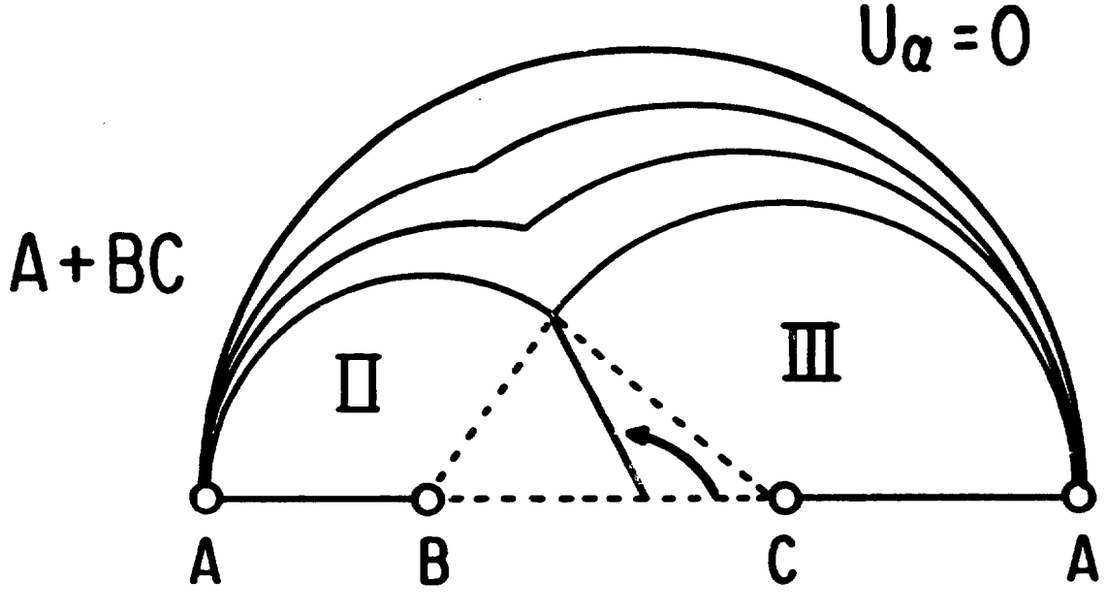
Fig. 5 Contributions to reactive cross section $(2J + 1)\, P_{(000)_o \rightarrow (0\ j\ \ell)_o}$ at E = .65 eV vs. total angular momentum, J. (▬) Basis shown in Table II. (●) Basis 7,5,3.

Fig. 6 As above for $P_{(0\ 1\ \ell)_p \rightarrow (0\ j\ \ell)_p}$. Odd parity x 20.

Fig. 7 Convergence with respect to basis of $P_{(000)_o \rightarrow (0\ j\ \ell)_o}$ for $J = 0$ vs. E. (—●— ·) Basis 13,11,7,5,1, 60 steps; (—✕—✕—) Basis 7,5,3,1, 60 steps; (--0---0--) Basis 7,5,3, 50 steps; (●—●—●) $P_{(000)_o \rightarrow (1, j, \ell)_o}$ basis 13,11,7,5,3,1.

Fig. 8 (—●—) $P_{(001)_o \rightarrow (0\ j\ l)_o}$, J = 1; (—⊙—) $P_{(001)_o \rightarrow (1\ j\ l)_o}$ J = 1, multiplied by two.

