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**The Effects of Potential Energy Surface Features
on Product Vibrational Distributions
for the Reaction $F + H_2 \rightarrow HF + H$**

by
Joel Evan Polowin, B.Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Master of Science
Department of Chemistry

Carleton University
Ottawa, Ontario
May 5, 1988

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on Product Vibrational Distributions
for the Reaction $F + H_2 \rightarrow HF + H$ "

Submitted by Joel Evan Polowin, B.Sc.
in partial fulfillment of the requirements
for the degree of Master of Science

Thesis Supervisor

for Chairman,
Department of Chemistry

Carleton University

May 10, 1988

Abstract

This thesis contains an investigation of reaction dynamics for the $F + H_2 \rightarrow HF + H$ reaction. An *ab initio* potential surface is used as a starting point. Trajectory calculations performed previously on that surface showed incorrect product vibrational energy distributions. The surface is therefore systematically modified using spline functions to investigate the effects on reaction cross-section and product distribution of: depth of reagent and product potential wells, barrier height, collision energy, and relative collision energy.

The distribution is broadened by deeper reagent channel wells, while product wells have no significant effect. Neither strongly affects the cross-section. Increased collinear barrier heights decrease the overall vibrational excitation of the products.

A higher collision energy increases the reactivity to the less-favoured states ($v' = 0, 3$), thereby broadening the distribution. Equal increases to the barrier and the collision energy decrease the reactivity to ($v' = 2$), broadening the distribution.

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1. Introduction

1.1 Potential Energy Surfaces in Common Use

Most of the potential energy surfaces which have been widely used can be classified into one of two broad categories. The first group consists of those that define the potential energy over all configuration space with a relatively simple mathematical function of the bond distances, using only five or six theoretically-, semi-empirically-, or arbitrarily-defined parameters. Examples of this category are the LEP and LEPS-type surfaces (Laidler [1][2] describes several of these; see also [3]) and Johnston's semi-empirical BEBO model [4]; and so on.

These models have several good features. The simplicity of the mathematical functions allows for relatively rapid, inexpensive computation for trajectory calculations. Furthermore, the derivatives of the potential energy function can be determined algebraically and calculated easily. The storage requirements of the database are small: only a few numbers. For these reasons, LEPS surfaces have been extensively used in reaction dynamics, especially by Polanyi and co-workers [5][6].

However, they also have some severe weaknesses. The worst of these is that the functions are rather inflexible: if the model does not fit the given data for some small region of the surface, it is difficult to improve the fit locally since any change made to the parameters will likely alter the remainder of the surface. It may be that there is no combination of the half-dozen parameters which will give an acceptably good fit to the 'true' surface or to known data, if the model is simply inappropriate for the case. Finally, if a great deal of potential energy data is available (for example, from *ab initio* calculations), then unless that data happens to fit the model perfectly, fitting all of the data to only half a dozen parameters is a waste of available information.

The second category of potential energy surfaces contains those whose large databases of potential energy values are calculated either from one of the models in

the first group or (more commonly) from *ab initio* studies. Potential energy values for points between the nodes are interpolated by some means, for example three-dimensional cubic splines [7][8]. This procedure gives a surface which is extremely flexible and which can be fit to data of almost any shape, since the surface is defined by a large number of nearly-independent points. Changing the value of one point affects the interpolated values only in a rather localized region, depending on the interpolation method used. Such a surface makes full use of a large data set if it is available.

This procedure has some great problems, however. One obvious disadvantage is the large storage requirement for a three-dimensional grid of data, multiplied by a factor of 7 or 8 to store the parameters needed for the interpolation. A potential energy surface defined by a 20-point grid (about the minimum for acceptable resolution) must take 8000 node values as input, as well as reading or calculating another 55000 to 65000 parameter values. Alternatively, parameter values could be calculated locally when needed but the computation time for running trajectories would be prohibitive. Furthermore, if the grid points are calculated by *ab initio* procedures, the cost in computer processing to calculate the large number of points is extremely high.

There are also inherent problems with the functions chosen to interpolate the three-dimensional grid. The first is of the 'spline-overshoot' type, where the behaviour of the interpolating function between nodal points can give a wrinkled or uneven surface if the curvature between nodal points is too great. Even if the surface is smooth, the interpolation may not precisely match the correct values; Sathyamurthy and Raff [8] found that the standard deviation of some values interpolated on a three-dimensional spline was rather large, although the increase in error associated with a change from two- to three-dimensional splines is less than that accompanying the change from one- to two-dimensional splines.

If the three dimensions of the grid refer to the three bond distances, another problem exists for *ab initio* surfaces: some of the grid points correspond to sets of bond distances that cannot physically occur [9][10]. This is the case whenever one of the distances is greater than the sum of the other two (the triangle inequality).

Either the missing grid points must be filled in (arbitrarily or by some form of extrapolation from points which are present) or some form of interpolation must be used which takes the missing points into account. For purposes of running trajectories the missing points are not a direct problem since they correspond to non-physical situations that the system cannot be in. They do, however, have an effect on the interpolation of points near the boundaries. This problem, of course, does not occur if the data is obtained from a calculation which does not require physical meaning for calculation (*e.g.* a LEPS-type calculation which operates on the three bond distances regardless of whether or not they can actually form a triangle), or if a coordinate system is chosen which does not have such non-physical points.

1.2 RMCS Potential Energy Surface

The Rotated Morse Curve, Cubic Spline (or RMCS) surface [10][11][12][13][14][15] is a potential energy surface which is able to combine the better features of the two extremes above. This model uses two-dimensional splines of Morse parameters, and thus has the flexibility and regionspecificity of spline interpolation. It operates in a bond-length bond-angle coordinate system, and thus avoids interpolation of non-physical points. The model has been used to construct several kinds of surfaces, including O_3 [16], H_2O [17], FOH [18], FHH [19][20], HFH [19], $O(^3P)$ and $O(^1D) + H_2$ [20][21], $H + H_2$ [22] and $H^* + FH$ [23]. The RMCS fit is enhanced if a five-parameter generalized Morse function (GMF5) [24][25] is used, since the additional two parameters extend the region of fit of the Morse-like curve to bond distances approaching the dissociation limit [19]. A change made to one of the nodes has a rather localized effect on interpolated values, since the resulting changes to the spline parameters tend to damp out fairly quickly. Finally, the use of two-dimensional splines results in a moderate storage requirement and a lower degree of error than is yielded by three-dimensional splines.

The method does have some problems, however. Even a two-dimensional spline will give an uneven or wrinkled surface due to oscillatory behaviour of the function if the change in curvature between two adjacent sets of nodes is too great; the curve must be examined carefully to ensure that this does not occur. Adjustments made

to improve the fit of a node to a curve in one dimension may ruin the fit in the other dimension.

There is an additional problem if the data to which the potential energy surface is being fitted is generated by *ab initio* procedures or other means which do not reduce the triatomic system to a set of essentially unrelated diatomics. When the two bond distances are approximately the same, the potential energy grows rapidly as the bond angle decreases, such that those data points cannot be described accurately by spline functions for angles of less than 60° . This is not directly a problem since in a triatomic system at least one of the bond angles must be greater than 60° ; one has only to create three surfaces (assuming three different atoms; for each identical atom one less surface is needed) and fit data for the bond angle γ where $180^\circ \geq \gamma \geq 60^\circ$ for each. The potential energy of the system is obtained from the surface corresponding to the largest bond angle.

During a trajectory, however, the system is continually changing, and which of the three angles is the largest, for the specific points on the surface over which the trajectory is being run, will change. The potential energy data will suddenly be taken from different surfaces, depending on how the geometry changes as the reagents meet and interact. Since the surfaces are fit to different sets of data and are fit in different directions in real space, the two may yield different values for the potential energy for the same physical coordinates of the atoms. Similarly, the derivatives of the potential energy with respect to the three bond distances, needed for the trajectory, may be different on the two surfaces. This lack of continuity may cause an error in the calculation of the trajectory and certainly will tend to indicate a poor energy conservation for the trajectory even if the calculation itself is good.

This continuity problem can be corrected by the use of some form of surface blending. Instead of abruptly changing from one surface to another when one bond angle grows larger than the others, both surfaces are used when two angles are large. Potential energies and their derivatives are taken from both surfaces, and weighted according to the bond angles to give a final average result which is used by the trajectory program [19][26].

Conversion from three bond distances to RMCS coordinates is straightforward. Bond angles are obtained from the cosine law, for example

$$\gamma = \cos^{-1} \left(\frac{R_{AB}^2 + R_{BC}^2 - R_{AC}^2}{2R_{AB}R_{BC}} \right).$$

Choosing a bond angle also selects the two adjacent bond distances, say R_{AB} (vertical axis; see Figure 1 on page 10) and R_{BC} (horizontal). If the swing point is at coordinates (s, s) then the swing angle θ is obtained from

$$\theta = \tan^{-1}((s - R_{AB})/(s - R_{BC}))$$

and the distance ℓ of the specified point from the swing point is given by

$$\ell = [(s - R_{BC})^2 + (s - R_{AB})^2]^{\frac{1}{2}}.$$

The γ , θ and ℓ values permit calculation of a potential energy (see Section 2.1). It should be noted that calculations in this coordinate system assume that the potential energy surface axes are at right angles. To draw a surface which could correctly represent a trajectory as a moving mass point, the vertical axis would have to be rotated by clockwise by an angle Φ where

$$\sin^2 \Phi = m_A m_C / (m_B + m_C)(m_A + m_B)$$

if the reaction is $A + BC \rightarrow AB + C$ [4].

1.3 The "Proper" Shape of a Potential Energy Surface

"Goodness of fit" to some functional form aside, assessment of the correctness of a potential energy surface is far from simple. Except for the diatomic limits, where the potential energy is fairly well defined, the true shape of no triatomic potential energy surface is known exactly. Even the reaction $F + H_2 \rightarrow HF + H$, which is perhaps the most thoroughly-studied simple reaction, both experimentally [27][28][29][30][31][32] and theoretically [3][19][33][34][35][36][37][38] (see also review articles [6],[39],[40]), occurs on a surface the details of whose structure are quite uncertain.

The problem is that experiments do not give direct information about a potential energy surface. Experimental data on product vibrational and rotational distributions allow inference as to whether the reaction barrier is early or late. Molecular scattering patterns, obtained by experiment, give information about the reaction intermediates' stabilities and thus about the presence or absence of potential wells at the barrier. Reaction rates, determined by kineticists, suggest the relative height of the barrier. Specific information about the variation of the barrier height with different geometries of reagents is not possible in a laboratory situation where the geometries cannot be selected for. No direct information is available with regard to the presence or absence of shallow wells in the reagent or product valleys of the surface.

What can be done is to perform trajectory calculations using a trial potential energy surface, and to compare such results as product rotational, vibrational and scattering angle distributions, reaction cross-section and calculated reaction rate to experimental data. If, according to such tests, the simulated reactions match experimental results, the surface at least may be correct. Some attempts have been made to correlate changes in the parameters of LEPS-type surfaces with changes in product distributions [6] and these have met with some success. Muckerman's surface M5 [40], obtained by such modifications of LEPS parameters, gives trajectory results whose product vibrational distributions (the most common test of surfaces) closely match experimental results. The reaction cross section and rate constant, however, are only about one-fifth of the correct values. This changing of parameters does not give much information about the correct shape of the surface, however, since changing a LEPS-type parameter changes the surface globally (see figures in [6], for example) and it is not simple to determine which change or changes in the surface shape have caused a change in trajectory results.

That the correct shape of the potential energy surface is unknown even for the most-studied reaction in the field is a bit surprising. A systematic investigation of the effect of changing surface features was needed to show precisely what the effects of those features are on the characteristics of the reaction products.

It was therefore decided to use the *ab initio* RMCS surface of Williams, Wright

and Donaldson [19][20] as the starting point for a surface of the correct general shape to study the effects of surface features on the product vibrational distributions of the reaction $F + H_2 \rightarrow HF + H$. Since the RMCS surface used splines as the interpolating functions, it was possible to systematically alter specific surface features such as reagent and product well depths and barrier height and location independently of the remainder of the surface. By determining the effects of each surface feature, the ultimate goal of this work was to be able to work from the experimental vibrational distribution of the products to what the potential energy surface would have to be like to produce that distribution.

Because there is some contention as to the depth of the potential wells on the reagent and product sides of the reaction barrier ("reagent and product wells"), and even as to whether or not they exist [3][6][40], a series of trajectories was performed on a set of surfaces identical except for the depths of these wells. Similarly, the height of the collinear reaction barrier is uncertain (most surfaces yield a cross-section σ which is too small, implying a too-high barrier); accordingly, a series of trajectories was run on surfaces identical except for barrier height. In each case, the product vibrational distribution was determined and, in comparison with experimental and previous theoretical values, used to determine the relative correctness of the surface. In a similar fashion, the hypothesis that a high collision energy will broaden the vibrational distribution of the products by allowing successful reactions to occur with a greater range of allowable motions (the reagents will be less 'channelled' by the potential energy valley) was tested. Finally, a series of trajectories was run with a constant difference between collinear barrier height and collision energy in order to separate the effects of higher collision energy from those of the higher barrier.

2. Method

2.1 Wright and Williams' Surface S0

The original *ab initio* surface S0 was constructed by Wright and Williams [19][20] by computing data points using the MRD-CI method and program of Buenker and Peyerimhoff and co-workers [41][42][43]. At the CI stage, the method makes use of multiple reference configurations, based on a single SCF wave function. Each reference configuration was explicitly included in the CI wave function only if its (squared) contribution exceeded 0.005 [44]. All single excitations of reference configurations were automatically included; double excitations were included only when they lowered the energy of a test secular equation by more than a specified threshold. The selection threshold was varied between 0–15 μ hartree for the different points so as to use not more than 3500 symmetry-adapted functions ("configurations") in the CI diagonalization. The energy at zero threshold was predicted by extrapolation; this approximates the computationally-expensive case in which all single and double excitations from all reference configurations would be included. Also, a correction was made to simulate the inclusion of quadruple excitations [45]. The resulting energy was used to construct the potential surface. In the CI calculations, the fluorine 1s core and its complement remained frozen.

The "balanced basis set" reported by Wright and Williams [46] was used in these calculations. It consists of a double-zeta + polarization set of Gaussian-type orbitals, with exponents from Huzinaga [47] and the Dunning [48] contraction (9s5p1d/4s2p1d) on fluorine (*d* exponent 0.90) and (4s1p/2s1p) on hydrogen (*p* exponent 1.0). The *d* orbitals also contained a sixth component, the $x^2 + y^2 + z^2$ function. One *s* and three *p* functions located at each bond midpoint were used to augment the double-zeta + polarization basis set, except for relatively linear geometries in which the long bond was not augmented (see below). The *s* and *p* exponents were chosen to be identical, and optimized for the FH diatomic as 0.35

for H-H, and 0.85 for F-H bonds. Finally, the atom-centered hydrogen exponents were scaled for molecular environments by a factor of 1.2, as suggested by Dunning [48].

The use of bond functions allows a more efficient description of bonding regions than use of atom-centered orbital functions alone. However, for purposes of constructing a surface they can lead to problems in consistency of procedure and continuity of results. For geometries which are collinear or nearly so, bond functions at the center of the long bond are very close to the central atom and tend to act as nuclear-centered diffuse polarization functions; this can artificially lower the molecular energy. However, for less linear geometries, having a set of bond functions along each bond is desired. Accordingly, for geometries with bond angles of 180° and 150° , only two sets of bond functions were employed (without the set on the long bond) while for 120° , 90° and 60° three were used [19].

For each of the molecular geometries described above, rays were selected through the swing point at (10,10) bohr [11][12][13] with swing angles θ between 0° and 90° so as to span the surface (see Figure 1).

For the FHH surfaces, angles of 0.0, 10.0, 20.0, 25.0, 27.5, 30.0, 32.5, 35.0, 37.0, 39.0, 40.0, 41.0, 43.0, 45.0, 48.0, 50.0, 55.0, 60.0, 70.0, 80.0 and 90.0° were used. For the HFH surfaces, the angles used were 0.0, 10.0, 20.0, 30.0, 35.0, 37.5, 40.0, 42.0, 44.0, 45.0, 46.0, 48.0, 50.0, 52.5, 55.0, 60.0, 70.0, 80.0 and 90.0° . The rays are closely spaced between 37° and 50° on the FHH surfaces, and 40° and 60° on the HFH surfaces, so as to accurately fit the important region around the reaction barrier and to minimize the risk of spline interpolation errors where the parameter values are changing rapidly. Nine or ten CI points were calculated along each ray, spanning 80 to 90% of the well depth. These data points were fitted to the five GMF5 parameters D_e , ℓ_e , β_0 , λ_1 and λ_2 by a non-linear least-squares program, where D_e is the depth of the Morse-like curve from the separated-atom limit, ℓ_e is the distance from the swing point to the curve minimum, β_0 is the curve steepness parameter, and λ_1 and λ_2 are parameters to improve the curve fit for

Figure 1.: Mapping PES With Rays Through Swing Point

Note the greater density of rays around the transition point.

smaller distances ℓ from the swing point, for

$$\begin{aligned} V(R_{AB}, R_{BC}, R_{AC}) &= V(\gamma, \theta, \ell) \\ &= D_e(\gamma, \theta) \left[1 - e^{\beta(\gamma, \theta, \ell)x} \right]^2 - D_e(\gamma, \theta) \end{aligned}$$

$$\text{where } x = \ell - \ell_e(\gamma, \theta)$$

$$\text{and } \beta(\gamma, \theta, \ell) = \beta_0(\gamma, \theta) [1 + \lambda_1(\gamma, \theta)x + \lambda_2(\gamma, \theta)x^2]$$

For both sets of surfaces, artificial data for the GMF5 parameters were generated for the non-interactive regions using exact relationships reported by Wright and Gray [10] and Williams [19]. For the reactant non-interaction region:

$$D(\theta) = D(0^\circ)$$

$$\ell_e(\theta) = \ell_e(0^\circ) / \cos \theta$$

$$\beta_0(\theta) = \beta_0(0^\circ) \cos \theta$$

$$\lambda_1(\theta) = \lambda_1(0^\circ) \cos \theta$$

$$\lambda_2(\theta) = \lambda_2(0^\circ) \cos^2 \theta$$

For the product non-interaction region, similar relationships were obtained by replacing 0° by 90° and 'cos' by 'sin' in the above expressions. Finally, some interpolated values of the parameters were included as nodal points to eliminate spline overshoots near the barrier on the FHH surfaces. In this way two distinct surfaces were created, the FHH and the HFH surfaces.

The results of the GMF5 fit to the CI data for the FHH surface at the five fixed bond angles are shown in Table 1. Splined curves showing the variation of each of the five parameters with θ for the collinear (180°) surface are shown in Figure 2, and similar curves showing the parameters for the other FHH fixed-bond-angle surfaces of S0 are shown in Figures 3 through 7. Figure 8 shows the actual potential energy surfaces generated from those parameters.

Similarly, the results of the GMF5 fit to the CI data for the HFH surface at the five fixed bond angles are shown in Table 2. The splined curves showing the variation of each of the five parameters with θ for the collinear (180°) surface are

Table 1.: a) GMF5 Fit of CI Data for S0 FHH 180°

$\theta/^\circ$	D_e/eV	β_0/bohr^{-1}	ℓ_e/bohr	$\lambda_1/\text{bohr}^{-1}$	$\lambda_2/\text{bohr}^{-2}$
0.00	4.7415	1.0468	8.6008	0.073405	0.064459
10.0	4.7415	1.0309	8.7335	0.072290	0.063480
20.0	4.7415	0.9837	9.1528	0.068978	0.060572
25.0	4.7559	0.9484	9.4295	0.064464	0.050742
27.5	4.7566	0.9251	9.6958	0.065909	0.051752
30.0	4.7602	0.9021	9.9316	0.065943	0.051623
32.5	4.7736	0.8830	10.1994	0.060776	0.044478
35.0	4.7849	0.8632	10.5001	0.054868	0.034678
37.0	4.7838	0.8402	10.7631	0.053456	0.032835
39.0	4.7668	0.8115	11.0357	0.048124	0.035388
40.0	4.7439	0.8040	11.1700	0.039366	0.025663
41.0	4.7529	0.7822	11.2995	0.040663	0.035472
43.0	5.1319	0.7947	11.4904	0.006271	0.025315
45.0	5.6446	0.8212	11.4536	0.011349	0.024871
48.0	6.0804	0.8795	11.0792	0.032494	0.030232
50.0	6.1756	0.9155	10.7818	0.038930	0.032320
55.0	6.2057	0.9836	10.0985	0.045482	0.038301
60.0	6.1881	1.0426	9.5526	0.046717	0.041780
70.0	6.1639	1.1294	8.8016	0.050312	0.052560
80.0	6.1639	1.1836	8.3984	0.052728	0.055084
90.0	6.1639	1.2019	8.2708	0.053541	0.055934

Table 1. (contd.): b) GMF5 Fit of CI Data for S0 FHH 150°

$\theta/^\circ$	D_e/eV	β_0/bohr^{-1}	ℓ_e/bohr	$\lambda_1/\text{bohr}^{-1}$	$\lambda_2/\text{bohr}^{-2}$
0.00	4.7415	1.0468	8.6008	0.073405	0.064459
10.0	4.7445	1.0309	8.7335	0.072290	0.063480
20.0	4.7415	0.9837	9.1528	0.068978	0.060572
25.0	4.7614	0.9561	9.4878	0.051763	0.042855
27.5	4.7675	0.9362	9.6962	0.054075	0.040973
30.0	4.7739	0.9143	9.9328	0.056144	0.039818
32.5	4.7820	0.8931	10.1975	0.049585	0.034126
35.0	4.7739	0.8684	10.4976	0.046036	0.030063
37.0	4.7543	0.8424	10.7630	0.050621	0.031683
39.0	4.7505	0.8183	11.0328	0.040320	0.028058
40.0	4.7345	0.8132	11.1707	0.029203	0.022679
41.0	4.7365	0.7999	11.3046	0.034112	0.027040
43.0	5.0876	0.8139	11.4840	-0.007990	0.016219
45.0	5.5981	0.8195	11.4377	0.004679	0.029344
48.0	6.0220	0.8804	11.0785	0.034331	0.038214
50.0	6.1376	0.9124	10.7753	0.030539	0.037166
55.0	6.1737	0.9932	10.0998	0.038947	0.036348
60.0	6.1657	1.0466	9.5507	0.039284	0.040042
70.0	6.1639	1.1294	8.8016	0.050312	0.052560
80.0	6.1639	1.1836	8.3984	0.052728	0.055084
90.0	6.1639	1.2019	8.2708	0.053541	0.055934

Table 1. (contd.): c) GMF5 Fit of CI Data for S0 FHH 120°

$\theta/^\circ$	D_c/eV	β_0/bohr^{-1}	ℓ_c/bohr	$\lambda_1/\text{bohr}^{-1}$	$\lambda_2/\text{bohr}^{-2}$
0.00	4.7415	1.0468	8.6008	0.073405	0.064459
10.0	4.7415	1.0309	8.7335	0.072290	0.063480
20.0	4.7415	0.9837	9.1528	0.068978	0.060572
25.0	4.7613	0.9587	9.4909	0.055901	0.041321
27.5	4.7703	0.9332	9.6947	0.056819	0.041545
30.0	4.7701	0.9138	9.9344	0.058662	0.041646
32.5	4.78	0.9080	10.2126	0.052899	0.033384
35.0	4.78	0.8676	10.4861	0.028587	0.024865
37.0	4.6360	0.8072	10.7106	0.011011	0.025850
39.0	4.8223	0.8191	11.0348	0.034586	0.026838
40.0	4.8247	0.8183	11.1680	0.016751	0.018676
41.0	4.8328	0.8051	11.3014	0.015	0.024565
43.0	5.0791	0.8129	11.4516	-0.015067	0.018786
45.0	5.5130	0.8167	11.4084	0.005197	0.027968
48.0	6.0117	0.8776	11.0652	0.030010	0.032845
50.0	6.1561	0.9144	10.7749	0.035656	0.033435
55.0	6.2196	0.9857	10.0979	0.042345	0.037716
60.0	6.1849	1.0424	9.5525	0.047425	0.042920
70.0	6.1639	1.1294	8.8016	0.050312	0.052560
80.0	6.1639	1.1836	8.3984	0.052728	0.055084
90.0	6.1639	1.2019	8.2708	0.053541	0.055934