Fig. 9 State-to-state transition probability $P_{(000)_o \rightarrow (0\ 1\ 1)_o}$ vs. E, J = 0. (—✱—✱—) Basis 13,11,9,5,3,3, 73 steps; (– – □ – –) Basis 7,5,3, 50 steps; X SK.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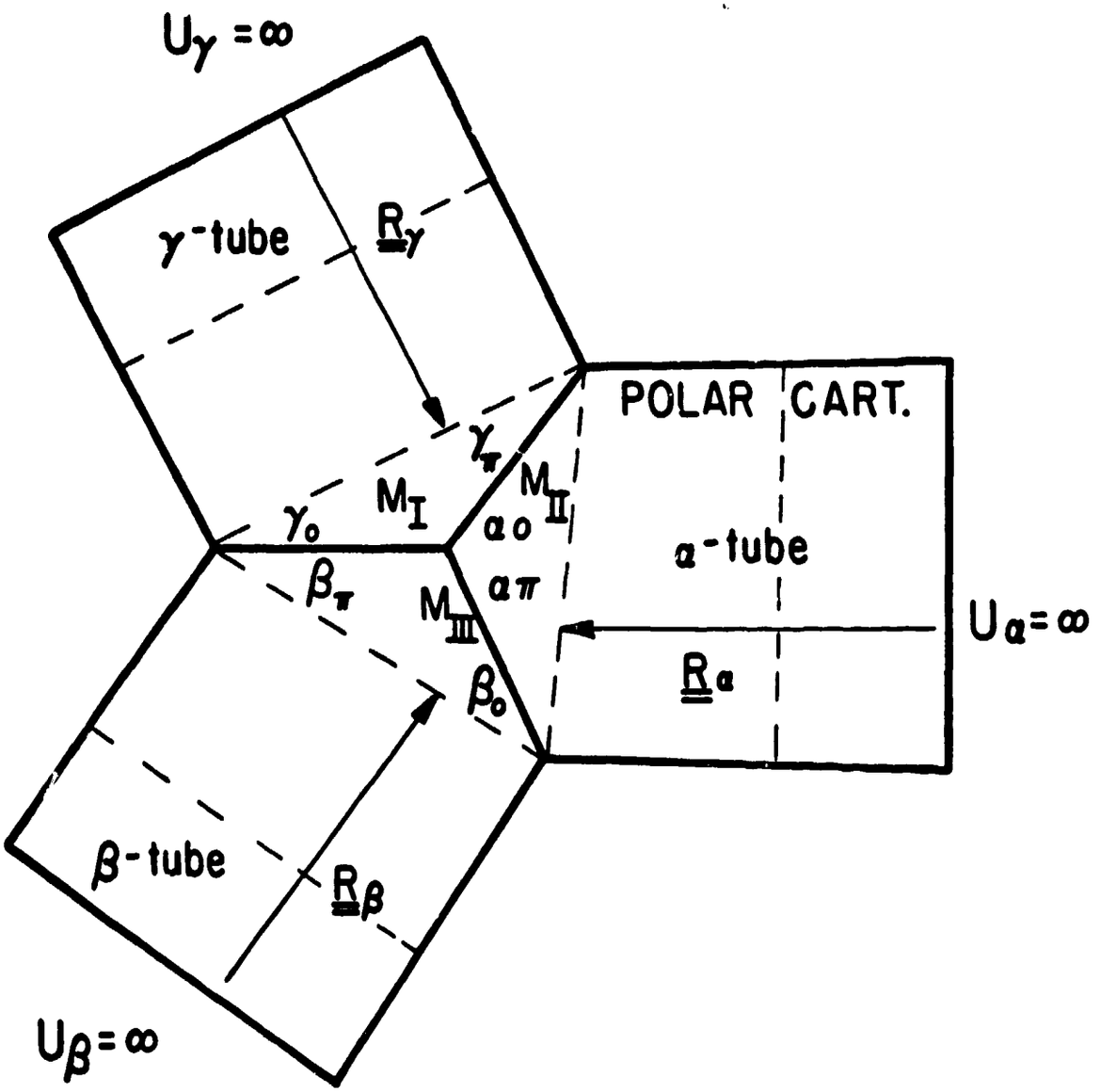
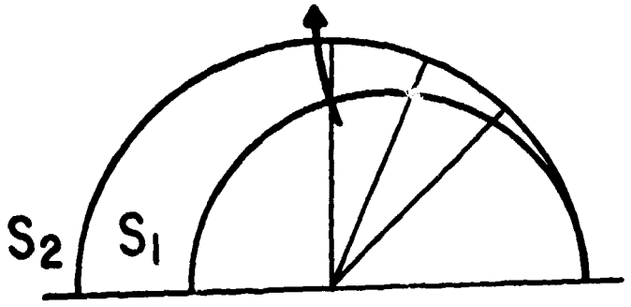
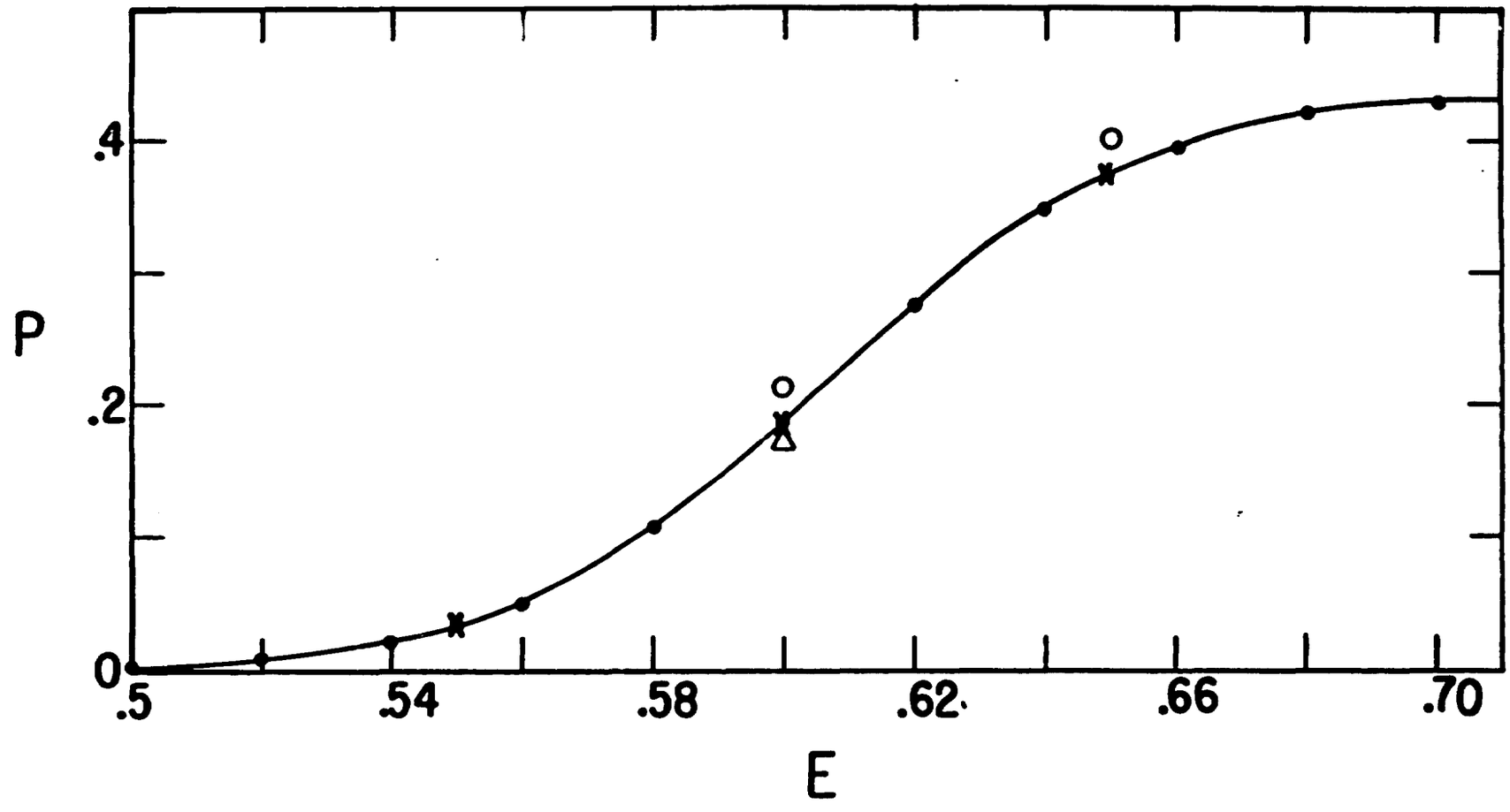
A+BC
II
III
A
B
C
A


$U_\gamma = \infty$
γ-tube
R_γ
γ_π
M_{II}
M_I
γ_o
α_o
POLAR
CART.