Table 1. (contd.): d) GMF5 Fit of CI Data for S0 FHH 90°

$\theta/^\circ$	D_e/eV	β_0/bohr^{-1}	ℓ_e/bohr	$\lambda_1/\text{bohr}^{-1}$	$\lambda_2/\text{bohr}^{-2}$
0.00	4.7415	1.0468	8.6008	0.073405	0.064459
10.0	4.7415	1.0309	8.7335	0.072290	0.063480
20.0	4.7415	0.9837	9.1528	0.068978	0.060572
25.0	4.7646	0.9551	9.4912	0.061135	0.043467
27.5	4.7753	0.9348	9.6993	0.071451	0.044173
30.0	4.7645	0.9102	9.9310	0.057537	0.038929
32.5	4.76	0.8826	10.1824	0.001469	0.018709
35.0	4.7045	0.8524	10.4512	-0.009344	0.011805
37.0	4.3950	0.8272	10.6996	0.044247	0.029750
39.0	4.8169	0.8071	11.0127	0.033343	0.035
40.0	4.8037	0.7998	11.1327	0.018579	0.030
41.0	4.7892	0.7870	11.2329	0.007524	0.035674
43.0	4.8501	0.8198	11.3328	-0.047836	0.010
45.0	5.1264	0.8143	11.2864	-0.031402	0.023
48.0	5.7548	0.8769	11.0193	0.014258	0.025232
50.0	6.0033	0.9155	10.7553	0.030160	0.027155
55.0	6.1830	0.9867	10.0953	0.043916	0.033914
60.0	6.1831	1.0434	9.5522	0.047966	0.039929
70.0	6.1639	1.1294	8.8016	0.050312	0.052560
80.0	6.1639	1.1836	8.3984	0.052728	0.055084
90.0	6.1639	1.2019	8.2708	0.053541	0.055934

Table 1. (contd.): e) GMF5 Fit of CI Data for S0 FHH 60°

$\theta/^\circ$	D_e/eV	β_0/bohr^{-1}	ℓ_e/bohr	$\lambda_1/\text{bohr}^{-1}$	$\lambda_2/\text{bohr}^{-2}$
0.00	4.7415	1.0468	8.6009	0.073405	0.064459
10.0	4.7415	1.0309	8.7335	0.072290	0.063480
20.0	4.7415	0.9837	9.1528	0.068978	0.060572
25.0	4.7720	0.9543	9.4921	0.064197	0.044946
27.5	4.77	0.9467	9.7012	0.056553	0.036143
30.0	4.7652	0.9152	9.9317	0.050895	0.034699
32.5	4.4709	0.8453	10.1814	0.051608	0.044062
35.0	4.4449	0.8070	10.4703	0.050	0.048
37.0	4.8235	0.8155	10.7296	0.045163	0.045
39.0	4.7887	0.7683	10.9469	0.025579	0.050
40.0	4.7932	0.7663	11.0217	-0.013287	0.035
41.0	4.7357	0.7439	11.0627	-0.021861	0.040
43.0	4.5405	0.7238	11.0174	-0.061335	0.047010
45.0	4.2536	0.7167	10.9412	-0.042686	0.054761
48.0	4.7712	0.8170	10.8557	0.004325	0.033704
50.0	5.4451	0.8778	10.6746	0.025563	0.033537
55.0	6.1040	0.9803	10.0810	0.037197	0.031925
60.0	6.1925	1.0440	9.5502	0.044843	0.035948
70.0	6.1639	1.1294	8.8016	0.050312	0.052560
80.0	6.1639	1.1836	8.3984	0.052728	0.055084
90.0	6.1639	1.2019	8.2708	0.053541	0.055934

Figure 2.: a) GMF5 Fit of S0 FHH 180°: D_e vs. θ

Actual points are circled; curve obtained by spline interpolation.

Figure 2. (contd.): b) GMF5 Fit of S0 FHH 180°: β_0 vs. θ

Figure 2. (contd.): c) GMF5 Fit of S0 FHH 180°: ℓ_e vs. θ

Figure 2. (contd.): d) GMF5 Fit of S0 FHH 180°: λ_1 vs. θ

Figure 2. (contd.): e) GMF5 Fit of S0 FHH 180°: λ_2 vs. θ

Figure 3.: GMF5 Fit of S0 FHH D_e vs. θ

a) 150° b) 120° c) 90° d) 60°

Figure 4.: GMF5 Fit of S0 FHH β_0 vs. θ

a) 150° b) 120° c) 90° d) 60°

Figure 5.: GMF5 Fit of S0 FHH ℓ_e vs. θ

a) 150° b) 120° c) 90° d) 60°

Figure 6.: GMF5 Fit of S0 FHH λ_1 vs. θ

a) 150° b) 120° c) 90° d) 60°

Figure 7.: GMF5 Fit of S0 FHH λ_2 vs. θ

a) 150° b) 120° c) 90° d) 60°

Figure 8.: a) S0 FHH 180° Potential Energy Surface

Contours shown are -3.0 (outer), -4.0, -4.5, -4.7, -4.76, -5.0, -5.5, -6.0 and -6.18 eV. These contours, and those following, were chosen by Williams [19] to display surface features for this system.

Figure 8. (contd.): b) S0 FHH 150° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.5, -4.7, -4.76, -5.0, -5.5, -6.0 and -6.18 eV.

Figure 8. (contd.): c) SO FHH 120° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.6, -4.7, -4.77, -5.0, -5.5, -6.0 and -6.18 eV.

Figure 8. (contd.): d) S0 FHH 90° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.5, -4.6, -4.74, -5.0, -5.5, -6.0 and -6.18 eV.

Figure 8. (contd.): e) S0 FHH 60° Potential Energy Surface.

Contours shown are -3.0, -4.0, -4.27, -4.5, -4.75, -5.0, -5.5, -6.0 and -6.18 eV.

shown in Figure 9, and the parameters for the other HFH fixed-bond-angle surfaces of S0 are shown in the curves in Figures 10 through 14. The actual potential energy surfaces generated from those parameters are shown in Figure 15.

The GMF5 parameters for the two surfaces were connected in two dimensions (γ, θ) by the two-dimensional spline-fitting program JPM5COEF1 (see Appendix B.1).

2.2. Scaled Surface S1

Although the S0 surfaces are similar to other surfaces for the $F + H_2$ reaction and have characteristics similar to what information is available from experiment, there are some important differences. The diatomic D_e values are incorrect: the S0 D_e for H_2 is 4.7415 eV whereas the experimental value is 4.7477 eV [49][50]; the HF D_e is calculated as 6.1639 eV, but the experimental value is 6.1224 eV [49][51]. Thus the exothermicity of the reaction is also not correct: the S0 ΔE is 32.78 kcal mol⁻¹, instead of 31.68 kcal mol⁻¹. The collinear reaction barrier height, found in most studies to be on the order of 1 kcal mol⁻¹, is only 0.10 kcal mol⁻¹ on S0; there is, however, a reagent well about 1 kcal mol⁻¹ deep right before the barrier, and the barrier height in the bottom of this well is therefore close to the expected value. Whether or not such wells should be present is currently a point of contention in the literature [3][6][40]. These problems, in addition to the fact that certain areas of the surfaces are uneven despite some smoothing done by Wright and Williams, make S0 in its original form unsuitable for detailed study of the effects of surface features on product properties. Therefore, S0 was altered to give the initial study surface, S1.

Each of the ten fixed-bond-angle surfaces of S0 was adjusted manually, as follows: first, the D_e values for the reagent and product non-interaction regions were corrected to the experimental values of 4.7477 eV for $F + H_2$ and 6.1224 eV for $HF + H$. Also, the values for the D_e and β_0 parameters for both the FHH and HFH surfaces, as well as for the ℓ_e parameter for the FHH surface, were adjusted to give smoother curves. This operation was performed by fitting data for each parameter

Table 2.: a) GMF5 Fit of CI Data for S0 HFH 180°

$\theta/^\circ$	D_e/eV	β_0/bohr^{-1}	ℓ_e/bohr	$\lambda_1/\text{bohr}^{-1}$	$\lambda_2/\text{bohr}^{-2}$
0.00	6.1639	1.2019	8.2708	0.053541	0.055934
10.0	6.1639	1.1836	8.3984	0.052728	0.055084
20.0	6.1639	1.1294	8.8016	0.050312	0.052560
30.0	6.1608	1.0431	9.5544	0.052788	0.043920
35.0	6.1302	0.9859	10.0955	0.047639	0.036741
37.5	6.0425	0.9505	10.4091	0.042886	0.033377
40.0	5.7415	0.9064	10.7382	0.042733	0.033122
42.0	5.1876	0.8359	10.9660	0.044843	0.051709
44.0	4.3937	0.7865	11.0651	-0.017555	0.032849
45.0	4.2405	0.7736	11.0589	-0.036157	0.025856
46.0	4.3937	0.7865	11.0651	-0.017555	0.032849
48.0	5.1876	0.8359	10.9660	0.044843	0.051709
50.0	5.7415	0.9064	10.7382	0.042733	0.033122
52.5	6.0425	0.9505	10.4091	0.042886	0.033377
55.0	6.1302	0.9859	10.0955	0.047639	0.036741
60.0	6.1608	1.0431	9.5544	0.052788	0.043920
70.0	6.1639	1.1294	8.8016	0.050312	0.052560
80.0	6.1639	1.1836	8.3984	0.052728	0.055084
90.0	6.1639	1.2019	8.2708	0.053541	0.055934

Table 2. (contd.): b) GMF5 Fit of CI Data for S0 HFH 150°

$\theta/^\circ$	D_e/eV	β_0/bohr^{-1}	ℓ_e/bohr	$\lambda_1/\text{bohr}^{-1}$	$\lambda_2/\text{bohr}^{-2}$
0.00	6.1639	1.2019	8.2708	0.053541	0.055934
10.0	6.1639	1.1836	8.3984	0.052728	0.055084
20.0	6.1858	1.1433	8.8029	0.041904	0.031263
30.0	6.2048	1.0415	9.5501	0.046148	0.034394
35.0	6.1859	0.9726	10.0922	0.056708	0.037364
37.5	6.1052	0.9350	10.4020	0.048146	0.032839
40.0	5.8342	0.8922	10.7288	0.042072	0.028017
42.0	5.3179	0.8433	10.9593	0.030884	0.030
44.0	4.5265	0.7652	11.0596	-0.018567	0.040288
45.0	4.3789	0.7451	11.0546	-0.037938	0.042313
46.0	4.5265	0.7652	11.0596	-0.018567	0.040288
48.0	5.3179	0.8433	10.9593	0.030884	0.030
50.0	5.8342	0.8922	10.7288	0.042072	0.028017
52.5	6.1052	0.9350	10.4020	0.048146	0.032839
55.0	6.1859	0.9726	10.0922	0.056708	0.037364
60.0	6.2048	1.0415	9.5501	0.046148	0.034394
70.0	6.1858	1.1433	8.8029	0.041904	0.031263
80.0	6.1639	1.1836	8.3984	0.052728	0.055084
90.0	6.1639	1.2019	8.2708	0.053541	0.055934

Table 2. (contd.): c) GMF5 Fit of CI Data for S0 HFH 120°

$\theta/^\circ$	D_e/eV	β_0/bohr^{-1}	ℓ_e/bohr	$\lambda_1/\text{bohr}^{-1}$	$\lambda_2/\text{bohr}^{-2}$
0.00	6.1639	1.2019	8.2708	0.053541	0.055934
10.0	6.1639	1.1836	8.3984	0.052728	0.055084
20.0	6.1837	1.1462	8.8050	0.044875	0.031399
30.0	6.1916	1.0410	9.5498	0.046113	0.038237
35.0	6.1685	0.9837	10.0916	0.044188	0.032003
37.5	6.0964	0.9474	10.4051	0.039721	0.029156
40.0	5.8347	0.9083	10.7337	0.029918	0.022053
42.0	5.3155	0.8572	10.9708	0.020428	0.023351
44.0	4.4241	0.7943	11.1056	-0.011514	0.028780
45.0	4.1048	0.8119	11.1364	-0.038557	0.021328
46.0	4.4241	0.7943	11.1056	-0.011514	0.028780
48.0	5.3155	0.8572	10.9708	0.020428	0.023351
50.0	5.8347	0.9083	10.7337	0.029918	0.022053
52.5	6.0964	0.9474	10.4051	0.039721	0.029156
55.0	6.1685	0.9837	10.0916	0.044188	0.032003
60.0	6.1916	1.0410	9.5498	0.046113	0.038237
70.0	6.1837	1.1462	8.8050	0.044875	0.031399
80.0	6.1639	1.1836	8.3984	0.052728	0.055084
90.0	6.1639	1.2019	8.2708	0.053541	0.055934

Table 2. (contd.): d) GMF5 Fit of CI Data for S0 HFH 90°

$\theta/^\circ$	D_e/eV	β_0/bohr^{-1}	ℓ_e/bohr	$\lambda_1/\text{bohr}^{-1}$	$\lambda_2/\text{bohr}^{-2}$
0.00	6.1639	1.2019	8.2708	0.053541	0.055934
10.0	6.1639	1.1836	8.3984	0.052728	0.055084
20.0	6.1638	1.1273	8.8019	0.053307	0.050719
30.0	6.2094	1.0414	9.5515	0.047993	0.038948
35.0	6.1829	0.9811	10.0915	0.044682	0.034855
37.5	6.1052	0.9453	10.4042	0.038856	0.031875
40.0	5.8561	0.8999	10.7305	0.029524	0.029555
42.0	5.3222	0.8479	10.9673	0.022250	0.030000
44.0	4.3677	0.8041	11.1157	-0.002560	0.038000
45.0	4.0936	0.7495	11.1056	-0.041787	-0.070000
46.0	4.3677	0.8041	11.1157	-0.002560	0.038000
48.0	5.3222	0.8479	10.9673	0.022250	0.030000
50.0	5.8561	0.8999	10.7305	0.029524	0.029555
52.5	6.1052	0.9453	10.4042	0.038856	0.031875
55.0	6.1829	0.9811	10.0915	0.044682	0.034855
60.0	6.2094	1.0414	9.5515	0.047993	0.038948
70.0	6.1638	1.1273	8.8019	0.053307	0.050719
80.0	6.1639	1.1836	8.3984	0.052728	0.055084
90.0	6.1639	1.2019	8.2708	0.053541	0.055934

Table 2. (contd.): e) GMF5 Fit of CI Data for S0 HFH 60°

$\theta/^\circ$	D_e/eV	β_0/bohr^{-1}	ℓ_e/bohr	$\lambda_1/\text{bohr}^{-1}$	$\lambda_2/\text{bohr}^{-2}$
0.00	6.1639	1.2019	8.2708	0.053541	0.055934
10.0	6.1639	1.1836	8.3984	0.052728	0.055084
20.0	6.1843	1.1431	8.8032	0.042366	0.032445
30.0	6.1928	1.0462	9.5503	0.040779	0.033506
35.0	6.1559	0.9855	10.0928	0.043831	0.033209
37.5	6.0480	0.9452	10.4025	0.038835	0.033356
40.0	5.7325	0.8858	10.7149	0.036029	0.037754
42.0	5.2002	0.8321	10.9115	0.005942	0.036
44.0	4.4349	0.7559	10.9553	-0.059418	0.035
45.0	4.2589	0.7295	10.9462	-0.035065	0.055
46.0	4.4349	0.7559	10.9553	-0.059418	0.035
48.0	5.2002	0.8321	10.9115	0.005942	0.036
50.0	5.7325	0.8858	10.7149	0.036029	0.037754
52.5	6.0480	0.9452	10.4025	0.038835	0.033356
55.0	6.1559	0.9855	10.0928	0.043831	0.033209
60.0	6.1928	1.0462	9.5503	0.040779	0.033506
70.0	6.1843	1.1431	8.8032	0.042366	0.032445
80.0	6.1639	1.1836	8.3984	0.052728	0.055084
90.0	6.1639	1.2019	8.2708	0.053541	0.055934

Figure 9.: a) GMF5 Fit of S0 HFH 180°: D_e vs. θ

Actual points are circled; curve obtained by spline interpolation.

Figure 9. (contd.): b) GMF5 Fit of S0 HFH.180°: β_0 vs. θ

Figure 9. (contd.): c) GMF5 Fit of S0 HFH 180°: ℓ_e vs. θ

Figure 9 (contd.): d) GMF5 Fit of S0 HFH 180°: λ_1 vs. θ

Figure 9. (contd.): e) GMF5 Fit of S0 HFH 180°: λ_2 vs. θ

Figure 10.: GMF5 Fit of S0 HFH D_e vs. θ

a) 150° b) 120° c) 90° d) 60°

Figure 11.: GMF5 Fit of S0 HFH β_0 vs. θ

a) 150° b) 120° c) 90° d) 60°

Figure 12.: GMF5 Fit of S0 HFH ℓ_e vs. θ

a) 150° b) 120° c) 90° d) 60°

Figure 13.: GMF5 Fit of S0 HFH λ_1 vs. θ

a) 150° b) 120° c) 90° d) 60°

Figure 14.: GMF5 Fit of S0 HFH λ_2 vs. θ

a) 150° b) 120° c) 90° d) 60°

Figure 15.: a) SO HFH 180° Potential Energy Surface

Contours shown are -3.0 (outer), -4.0, -4.3, -4.5, -5.0, -5.5, -6.0 and -6.1 eV.

Figure 15. (contd.): b) S0 HFH 150° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.3, -4.7, -5.0, -5.5, -5.75 and -6.05 eV.

Figure 15. (contd.): c) S0 HFH 120° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.22, -4.5, -5.0, -5.5, -6.0 and -6.18 eV.

Figure 15. (contd.): d) S0 HFH 90° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.5, -5.0, -5.5, -6.0, -6.1 and -6.18 eV.

Figure 15. (contd.): e) S0 HFH 60° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.2, -4.5, -5.0, -5.5, -6.0 and -6.18 eV.

to a 1-dimensional spline, using the spline data to interpolate large numbers of points, then visually examining plots of the interpolated points to ensure that no irregularities were present. (Programs JPSPLINFIT, JPSPLINSHOW and MPXY, shown in Appendices B.2, B.3, and B.4, were used.) The λ_1 and λ_2 parameters were not adjusted; as higher-order parameters, their function is to aid in the fitting of *ab initio* data to the GMF5 functional form, and their values, if kept reasonable, become largely irrelevant when more arbitrary changes are made to the data values. These additional parameters were retained for consistency of functional form and calculation procedure.

Other changes made were the elimination of most traces of the reagent and product wells, and the scaling of the reaction barrier up by 1 kcal mol⁻¹ from the S0 level for each bond angle, so that the collinear reaction barrier was about 1.05 kcal mol⁻¹, similar to the 1.062 kcal mol⁻¹ value for Muckerman's M5 [40]. These changes were made by adjusting the spline nodal points to higher or lower values, more or less arbitrarily, to produce the desired results while minimizing the effects on other parts of the curves. The result was the smoothed and simplified set of surfaces, S1, which were more suitable for detailed study of surface feature effects than S0. The correction of the gross features such as exothermicity and collinear barrier height permitted meaningful comparison with results of experiments and other trajectory studies. Global surfaces were constructed from the fixed-angle surfaces by the two-dimensional spline-fitting program JPM5COEF1 (Appendix B.1).

2.3 Blending Functions

Trajectory calculations were performed with Muckerman's program [52] as modified to operate on the Honeywell CP6 computer with attached FPS processor, using the GMF5 potential energy surfaces. (See Appendix A; see also sample data file JPFHH_DATA5 in Appendix B.5 and submission job control language (JCL) JPFPSBATCH in Appendix B.6.) The first sequence of calculations was performed to assess the need for blending functions and their effectiveness at improving the energy conservation of trajectories.

The first set of trajectories was run on smoothed surface S1 with no blending. Surface switching was permitted with no attempt to maintain continuity of potential energy or of the derivatives of the potential energy with respect to bond distance. This set was the control, for comparison with later calculations. These trajectories, and others run for testing the blending function, were run with a collision energy of $3.00 \text{ kcal mol}^{-1}$ and the reagent H_2 in state $v=0$, $J=1$. This collision energy is common in the literature [40] and so is good for comparison purposes; the (0,1) state of H_2 gives reaction cross-sections and rates about the same as the average for all accessible H_2 states at 300 K [40].

The second set of trajectories was run on surface S1 with a linear-ramp blending function. In this case, if the largest bond angle γ_i was less than 90° and the next-largest bond angle γ_j was in the range $60^\circ < \gamma_j < 90^\circ$, the blended potential was calculated as

$$V = c_i V_i + c_j V_j$$

where

$$c'_i = (\gamma_i - 60^\circ)/30^\circ, \quad c'_j = (\gamma_j - 60^\circ)/30^\circ$$

and

$$c_i = c'_i / (c'_i + c'_j) \quad (\text{normalization}).$$

The same approach was applied to the derivatives, so that $\partial V / \partial R_1 = c_i \partial V_i / \partial R_1 + c_j \partial V_j / \partial R_1$, etc.

The third set of trajectories, also run on S1, used a *cosine blending function*, whose coefficients were calculated from

$$c'_i = \frac{1}{\cos \gamma_i} - 2.$$

This cosine function assigns a very high unnormalized weight to the angle near 90° , so normalization brings its weight to just below 1 and the weight of the other surface to a correspondingly very small number. This allows smooth blending with points just outside the blending region, say for $\gamma_i = 90.1^\circ$. The linear ramp function suffered from the problem that if the large angle dropped below 90° when the next

angle was fairly large — say, 75° — the weight assigned to the second surface, after normalization, would still be large and there ~~would still~~ be a discontinuity in the potential energy and its derivatives.

Another change made for this third set was a change in the blending procedure for the derivatives. Since the weights themselves are functions of the bond distances R_i , the correct expression for the derivative is [26]

$$\frac{\partial V}{\partial R_i} = c_1 \frac{\partial V_1}{\partial R_i} + c_2 \frac{\partial V_2}{\partial R_i} + V_1 \frac{\partial c_1}{\partial R_i} + V_2 \frac{\partial c_2}{\partial R_i}.$$

A complete derivation of the function and its derivatives, as included in the trajectory program (Appendix A.7), is given in Appendix C.

2.4 Surface Series 3: Reagent Well

In order to test the effects of the depth of the reagent well on the product vibrational distribution of the $F + H_2 \rightarrow HF + H$ reaction, the D_e parameter values of scaled surface S1 FHH were adjusted slightly to remove all traces of the reagent wells, giving smoothed surface S1A. The curves were examined at high magnification to ensure that all spline overshoots and wells had been eliminated. (See programs JPSPLINFIT, JPSPLINSHOW and MPXY in Appendices B.2, B.3, and B.4.) By changing the D_e values in the well region only, the S1A FHH surface was itself then modified into surface S3A FHH, which had reagent wells of about $0.5 \text{ kcal mol}^{-1}$ but was otherwise identical with S1A. The S1 HFH surface was examined and found to contain no wells, and renamed to S1A HFH.

A program was written to automatically generate surfaces with any desired reagent well depths, by interpolation or extrapolation from surfaces S1A and S3A. For each fixed bond angle, it read the data from surfaces S1A and S3A, and took as input the desired reagent well depths and a tolerance limit on those values. From the known well depth of $0.5 \text{ kcal mol}^{-1}$, and assuming a linear change of the interpolated minimum value with a change in node height, it calculated a new set of nodes to give a curve with what should have been the desired well depth had the linearity assumption been correct. It calculated the new spline parameters, then

scanned the new curve in a quinary search to determine the actual well depth. If that value was not within the tolerance limit of the desired value, it calculated a new scaling factor based on the current depth to give a new surface. This new factor was averaged with the old factor, to damp out overshoot/undershoot swings, and the program then looped back to calculate a new set of nodes. This procedure was repeated for each of the five bond angles on the FHH surfaces. (See program JPRGTWELLBUILD in Appendix B.8.)

This program was used initially to adjust the original S3A into a slightly scaled S3A whose reagent well depths were at exactly $0.500 \text{ kcal mol}^{-1}$ for all bond angles. Global surfaces in the S3 sequence were then constructed by creating single-bond-angle surfaces with specified well depths, then joining these surfaces with the two-dimensional spline-fitter program (JPM5COEF1 in Appendix B.1). Trajectories were run on the global surfaces -- S3A for the FHH, S1A for the HFH -- with reagent wells of 0.00, 0.200, 0.400, 0.500, 0.600, 0.800 and $1.000 \text{ kcal mol}^{-1}$, with a collision energy of $3.00 \text{ kcal mol}^{-1}$, and the hydrogen initially in state $v=0, J=1$. Two thousand trajectories were run for each surface. The tolerance on the well depth was specified as $0.001 \text{ kcal mol}^{-1}$ for all but the $0.00 \text{ kcal mol}^{-1}$ surface for which the tolerance was $0.01 \text{ kcal mol}^{-1}$ since the program had difficulty in totally eliminating spline overshoot errors in the generated surface for small bond angles. The generated surface with $1.000 \text{ kcal mol}^{-1}$ wells was examined manually to ensure that in this most extreme case of extrapolation the curve was still smooth and continuous; no problem was observed, and no corrections had to be made. The submission and execution of the program was controlled by JCL similar to the file JPWELLBATCH (Appendix B.7).