α-tube
β_π
α_π
M_{III}
$U_\alpha = \infty$
R_α
β_o
β-tube
R_β
$U_\beta = \infty$


S2
S1


P
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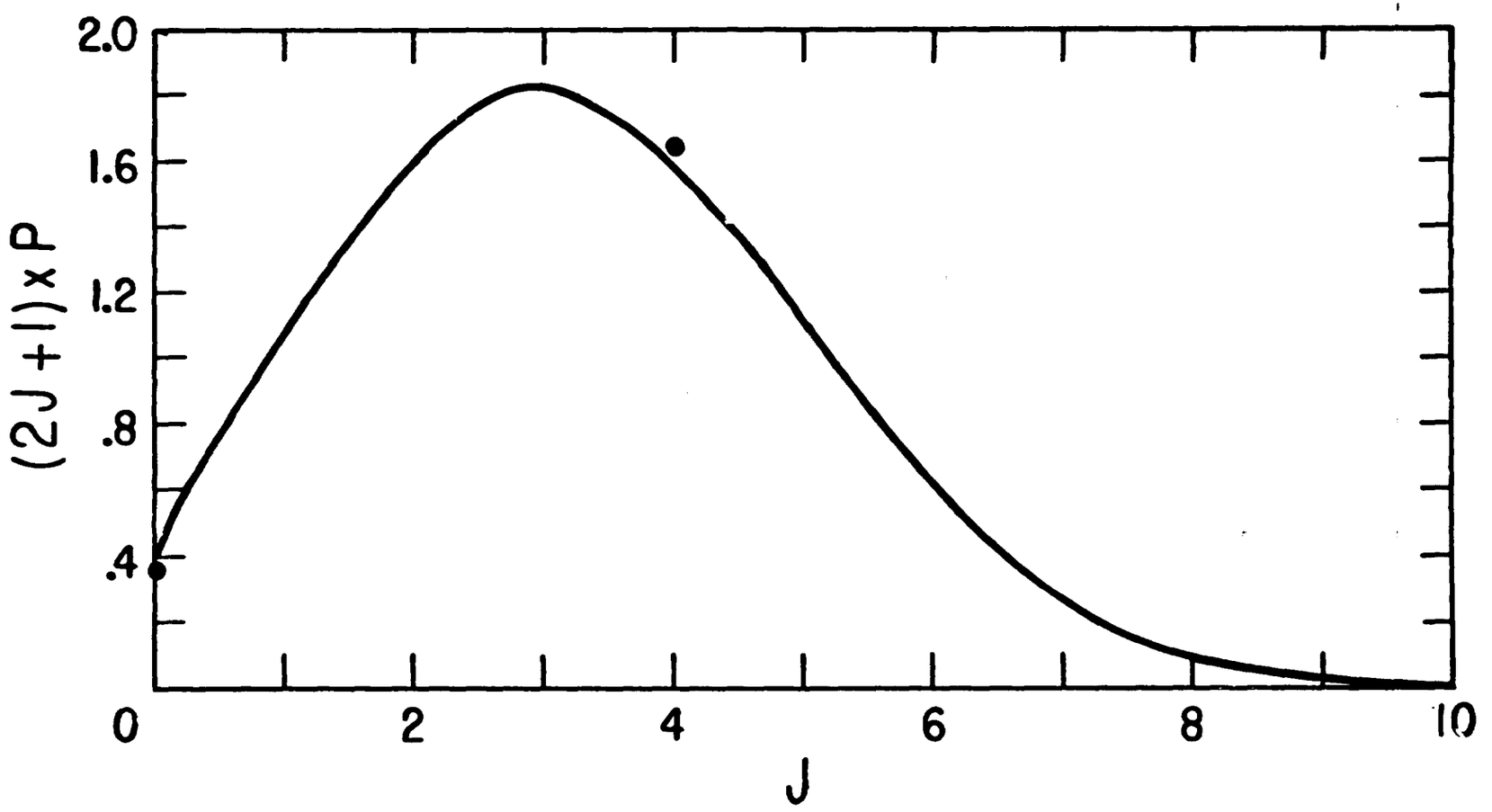