2.5 Surface Series 5: Product Well

To test the effects of varying depths of product wells on the vibrational distribution of the products, a series of surfaces was needed which were identical except for the depths of their product wells. The D_c parameter values of smoothed surface S1A (no reagent wells) were adjusted to remove any traces of product wells, giving

surface S1B. (The HFH surface had already been treated so for the last series.) The S1B FHH surfaces were then modified to give the S5B FHH surfaces, which had product wells with depths of $0.5 \text{ kcal mol}^{-1}$, by adjustments to the D_e values in that region only; similarly, the S1A HFH surfaces were modified to give the S3A HFH surfaces which also had $0.5 \text{ kcal mol}^{-1}$ wells. As before, the modified surfaces were examined closely to ensure the smoothness of the curves.

Fixed-bond-angle FHH and HFH surfaces were then constructed by interpolation or extrapolation from the S1B and S5B FHH, and S1A and S3A HFH surfaces, according to specified well depths and tolerance values. (See programs JPPRDWELLBUILD and JPHFHWELLBUILD in Appendices B.9 and B.10.) The manner of their construction was essentially the same as that of the reagent well surfaces; the major difference is that where a reagent well for the $F + H_2 \rightarrow HF + H$ reaction is beside a slight barrier, a product well (or a well on either side of the HFH surface) is beside a very steep slope, which tends to cause spline overshoots, which cause the surface to be very irregular. In this region, the variation in interpolated values with node values is extremely non-linear, and to assume linear behaviour would tend to produce wildly oscillating extrapolated values. Accordingly, the damping of the scaling factor is much more severe here: for the FHH well-builder program, the new scaling factor was based 90% on the previous value and only 10% on the new calculated value. This weighting was found to converge fairly quickly on the desired well depths. The best HFH wells that could be constructed using the same nodal points were smoother and broader, and did not suffer from this problem to such an extent; accordingly, a simple averaging sufficed.

As before, the fixed-bond-angle surfaces were merged into global surfaces. (See the two-dimensional spline-fitter program, JPM5COEF1, in Appendix B.1.) Trajectories were run for surfaces with product well depths of 0.00, 0.200, 0.400, 0.600, 0.800 and $1.000 \text{ kcal mol}^{-1}$, all with collision energies of $3.00 \text{ kcal mol}^{-1}$ and initial H_2 state of $v=0, J=1$. Two thousand trajectories were run on each surface. As before, the surfaces with $1.000 \text{ kcal mol}^{-1}$ wells were visually inspected to ensure smoothness; no adjustments were needed.

2.6 Surface Series 6: Barrier Height

It was desired to determine the effect of the reaction barrier height on the product vibrational distributions. Series of surfaces, differing only in the reaction barrier height, were needed. The D_e values for the S1B FHH surfaces (no reagent or product wells) were adjusted manually to give the S6A FHH surface by eliminating the reaction barriers. In the case of the 60° and 90° surfaces, which have two barriers, only the barrier corresponding to the real reaction barrier, not to the growing singularity (see Figure 3), was removed. (This singularity at $\theta = 45^\circ$ is due to the close proximity of atoms with the same bond lengths at small bond angles causing significant repulsion and thus a high potential energy.) The heights of the S1B reaction barriers for the different angles were recorded.

Fixed-angle surfaces were constructed with specified reaction barrier heights, within designated tolerances. (See JPBARRIERBUILD, in Appendix B.11.) In most respects this was accomplished much as the generation of other surfaces except that a local minimum was found on the D_e curves instead of a local maximum. It was assumed that the difference in barrier heights between two fixed-angle surfaces on S1B would be the same for the fixed-angle surfaces on all other global surfaces, so that if the input collinear barrier height was increased by some amount, the barrier would be increased globally by that amount. Because the barrier is at the top of a steep slope, the variation of spline-interpolated values with node heights was rather non-linear. Fairly strong damping of the oscillations of the extrapolated scale factor was needed, and so the new scale factor value was taken 30% from the calculation and 70% from its previous value. This weighting was found to converge fairly rapidly and smoothly to the desired barrier heights. After the fixed-angle surfaces were constructed, the two-dimensional spline-fitter program (JPM5COEF1 in Appendix B.1) was used to construct a global surface.

Two thousand trajectories were run on each surface, for reaction barriers of 0.00, 0.250, 0.500, 0.750, 1.000, 1.250, 1.500, 1.750, 2.000, 2.500 and 3.000 kcal mol⁻¹, at a collision energy of 3.00 kcal mol⁻¹ and with the H₂ in its usual (0,1) state. (It

should be noted that even when the collision energy is close to or even a bit smaller than the reaction barrier height, some of the $6.21 \text{ kcal mol}^{-1}$ of zero-point energy of the H_2 [49] will act towards moving over the barrier.) As before, the most extreme surface was checked visually for smoothness and found to be problem-free. (JCL JPWELLBATCH, in Appendix B.7, was used to run trajectories in this series.)

2.7 Trajectory Series 6H: Collision Energy

In order to determine the effect of reagent collision energy on the product vibrational distribution, series of trajectories had to be run with different energies on a simple smooth surface. Surface 6H (no wells, $2.000 \text{ kcal mol}^{-1}$ collinear reaction barrier) was constructed as part of the previous series. A series of trajectories was run on this surface with the following collision energies: 1.000, 1.500, 2.000, 2.500, 3.000 (results taken from the previous series), 3.500, 4.000, 4.500, and $5.000 \text{ kcal mol}^{-1}$. In each case two thousand trajectories were run, except for the $1.000 \text{ kcal mol}^{-1}$ case whose low reactivity required four thousand trajectories to give enough reactions to give good statistics. All were run for H_2 in its usual (0,1) state. (Execution was controlled by a version of JPWELLBATCH that had had the surface-construction commands commented out - see Appendix B.7.)

2.8 "Diagonal" Trajectory Series: Constant Difference Between Collision Energy and Barrier Height

To separate the effects of high transition-state energy from high reaction barrier, trajectories were run on surfaces with different barrier heights and collision energies consistently $2.000 \text{ kcal mol}^{-1}$ greater than the barrier heights ("diagonal" on a chart of collision energy vs. barrier height). JPWELLBATCH was used to run two thousand trajectories each on surfaces with collinear reaction barriers of 0.00, 0.500, 1.000 (results from series 6), 1.500, 2.000 (from series 6H), 2.500 and $3.000 \text{ kcal mol}^{-1}$; again the (0,1) state was used for the reagent H_2 .

3. Results and Discussion

3.1 Scaled Surface S1

The results of the adjustments to the D_e , β_0 and ℓ_e parameters of the S0 FHH fixed-bond-angle surfaces, giving the S1 FHH surface, are shown in Table 3. Spline-interpolated curves showing the variation of these parameters with θ for the collinear surface are shown in Figure 16, and similar curves showing the parameters for the other FHH fixed-bond-angle surfaces of S1 are shown in Figures 17 through 19. The potential energy surfaces generated from these modified parameters are shown in Figure 20.

Comparison of the collinear S0 and S1 parameter figures shows that the adjustments needed to smooth the data were relatively minor. The most apparent changes in the D_e values occur on the reagent side of the barrier, where the S0 values are noticeably uneven. The β_0 values were almost unchanged except in the immediate vicinity of the barrier where the S0 curve shows a slight shoulder. The ℓ_e values were not changed at all; the curve was already smooth.

The adjustments made to the other FHH fixed-bond-angle surfaces were similar. In each case, the reagent side of the D_e curve was smoothed and most of the original wells were removed. Close examination of the 150° , 120° and 60° D_e vs. θ curves shows that these still have small product wells or other irregularities due to spline oscillations but that these features are much smaller than on the original surfaces. A shoulder on the 120° curve, immediately after the barrier (and possibly due to the first appearance of the potential increase due to the close approach of the end atoms) was smoothed over. Some irregularities in the region between the two barriers on the 60° D_e curve were eliminated.

The non-collinear β_0 curves show considerably more structure than the 180° curve does in the S0 FHH surface. These irregularities were smoothed to give

Table 3.: a) S1-FHH D_e Parameters for all θ , γ

$\theta/^\circ$	$\gamma = 180^\circ$	150°	120°	90°	60°
0.0	4.7477	4.7477	4.7477	4.7477	4.7477
10.0	4.7477	4.7477	4.7477	4.7477	4.7477
20.0	4.7477	4.7477	4.7477	4.7477	4.7477
25.0	4.7477	4.7477	4.7477	4.7477	4.7477
27.5	4.7477	4.7477	4.7477	4.7477	4.7445
30.0	4.7477	4.7477	4.7440	4.7312	4.7000
32.5	4.7475	4.7475	4.7370	4.6754	4.4400
35.0	4.7445	4.7440	4.7000	4.4661	4.3800
37.0	4.7410	4.7400	4.6000	4.3871	4.7500
39.0	4.7271	4.7240	4.7150	4.8000	4.8250
40.0	4.7097	4.7080	4.8050	4.8037	4.7932
41.0	4.7236	4.7110	4.9000	4.7892	4.7357
43.0	5.1319	5.0876	5.1750	4.8501	4.5405
45.0	5.6446	5.5981	5.5130	5.1264	4.2200
48.0	6.0000	5.9600	6.0117	5.6500	4.7712
50.0	6.0800	6.0500	6.0880	5.8500	5.4000
55.0	6.1224	6.1224	6.1224	6.0650	5.9400
60.0	6.1224	6.1224	6.1224	6.1125	6.0900
70.0	6.1224	6.1224	6.1224	6.1224	6.1224
80.0	6.1224	6.1224	6.1224	6.1224	6.1224
90.0	6.1224	6.1224	6.1224	6.1224	6.1224

Table 3. (contd.): b) S1 FHH β_0 Parameters for all θ , γ

$\theta/^\circ$	$\gamma = 180^\circ$	150°	120°	90°	60°
0.0	1.0468	1.0468	1.0468	1.0468	1.0468
10.0	1.0309	1.0309	1.0309	1.0309	1.0309
20.0	0.9837	0.9900	0.9850	0.9870	0.9900
25.0	0.9484	0.9561	0.9587	0.9551	0.9600
27.5	0.9251	0.9362	0.9450	0.9348	0.9375
30.0	0.9021	0.9143	0.9300	0.9102	0.9100
32.5	0.8783	0.8931	0.9080	0.8826	0.8750
35.0	0.8523	0.8684	0.8676	0.8450	0.8300
37.0	0.8309	0.8424	0.8072	0.8100	0.8000
39.0	0.8065	0.8160	0.7950	0.7850	0.7683
40.0	0.7935	0.8070	0.7940	0.7800	0.7550
41.0	0.7822	0.7999	0.7960	0.7810	0.7439
43.0	0.7947	0.8035	0.8010	0.7900	0.7238
45.0	0.8290	0.8195	0.8167	0.8143	0.7167
48.0	0.8795	0.8804	0.8776	0.8769	0.8170
50.0	0.9155	0.9124	0.9144	0.9155	0.8778
55.0	0.9836	0.9932	0.9857	0.9867	0.9803
60.0	1.0426	1.0466	1.0424	1.0434	1.0440
70.0	1.1294	1.1294	1.1294	1.1294	1.1294
80.0	1.1836	1.1836	1.1836	1.1836	1.1836
90.0	1.2019	1.2019	1.2019	1.2019	1.2019

Table 3. (contd.): c) S1 FHH ℓ_e Parameters for all θ , γ

$\theta/^\circ$	$\gamma = 180^\circ$	150°	120°	90°	60°
0.0	8.6008	8.6008	8.6008	8.6008	8.6009
10.0	8.7335	8.7335	8.7335	8.7335	8.7335
20.0	9.1528	9.1528	9.1528	9.1528	9.1528
25.0	9.4895	9.4878	9.4909	9.4912	9.4921
27.5	9.6958	9.6962	9.6947	9.6993	9.7012
30.0	9.9316	9.9328	9.9344	9.9310	9.9317
32.5	10.1994	10.1975	10.2000	10.1824	10.1814
35.0	10.5001	10.4976	10.4861	10.4512	10.4703
37.0	10.7631	10.7630	10.7400	10.7500	10.7296
39.0	11.0357	11.0328	11.0600	11.0127	10.9469
40.0	11.1700	11.1707	11.2000	11.1327	11.0217
41.0	11.2995	11.3046	11.3200	11.2329	11.0627
43.0	11.4904	11.4840	11.4516	11.3328	11.0174
45.0	11.4536	11.4377	11.4084	11.2864	10.9412
48.0	11.0792	11.0785	11.0800	11.0193	10.8557
50.0	10.7818	10.7753	10.7749	10.7553	10.6746
55.0	10.0985	10.0998	10.0979	10.0953	10.0810
60.0	9.5526	9.5507	9.5525	9.5522	9.5502
70.0	8.8016	8.8016	8.8016	8.8016	8.8016
80.0	8.3984	8.3984	8.3984	8.3984	8.3984
90.0	8.2708	8.2708	8.2708	8.2708	8.2708

Figure 16.: a) Plot of D_e vs. θ for S1 FHH 180°

Actual points are circled; curve obtained by spline interpolation.