.2
0
.5
.54
.58
.62
.66
.70
E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1.2
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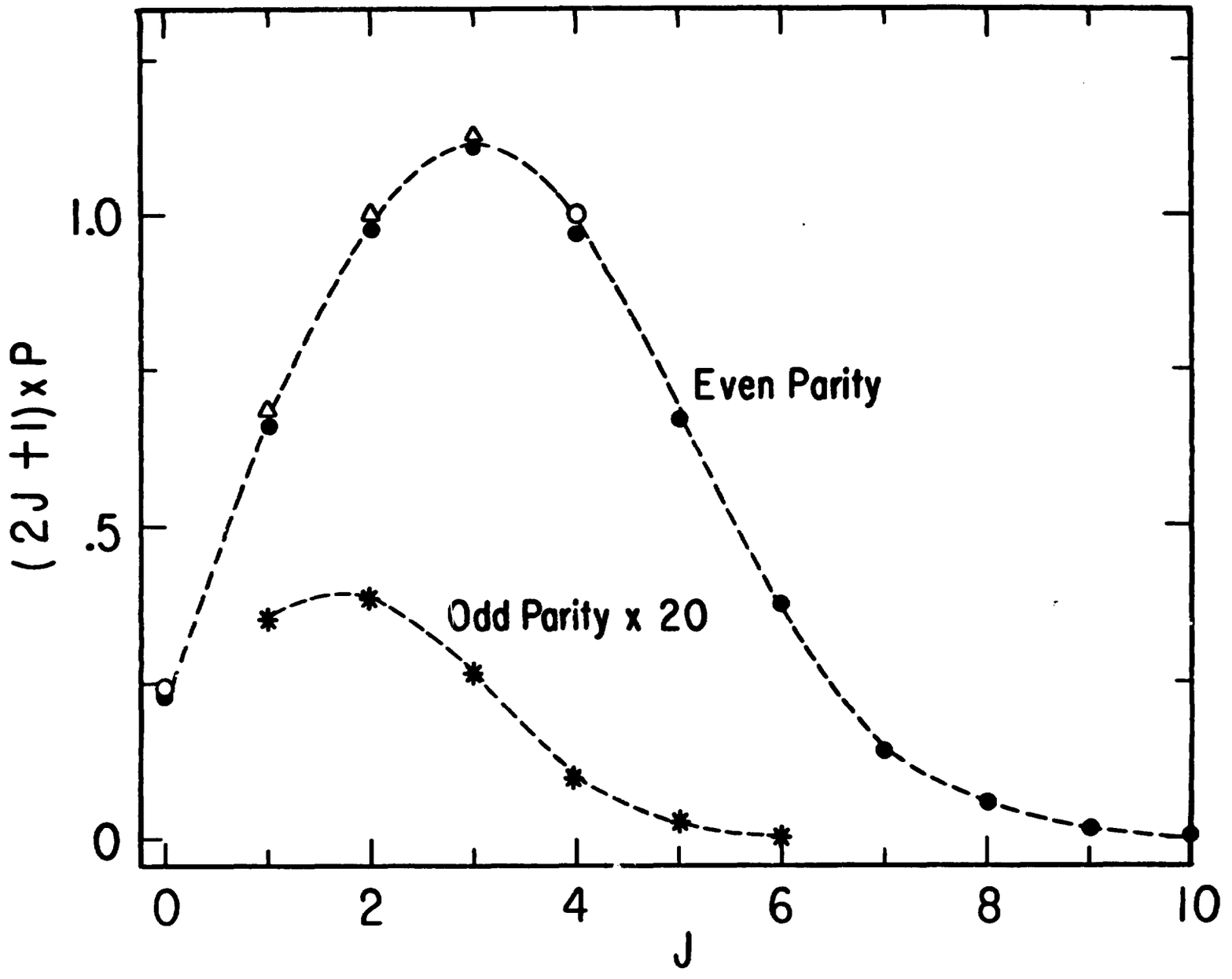
0
2
4
6
8
10
(2J+1)xP
J


1.0
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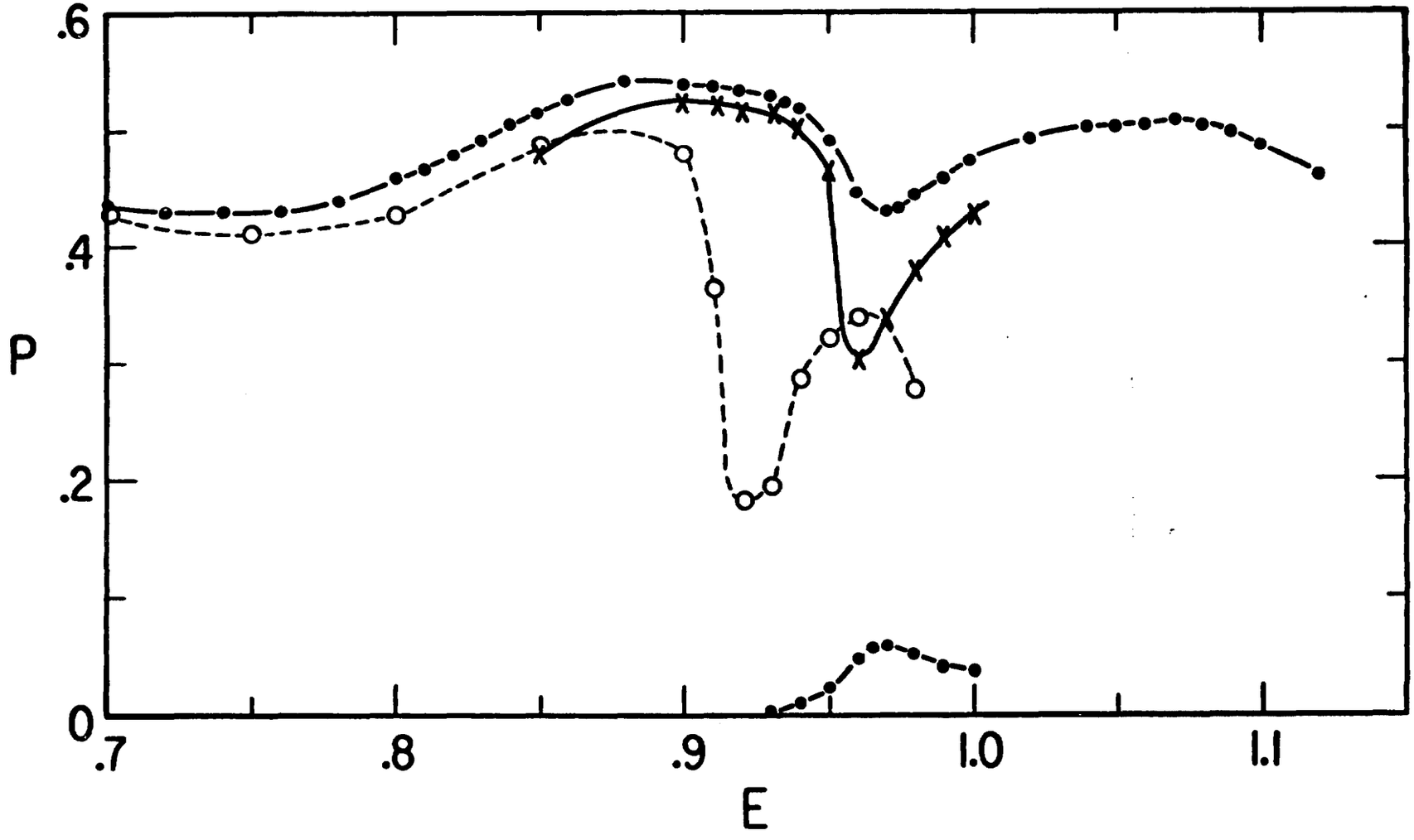
0
(2J+1)xP
Even Parity
Odd Parity x 20