Figure 16. (contd.): b) Plot of β_0 vs. θ for S1 FHH 180°

Figure 16. (contd.): c) Plot of ℓ_e vs. θ for S1 FHH 180°

Figure 17.: Plot of D_e vs. θ for S1 FHH

a) 150° b) 120° c) 90° d) 60°

Figure 18.: Plot of β_0 vs. θ for S1 FHH

a) 150° b) 120° c) 90° d) 60°

Figure 19.: Plot of ℓ_e vs. θ for S1 FHH

a) 150° b) 120° c) 90° d) 60°

Figure 20.: a) S1 FHH 180° Potential Energy Surface

Contours shown are -3.0 (outer), -4.0, -4.5, -4.7, -4.76, -5.0, -5.5, -6.0 and -6.18 eV.

Figure 20. (contd.): b) S1 FHH 150° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.5, -4.7, -4.76, -5.0, -5.5, -6.0 and -6.18 eV.

Figure 20. (contd.): c) S1 FHH 120° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.6, -4.7, -4.77, -5.0, -5.5, -6.0 and -6.18 eV.

Figure 20. (contd.): d) S1 FHH 90° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.5, -4.6, -4.74, -5.0, -5.5, -6.0 and -6.18 eV.

Figure 20. (contd.): e) S1 FHH 60° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.27, -4.5, -4.75, -5.0, -5.5, -6.0 and -6.18 eV.

simple curves; in some cases, most notably the 120° , the result was a rather broad, flat minimum that approximated the original shape fairly well.

Of the S0 FHH ℓ_e curves, only the 120° and 90° parameters were altered. In all cases the changes were minor and intended to smooth some slight irregularities of the original curves.

The changes are more apparent upon comparison of the fixed-bond-angle potential energy surfaces. The S0 FHH collinear surface (Figure 8) clearly shows the reagent and product wells which the S1 surface lacks. The pinching together of the contour lines at the barrier on the S1 collinear surface shows that the barrier is higher on that surface (since the contour values are the same). The overall shapes of the surfaces are quite similar, however; although the D_e values, which affect the minimum of the curve, are changed, the β_0 and ℓ_e , which affect the curvature at the bottom of the curve and the position of the minimum, are close to their original values.

The S0 FHH 150° surface also has wells which are absent from the S1 surface. The two are otherwise much alike.

The changes in the FHH 120° surface are more drastic. The removal of the shoulder from the D_e curve made the region slightly to the product side of the barrier connect much more smoothly with the main valley. Alterations in the ℓ_e values made the entrance valley much straighter. As with the other surfaces, wells were removed, including the double reagent well that was due to a spline oscillation.

The product side of the FHH 90° curve looks much the same both before and after alterations, except for the eliminated well. The entrance valley is a bit smoother in the S1 surface. In both cases, the new barrier at $\theta = 45^\circ$ can be seen starting to appear.

The FHH 60° surface, with its two large barriers and well between them, is difficult to smooth within the limitations imposed by the selected nodes. It may be seen, however, that the shape of the interbarrier well is more rounded in S1 than in S0; this is the result of changes to both the D_e and β_0 values.

The results of the changes made to the D_e and β_0 parameters of the S0 HFH surface to give the S1 HFH surface are shown in Table 4. The parameter values are shown in spline-interpolated curves in Figures 21 (collinear surface), 22 and 23 (other fixed-bond-angle surfaces). The S1 HFH potential energy surfaces generated from these parameters are shown in Figure 24.

As may be seen from the D_e plots, the original S0 HFH D_e curves were already quite smooth; after scaling to the correct experimental potential energy value, only slight adjustment was needed to remove the small wells. The original β_0 values were less smooth and required more adjustment. The 180° , 150° and 60° curves were adjusted to remove some discontinuities in slope; in fact, the 150° curve required extensive minor correction for smoothness over most of the curve. In addition, the 120° β_0 value was decreased at the barrier ($\theta = 45^\circ$) to eliminate an anomalous local maximum, and the 90° curve was adjusted to remove a pair of shoulders near the barrier.

The effects of these changes on the potential energy surfaces are rather small, apart from the scaling of D_e values. Only the two surfaces whose β_0 values were significantly altered show any great change. The barrier on the 120° S1 surface is somewhat broader than on the S0 surface since the smaller β_0 value results in the valley being less pinched in cross-section. The outer contours on the 90° fixed-angle surface became more regular with the removal of the shoulders from the β_0 curve.

3.2 Blending Functions

The first set of twelve hundred trajectories, computed without a blending function, yielded many reactive trajectories that had to be discarded due to poor energy conservation. About 15% of reactive trajectories did not conserve energy to within 8% of the total energy. A sample of one hundred reactive trajectories showed a root-mean-square deviation of 0.025 eV between the initial and final total energies; this is roughly 6% of the total energy of 0.436 eV. (The initial total energy is the sum of the initial rotational and vibrational energies of the reagent molecule and the collision energy; the final total energy is the total vibrational, rotational and kinetic

Table 4.: a) S1 HFH D_e Parameters for all θ , γ

$\theta/^\circ$	$\gamma = 180^\circ$	150°	120°	90°	60°
0.0	6.1224	6.1224	6.1224	6.1224	6.1224
10.0	6.1224	6.1224	6.1224	6.1224	6.1224
20.0	6.1224	6.1224	6.1224	6.1224	6.1224
30.0	6.1193	6.1193	6.1192	6.1191	6.1193
35.0	6.0887	6.0885	6.0879	6.0861	6.0890
37.5	6.0010	6.0003	5.9981	5.9917	6.0022
40.0	5.7000	5.6977	5.6900	5.6677	5.7040
42.0	5.1461	5.1408	5.1229	5.0715	5.1554
44.0	4.3522	4.3425	4.3101	4.2170	4.3691
45.0	4.1990	4.1885	4.1533	4.0521	4.2174
46.0	4.3522	4.3425	4.3101	4.2170	4.3691
48.0	5.1461	5.1408	5.1229	5.0715	5.1554
50.0	5.7000	5.6977	5.6900	5.6677	5.7040
52.5	6.0010	6.0003	5.9981	5.9917	6.0022
55.0	6.0887	6.0885	6.0879	6.0861	6.0890
60.0	6.1193	6.1193	6.1192	6.1191	6.1193
70.0	6.1224	6.1224	6.1224	6.1224	6.1224
80.0	6.1224	6.1224	6.1224	6.1224	6.1224
90.0	6.1224	6.1224	6.1224	6.1224	6.1224

Table 4. (contd.): b) S1 HFH β_0 Parameters for all θ , γ

$\theta/^\circ$	$\gamma = 180^\circ$	150°	120°	90°	60°
0.0	1.2019	1.2019	1.2019	1.2019	1.2019
10.0	1.1836	1.1836	1.1836	1.1836	1.1836
20.0	1.1294	1.1450	1.1450	1.1273	1.1431
30.0	1.0431	1.0590	1.0500	1.0414	1.0500
35.0	0.9859	1.0030	0.9837	0.9811	0.9855
37.5	0.9510	0.9650	0.9474	0.9453	0.9452
40.0	0.9000	0.9140	0.9000	0.8999	0.8858
42.0	0.8359	0.8600	0.8572	0.8479	0.8321
44.0	0.7865	0.8020	0.7943	0.7900	0.7559
45.0	0.7736	0.7940	0.7850	0.7495	0.7295
46.0	0.7865	0.8020	0.7943	0.7900	0.7559
48.0	0.8359	0.8600	0.8572	0.8479	0.8321
50.0	0.9000	0.9140	0.9000	0.8999	0.8858
52.5	0.9510	0.9650	0.9474	0.9453	0.9452
55.0	0.9859	1.0030	0.9837	0.9811	0.9855
60.0	1.0431	1.0590	1.0500	1.0414	1.0500
70.0	1.1294	1.1450	1.1450	1.1273	1.1431
80.0	1.1836	1.1836	1.1836	1.1836	1.1836
90.0	1.2019	1.2019	1.2019	1.2019	1.2019

Figure 21.: a) Plot of D_e vs. θ for S1 HFH 180°

Actual points are circled; curve obtained by spline interpolation.

Figure 21. (contd.): b) Plot of β_0 vs. θ for S1 HFH 180°

Figure 22.: Plot of D_e vs. θ for S1 HFH

a) 150° b) 120° c) 90° d) 60°

Figure 23.: Plot of β_0 vs. θ for S1 HFH

a) 150° b) 120° c) 90° d) 60°

Figure 24.: a) S1 HFH 180° Potential Energy Surface

Contours shown are -3.0 (outer), -4.0, -4.3, -4.5, -5.0, -5.5, -6.0 and -6.1 eV.

Of the original distribution of 100% of reactive trajectories, 2% were moved from ($v' = 0$) and 4% from ($v' = 1$) up to ($v' = 2$), and 6% down from ($v' = 3$). This seems to represent a moderate increase in vibrational excitation, especially since most of the trajectories sorted into the ($v' = 3$) bin are only slightly over the cutoff margin and a shift of these down into ($v' = 2$) represents a smaller change than the increase from the lower states.

It must be remembered, however, that surface S0 contains some features that are absent from S1, in particular the wells and the very low barrier, which might affect the product distributions. Certainly the S1 results are closer than those of S0 to those obtained by Muckerman with his M5 surface [40] and the experimental results of Perry and Polanyi [30] and Berry [27], for all product properties except translational energy (compared to M5) and $F(v' \neq 3)$ (to experiment). Of the properties available for comparison, the S1 results are fairly close to experimental values (in some cases closer than M5 is) and so this surface appears to be a reasonable starting point for further studies.

Of the various trajectory product properties, the product vibrational distribution is one of the simplest to study because it refers to a division of the reactions into only four groups, since only the four lowest states are accessible for low collision energies. One of the most significant reasons that this reaction is of interest is that most of the energy of reaction goes into vibrational excitation, causing a population inversion; this means that the vibrational distribution is a property which is relatively well-documented. Other features, such as the distribution of the reaction energy into vibration, rotation and translation, or the rotational distribution of the products, are not always described. Features such as the scattering angle distribution, or the product rotational distribution, tend to be more complex and harder to characterize in terms of effects of specific surface features. It is for these reasons that this study was focussed on the product vibrational distributions.

It is of interest to consider the relationship between the computed results and those obtained from chemiluminescence studies. The IR emission occurs with a typical lifetime of about 2 to 5 ms [31], much longer than the average total trajectory time which (at collision energies of 3 kcal mol^{-1}) is about $2 \times 10^{-13} \text{ s}$. It is therefore clear that the trajectory results show the product states immediately after reaction

Figure 24. (contd.): c) S1 HFH 120° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.22, -4.5, -5.0, -5.5, -6.0 and -6.18 eV.

Figure 24. (contd.): d) S1 HFH 90° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.5, -5.0, -5.5, -6.0, -6.1 and -6.18 eV.

Figure 24. (contd.): e) S1 HFH 60° Potential Energy Surface

Contours shown are -3.0, -4.0, -4.2, -4.5, -5.0, -5.5, -6.0, and -6.18 eV.

energy of the product system, less the exothermicity of the reaction so that the total energy value should be constant.) Figure 25a shows a plot of energy deviation as a function of reaction time in the trajectory, for a typical reactive trajectory. In this case, the first sudden energy change, when the trajectory changed surfaces at about 1.12×10^{-13} s, had a magnitude of 0.025 eV. Another change at 1.40×10^{-13} s increased the energy so that the final total energy was not so far from the initial value. Also, about one trajectory in two thousand 'blew up' (failed utterly) when the deviations were severe enough to cause FORTRAN run-time errors.

The average deviation was observed to increase with the vibrational quantum number assigned to the product, so that the ($v' = 0$) reactive trajectories tended to have small deviations but the ($v' = 3$) reactives had large ones. It was conjectured that the more rapid and larger oscillations of the latter trajectories caused them to cross between the three global surfaces more frequently. It is also possible that reaction paths which happen to cross between surfaces in regions with large energy differences also happen to be those that yield high vibrational excitation of the products. In either case, if the trajectories with higher vibrational excitation of the products are preferentially discarded, clearly the resulting population distribution will be erroneously shifted to lower states.

The second set of trajectories, calculated by a program version that included linear-ramp blending, gave similar results. Figure 25b shows a trajectory with the same starting conditions as the one described above; it helps to explain the lack of significant improvement in energy continuity. The same discontinuities as before are seen; the only difference seems to be that the jump in energy occurs over several steps instead of between one step and the next. This suggests that blending of energies is not sufficient, or that the ramp blending is inadequate. The difference in energies between the surfaces has not been decreased, nor have the surfaces been smoothly joined; the sudden inclusion of a second surface still causes a large change. The blending of the derivatives, too, gives a discontinuous change of forces on the system.

Figure 25.: Energy Change as a Function of Reaction Time

Plot of change in total energy from its initial value, as a function of time along the trajectory, for a typical reactive trajectory. (a) shows a trajectory calculated with no blending of surfaces; (b) shows a trajectory from the same initial conditions, with a linear-ramp blending function.

Figure 26 shows the energy changes in a trajectory from the same initial conditions calculated with the cosine blending function applied to the energies and their derivatives, and with the correct application of the weights to the derivatives. It may be seen that the surfaces have been successfully and smoothly joined. Energy conservation has been maintained to within 0.0001 eV. Also worthy of note is the shorter time required for the trajectory to finish; this may be because a different reaction path was followed, but may in part be due to the system maintaining its full kinetic energy and so causing the products to separate more quickly.

A sample of one hundred reactive trajectories showed an r.m.s. deviation of only 0.0021 eV between the initial and final total energies, less than one-tenth of the deviation originally observed. No trajectories had such poor conservation of energy that they had to be discarded. Also, the incidence of trajectories that 'blew up' was greatly reduced, to about one in forty thousand. These remaining errors were probably due to computation problems with taking the secant of a number which was within the computer's rounding error of 90° .

It is therefore apparent that some form of blending function is needed to properly perform this sort of trajectory study, and that the cosine blending function, when properly applied, can fulfill the necessary role.

The results of five hundred trajectories computed with surface S1 by the program with the cosine blending function are shown in Table 5. Also shown are results of trajectories computed with Muckerman's surface M5, widely accepted as one of the standards of comparison for $F + H_2$ potential energy surfaces [40], and the original surface S0, along with experimental results for the reaction.

As may be seen, the properties of the S0 and S1 products are very similar. This suggests that the smoothing had little effect upon the properties of the surface. The significant changes lie in the reaction cross-section and the vibrational distribution of the products. The change in cross-section is within the Monte-Carlo uncertainty of the calculation (see Appendix B); the change in population distribution is not. Since the exothermicity of the S0 surface was decreased by $1.1 \text{ kcal mol}^{-1}$ to give the S1 surface, a shift to lower vibrational distributions would be expected, but the observed effect is in fact a sharpening of the distribution, into the ($v' = 2$) state.

Figure 26.: Energy Change as a Function of Reaction Time

Plot of the change in total energy as a function of trajectory reaction time for the same initial conditions as before, with cosine-function blending.

Table 5.: Summary of Significant F + H₂ Product Properties

Trajectories were run with a collision energy of 3.0 kcal mol⁻¹ for H₂ in its (0,1) state on surfaces M5 [40], S0 and S1; experimental results are by Perry and Polanyi (P and P²) [30] and Berry [27].

Property	M5	S0	S1	P and P	Berry
N	10 000	1099	500		
N_r	2595	348	163		
$\sigma_v / \text{\AA}^2$	3.26 ± 0.05	5.26 ± 0.23	5.42 ± 0.35		
$\langle b \rangle_r / \text{\AA}$	0.973	1.213	1.169		
$\langle \theta \rangle_r / ^\circ$	113.1	94.3	86.9		
$F(v' = 0)$	0	0.08	0.06	0.02	0.03
$F(v' = 1)$	0.1233	0.29	0.25	0.15	0.15
$F(v' = 2)$	0.5661	0.34	0.47	0.53	0.50
$F(v' = 3)$	0.3106	0.29	0.23	0.29	0.32
E'_{tot}	41.30	42.61	42.51	40.86	
$\langle E'_v \rangle$	29.43	26.6	26.8	27.13	
$\langle E'_r \rangle$	4.53	6.0	4.9	3.39	
$\langle E'_t \rangle$	7.34	10.0	10.8	10.6	
$\langle f'_v \rangle$	0.713	0.62	0.63	0.664	0.67
$\langle f'_r \rangle$	0.110	0.14	0.12	0.083	
$\langle f'_t \rangle$	0.178	0.23	0.25	0.260	

Notation: N refers to a number of trajectories; the subscript r refers to reactive trajectories only. σ is a collision cross-section, b an impact parameter, and θ a scattering angle; quantities in angle brackets are averaged. $F(v' = n)$ describes the fraction of reactive trajectories ending in vibrational state n . E' refers to product energy in units of kcal mol⁻¹; the subscripts v , r and t to vibration, rotation and translation, respectively; f'_m to the fraction of energy ending in mode m .

Of the original distribution of 100% of reactive trajectories, 2% were moved from ($v' = 0$) and 4% from ($v' = 1$) up to ($v' = 2$), and 6% down from ($v' = 3$). This seems to represent a moderate increase in vibrational excitation, especially since most of the trajectories sorted into the ($v' = 3$) bin are only slightly over the cutoff margin and a shift of these down into ($v' = 2$) represents a smaller change than the increase from the lower states.

It must be remembered, however, that surface S0 contains some features that are absent from S1, in particular the wells and the very low barrier, which might affect the product distributions. Certainly the S1 results are closer than those of S0 to those obtained by Muckerman with his M5 surface [40] and the experimental results of Perry and Polanyi [30] and Berry [27], for all product properties except translational energy (compared to M5) and $F(v' = 3)$ (to experiment). Of the properties available for comparison, the S1 results are fairly close to experimental values (in some cases closer than M5 is) and so this surface appears to be a reasonable starting point for further studies.

Of the various trajectory product properties, the product vibrational distribution is one of the simplest to study because it refers to a division of the reactions into only four groups, since only the four lowest states are accessible for low collision energies. One of the most significant reasons that this reaction is of interest is that most of the energy of reaction goes into vibrational excitation, causing a population inversion; this means that the vibrational distribution is a property which is relatively well-documented. Other features, such as the distribution of the reaction energy into vibration, rotation and translation, or the rotational distribution of the products, are not always described. Features such as the scattering angle distribution, or the product rotational distribution, tend to be more complex and harder to characterize in terms of effects of specific surface features. It is for these reasons that this study was focussed on the product vibrational distributions.

It is of interest to consider the relationship between the computed results and those obtained from chemiluminescence studies. The IR emission occurs with a typical lifetime of about 2 to 5 ms [31], much longer than the average total trajectory time which (at collision energies of 3 kcal mol^{-1}) is about $2 \times 10^{-13} \text{ s}$. It is therefore clear that the trajectory results show the product states immediately after reaction

and long before vibrational emission would occur.

3.3 Surface Series 3: Reagent Well

This series of surfaces was used to investigate the effects of changing reagent well depths. Tables 6 and 7 show the adjusted D_e parameters used for the S1A and S3A FHH surfaces. Figure 27 shows spline-interpolated plots of the modified S1A and S3A FHH D_e parameters, as well as the original S1 FHH parameters, from which the other values were determined, for comparison purposes.

It was expected that the increasing reagent well depth would have little effect on the reaction cross-section, since the well would not be encountered until the trajectory was already directed in a reactive or non-reactive path. Only a very few trajectories would be deflected into or out of the reactive channel. However, it was expected that the product distribution might be broadened since the reactive trajectories might be slightly deflected into a greater variety of pathways over the barrier. The results of the Series 3 calculations are shown in Table 8; Figure 28 shows a plot of the product vibrational distribution as a function of reagent well depth.

As may be seen from Table 8, changing reagent well depth had no significant effect on the reaction cross-section. A least-squares analysis of σ_r vs. well depth showed that there is no significant linear correlation between the two parameters.

There was a fairly steady decrease in the fraction of the product HF ending up in the ($v' = 2$) state as the well depth increased. Although there may have been a slight increase in the fractions going into ($v' = 0, 3$) most of the increase seems to have been in ($v' = 1$), thereby broadening the distribution. Conversely, the sharpest distribution should be obtained when there are no reagent wells. A consequence of this is that alterations to reagent well depth can be used to broaden the distribution, if desired, but only to a limited extent to sharpen it since the well depths can be reduced only to zero.

3.4 Surface Series 5: Product Well

This series of surfaces was used to determine the effects of varying product

Table 6.: S1A FHH D_e Parameters for all θ, γ

$\theta/^\circ$	$\gamma = 180^\circ$	150°	120°	90°	60°
0.0	4.7477	4.7477	4.7477	4.7477	4.7477
10.0	4.7477	4.7477	4.7477	4.7477	4.7477
20.0	4.7477	4.7477	4.7477	4.7477	4.7477
25.0	4.7477	4.7477	4.7477	4.7477	4.7477
27.5	4.7477	4.7477	4.7477	4.7477	4.7445
30.0	4.7477	4.7477	4.7440	4.7442	4.7000
32.5	4.7475	4.7475	4.7370	4.7054	4.4400
35.0	4.7445	4.7440	4.7000	4.4761	4.3800
37.0	4.7410	4.7400	4.6000	4.3871	4.7500
39.0	4.7271	4.7240	4.7150	4.8000	4.8250
40.0	4.7097	4.7080	4.8050	4.8037	4.7932
41.0	4.7236	4.7110	4.9000	4.7892	4.7357
43.0	5.1319	5.0876	5.1750	4.8501	4.5405
45.0	5.6446	5.5981	5.5130	5.1264	4.2200
48.0	6.0000	5.9600	6.0117	5.6500	4.7712
50.0	6.0800	6.0500	6.0880	5.8500	5.4000
55.0	6.1224	6.1224	6.1224	6.0650	5.9400
60.0	6.1224	6.1224	6.1224	6.1125	6.0900
70.0	6.1224	6.1224	6.1224	6.1224	6.1224
80.0	6.1224	6.1224	6.1224	6.1224	6.1224
90.0	6.1224	6.1224	6.1224	6.1224	6.1224

Table 7.: S3A FHH D_e Parameters for all θ , γ

$\theta/^\circ$	$\gamma = 180^\circ$	150°	120°	90°	60°
0.0	4.7477	4.7477	4.7477	4.7477	4.7477
10.0	4.7477	4.7477	4.7477	4.7477	4.7477
20.0	4.7477	4.7477	4.7477	4.7477	4.7490
25.0	4.7477	4.7477	4.7477	4.7478	4.7594
27.5	4.7477	4.7477	4.7515	4.7480	4.7693
30.0	4.7480	4.7550	4.7651	4.7564	4.7000
32.5	4.7531	4.7684	4.7694	4.7502	4.4400
35.0	4.7682	4.7614	4.7201	4.5167	4.3800
37.0	4.7620	4.7360	4.6050	4.3898	4.7500
39.0	4.7271	4.7111	4.7150	4.8000	4.8250
40.0	4.7097	4.7001	4.8050	4.8037	4.7932
41.0	4.7230	4.7100	4.9000	4.7892	4.7357
43.0	5.1319	5.0876	5.1750	4.8501	4.5405
45.0	5.6446	5.5981	5.5130	5.1264	4.2200
48.0	6.0000	5.9600	6.0117	5.6500	4.7712
50.0	6.0800	6.0500	6.0880	5.8500	5.4000
55.0	6.1224	6.1224	6.1224	6.0650	5.9400
60.0	6.1224	6.1224	6.1224	6.1125	6.0900
70.0	6.1224	6.1224	6.1224	6.1224	6.1224
80.0	6.1224	6.1224	6.1224	6.1224	6.1224
90.0	6.1224	6.1224	6.1224	6.1224	6.1224

Figure 27.: Plots of S1, S1A and S3A FHH D_e Values

Surface S1A: ————— ; S3A: - - - - - ; original S1:

Where S1 is not visible it is identical to S1A. (a) 180° surfaces.

Figure 27. (contd.): Plots of S1, S1A and S3A FHH D_e Values

(b) 150° surfaces (c) 120° surfaces

Figure 27. (contd.): Plots of S1, S1A and S3A FHH D_e Values

(d) 90° surfaces (e) 60° surfaces. Note that the S1A 90° surface is flat in the well region, as it was changed from S1.