0
2
4
6
8
10
J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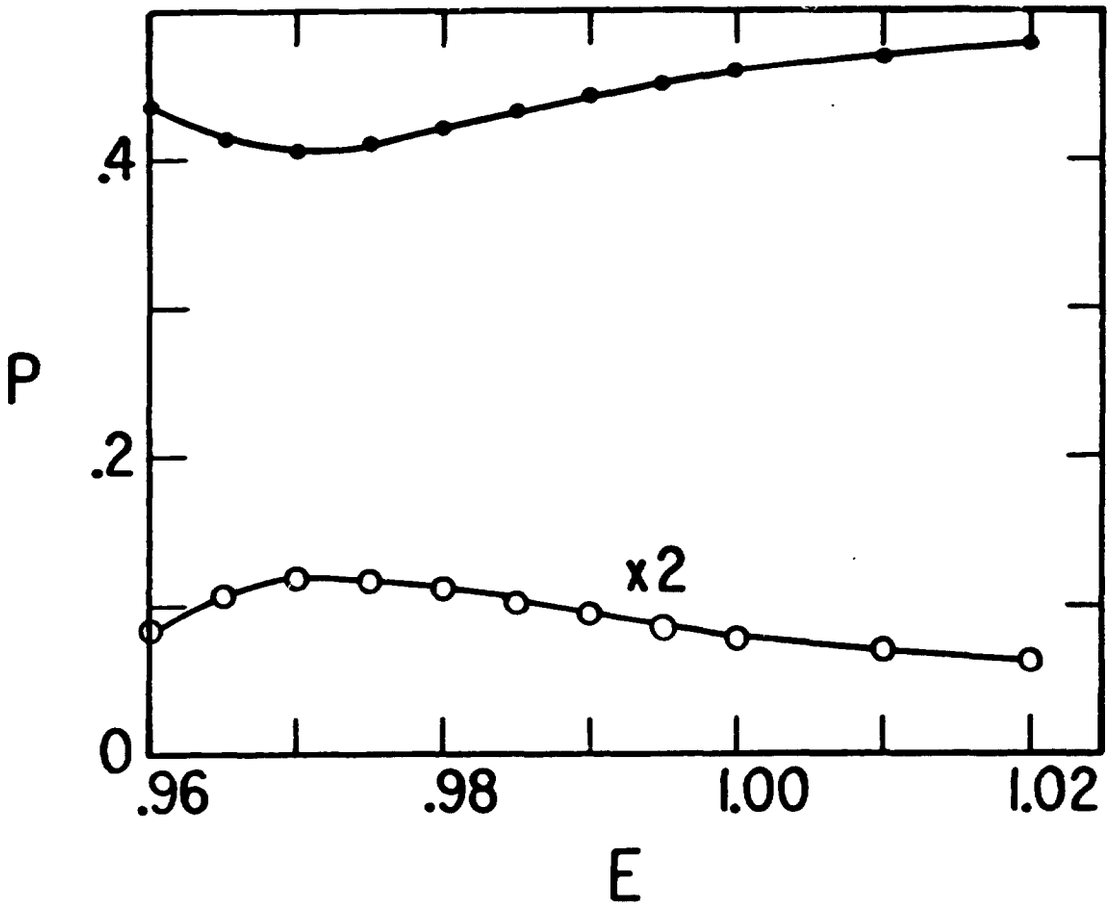
.4
.2
0
P
.7
.8
.9
1.0
1.1
E


P
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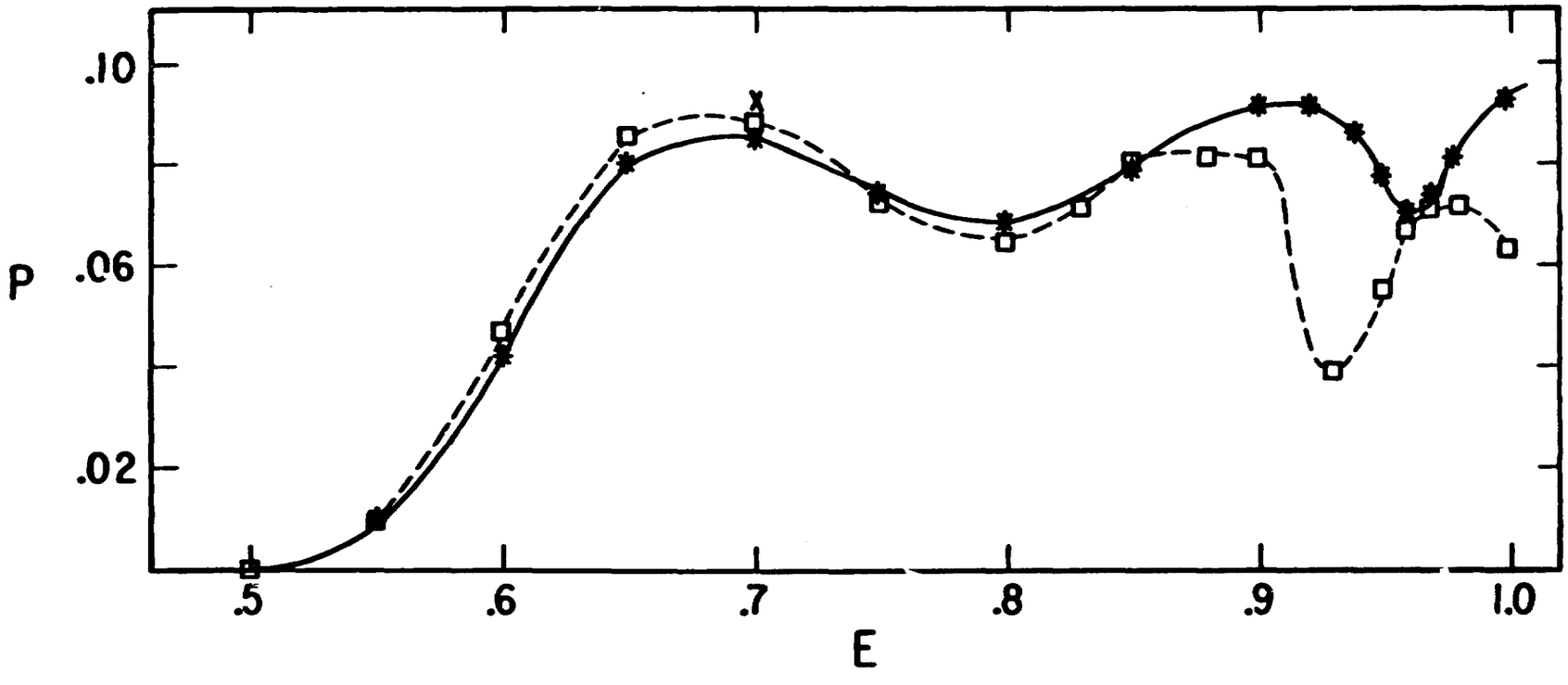
0
x2
.96
.98
1.00
1.02
E


.10
.06
.02
P
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.7
.8
.9
1.0
E