Table 8.: Results of Series S3 Calculations

Surface	Reagent Well Depth / kcal mol ⁻¹	σ_r / Å ²	$F(v' = 0)$	$F(v' = 1)$	$F(v' = 2)$	$F(v' = 3)$
3 ₋	0.00	3.82 ± 0.13	0.067 ± 0.010	0.260 ± 0.018	0.477 ± 0.020	0.196 ± 0.016
3B	0.200	3.53 ± 0.13	0.066 ± 0.010	0.282 ± 0.019	0.488 ± 0.021	0.164 ± 0.016
3C	0.400	3.71 ± 0.13	0.080 ± 0.011	0.273 ± 0.018	0.459 ± 0.021	0.188 ± 0.016
3A	0.500	3.59 ± 0.13	0.093 ± 0.012	0.262 ± 0.018	0.458 ± 0.021	0.187 ± 0.016
3D	0.600	3.87 ± 0.13	0.071 ± 0.010	0.298 ± 0.018	0.446 ± 0.020	0.183 ± 0.016
3E	0.800	3.69 ± 0.13	0.078 ± 0.011	0.301 ± 0.019	0.427 ± 0.020	0.194 ± 0.016
3F	1.000	3.58 ± 0.13	0.084 ± 0.012	0.295 ± 0.019	0.428 ± 0.021	0.193 ± 0.017

well depths on the trajectory products. Tables 9 and 10 show the adjusted D_e parameters used for the S1B and S5B FHH surfaces; Table 11 shows the S3A HFH D_e parameters. Figures 29 and 30 show interpolated plots of these parameters, along with the S1A parameters for comparison.

It was expected that the results of the Series 5 calculations would be very similar to those of Series 3: since the product well occurs after the barrier, it should have little or no effect on the reaction cross-section. Only trajectories which swing wildly around the bend in the potential energy valley could be influenced by the wells to change from reactivity to non-reactivity or *vice versa*. The effect of a deep well on the product distribution should be to broaden it slightly as the well diffuses the trajectories passing through it to a broader range of paths, much as a lens will spread out a partially-focussed beam of light. Table 12 shows the numerical results from this series of calculations; Figure 31 shows a plot of the product vibrational

Figure 28.: Product Distribution *vs.* Reagent Well Depth

Results of Series 3 calculations; all trajectories calculated with collision energy of 3.000 kcal mol⁻¹ with H₂ initially in (0,1) state.

Table 9.: S1B FHH D_e Parameters for all θ , γ

$\theta/^\circ$	$\gamma \neq 180^\circ$	150°	120°	90°	60°
0.0	4.7477	4.7477	4.7477	4.7477	4.7477
10.0	4.7477	4.7477	4.7477	4.7477	4.7477
20.0	4.7477	4.7477	4.7477	4.7477	4.7477
25.0	4.7477	4.7477	4.7477	4.7477	4.7477
27.5	4.7477	4.7477	4.7477	4.7477	4.7445
30.0	4.7477	4.7477	4.7440	4.7442	4.7000
32.5	4.7475	4.7475	4.7370	4.7054	4.4400
35.0	4.7445	4.7440	4.7000	4.4761	4.3800
37.0	4.7410	4.7400	4.6000	4.3871	4.7500
39.0	4.7271	4.7240	4.7150	4.8000	4.8250
40.0	4.7097	4.7080	4.8050	4.8037	4.7932
41.0	4.7236	4.7110	4.9000	4.7892	4.7357
43.0	5.1319	5.0876	5.1750	4.8501	4.5405
45.0	5.6446	5.5981	5.5130	5.1264	4.2200
48.0	6.0000	5.9600	6.0117	5.6500	4.7712
50.0	6.0800	6.0620	6.0980	5.8500	5.4000
55.0	6.1224	6.1224	6.1224	6.0650	5.9920
60.0	6.1224	6.1224	6.1224	6.1125	6.0900
70.0	6.1224	6.1224	6.1224	6.1224	6.1224
80.0	6.1224	6.1224	6.1224	6.1224	6.1224
90.0	6.1224	6.1224	6.1224	6.1224	6.1224

Table 10.: S5B FHH D_e Parameters for all θ , γ

$\theta/^\circ$	$\gamma = 180^\circ$	150°	120°	90°	60°
0.0	4.7477	4.7477	4.7477	4.7477	4.7477
10.0	4.7477	4.7477	4.7477	4.7477	4.7477
20.0	4.7477	4.7477	4.7477	4.7477	4.7477
25.0	4.7477	4.7477	4.7477	4.7477	4.7477
27.5	4.7477	4.7477	4.7477	4.7477	4.7445
30.0	4.7477	4.7477	4.7440	4.7442	4.7000
32.5	4.7475	4.7475	4.7370	4.7054	4.4400
35.0	4.7445	4.7440	4.7000	4.4761	4.3800
37.0	4.7410	4.7400	4.6000	4.3871	4.7500
39.0	4.7271	4.7240	4.7150	4.8000	4.8250
40.0	4.7097	4.7080	4.8050	4.8037	4.7932
41.0	4.7236	4.7110	4.9000	4.7892	4.7357
43.0	5.1319	5.0876	5.1750	4.8501	4.5405
45.0	5.6446	5.5981	5.5130	5.1264	4.2200
48.0	6.0000	5.9600	6.0117	5.6500	4.7712
50.0	6.1038	6.0871	6.1210	5.8500	5.4000
55.0	6.1325	6.1335	6.1318	6.1141	6.0870
60.0	6.1224	6.1224	6.1224	6.1371	6.1375
70.0	6.1224	6.1224	6.1224	6.1224	6.1224
80.0	6.1224	6.1224	6.1224	6.1224	6.1224
90.0	6.1224	6.1224	6.1224	6.1224	6.1224

Table 11.: S3A HFH D_e Parameters for all θ , γ

$\theta/^\circ$	$\gamma = 180^\circ$	150°	120°	90°	60°
0.0	6.1224	6.1224	6.1224	6.1224	6.1224
10.0	6.1224	6.1224	6.1224	6.1224	6.1224
20.0	6.1224	6.1224	6.1224	6.1224	6.1224
30.0	6.1394	6.1394	6.1394	6.1409	6.1440
35.0	6.1124	6.1123	6.1118	6.1089	6.1050
37.5	6.0010	6.0003	5.9981	5.9917	6.0022
40.0	5.7000	5.6977	5.6900	5.6677	5.7040
42.0	5.1461	5.1408	5.1229	5.0715	5.1554
44.0	4.3522	4.3425	4.3101	4.2170	4.3691
45.0	4.1990	4.1885	4.1533	4.0521	4.2174
46.0	4.3522	4.3425	4.3101	4.2170	4.3691
48.0	5.1461	5.1408	5.1229	5.0715	5.1554
50.0	5.7000	5.6977	5.6900	5.6677	5.7040
52.5	6.0010	6.0003	5.9981	5.9917	6.0022
55.0	6.1124	6.1123	6.1118	6.1089	6.1050
60.0	6.1394	6.1394	6.1394	6.1409	6.1440
70.0	6.1224	6.1224	6.1224	6.1224	6.1224
80.0	6.1224	6.1224	6.1224	6.1224	6.1224
90.0	6.1224	6.1224	6.1224	6.1224	6.1224

Figure 29.: Plots of S1B, S5B and S1A FHH D_e Values

Surface S1B: ————— ; S5B: - - - - - ; S1A:

Where S1A is not visible it is identical to S1B. (a) 180° surfaces.

Figure 29. (contd.): Plots of S1B, S5B and S1A FHH D_e Values

(b) 150° surfaces (c) 120° surfaces

Figure 29. (contd.): Plots of S1B, S5B and S1A FHH D_e Values

(d) 90° surfaces (e) 60° surfaces. Note that the S1B 60° surface has been smoothed in the product well-region from S1A.

Figure 30.: Plots of S1A and S3A HFH D_e Values

Surface S1A: ————— ; S3A: - - - - - . (a) 180° surfaces.

Figure 30. (contd.): Plots of S1A and S3A HFH D_e Values

(b) 150° surfaces (c) 120° surfaces

Figure 30. (contd.): Plots of S1A and S3A HFH D_e Values

(b) 90° surfaces (c) 60° surfaces

Table 12.: Results of Series S5 Calculations

Surface	Product Well Depth / kcal mol ⁻¹	σ_r / Å ²	$F(v' = 0)$	$F(v' = 1)$	$F(v' = 2)$	$F(v' = 3)$
5 ₋	0.00	3.93 ± 0.13	0.075 ± 0.011	0.262 ± 0.018	0.476 ± 0.020	0.187 ± 0.016
5A	0.200	4.22 ± 0.13	0.064 ± 0.009	0.280 ± 0.017	0.488 ± 0.019	0.168 ± 0.014
5B ₁	0.400	3.97 ± 0.13	0.051 ± 0.009	0.241 ± 0.017	0.498 ± 0.020	0.210 ± 0.016
5C	0.600	3.89 ± 0.13	0.081 ± 0.011	0.234 ± 0.017	0.502 ± 0.020	0.183 ± 0.016
5D	0.800	4.05 ± 0.13	0.082 ± 0.011	0.278 ± 0.018	0.466 ± 0.020	0.174 ± 0.015
5E	1.000	3.82 ± 0.13	0.082 ± 0.010	0.273 ± 0.018	0.456 ± 0.020	0.189 ± 0.016

distribution as a function of product well depth.

As Figure 31 shows, the effect of increasing product well depth on the product vibrational distribution is minimal, or at least not very consistent. There is very little change in the distributions between surfaces with no wells and those with 1.0 kcal mol⁻¹ deep wells. Surfaces with wells which are moderately deep (around 0.5 kcal mol⁻¹) actually gave sharper distributions, with some products moving from the ($v' = 1$) to the ($v' = 2$) state. This effect is within the uncertainty of the measurements, however; if real, it could be because the 'lens' of the well happens to focus the trajectories when it is of the correct depth. That the effect is small may be due to the numerous reactive trajectories which do not encounter the well at all; on the potential energy surface, they would bank off the wall opposite the entrance valley and swing past the well.

As expected, there was little or no effect of product well depth on reaction cross-section, as may be seen in Table 12. Least squares analysis demonstrates the lack of correlation between the two. The overall reactivity of the S5 series,

Figure 31.: Product Distribution *vs.* Product Well Depth

Results of Series 5 calculations; all trajectories calculated with collision energy of 3.000 kcal mol⁻¹ with H₂ initially in (0,1) state.

seems to be slightly greater than that of the S3 series. Since the FHH surfaces are identical up to the reaction barrier, it appears that the addition of wells to the HFH surfaces promote reaction. However, Series S5 shows that systematically increasing the product well depths does not consistently increase the reactivity. The perceived difference between the two series may be attributable to one point; if the anomalously high S5A datum is ignored, the average σ_r values for the two surface series are then less than two standard deviations apart, so they may be said to correspond within their margins of error.

On the whole it appears that the only possible effect on the product distribution of varying depths of product wells is a small maximum in distribution sharpness for wells of about $0.5 \text{ kcal mol}^{-1}$, and the possibility that deeper wells broaden the distribution. Neither effect is very large.

3.5 Surface Series 6: Barrier Height

Surfaces in this series were constructed for the purpose of determining the effects of differing barrier heights on the reaction products. Table 13 shows the D_r parameters used to construct the S6A FHH surface; Figure 32 shows spline-interpolated plots of these parameters, along with the S1B parameters (also used in this series of calculations) and the S1A parameters (from which the others were created).

The reaction cross-section was expected to decrease sharply with increasing collinear barrier height. As the barrier increases, only trajectories with an increasingly narrow range of paths are able to cross over it. Under ordinary circumstances, most reactive trajectories do not go over the barrier precisely at its minimum but rather somewhere near it. As the minimum increases, the range of paths that can pass over the barrier other than at the minimum decreases. In the extreme case where the barrier height was as high as possible but still allowing reaction, only trajectories following a single specific path could get by. Thus it was also expected that the product vibrational distribution would sharpen as fewer paths could be successful, meaning that only a restricted set of product outcomes would be possible.

Table 13.: S6A FHH D_e Parameters for all θ , γ

$\theta/^\circ$	$\gamma = 180^\circ$	150°	120°	90°	60°
0.0	4.7477	4.7477	4.7477	4.7477	4.7477
10.0	4.7477	4.7477	4.7477	4.7477	4.7477
20.0	4.7477	4.7477	4.7477	4.7477	4.7477
25.0	4.7477	4.7477	4.7477	4.7477	4.7477
27.5	4.7477	4.7477	4.7477	4.7477	4.7477
30.0	4.7477	4.7477	4.7477	4.7477	4.7477
32.5	4.7477	4.7477	4.7477	4.7477	4.7477
35.0	4.7477	4.7477	4.7477	4.7477	4.7477
37.0	4.7477	4.7477	4.7477	4.7600	4.7700
39.0	4.7477	4.7477	4.7630	4.8000	4.8250
40.0	4.7477	4.7479	4.8050	4.8037	4.7932
41.0	4.7700	4.7700	4.9000	4.7892	4.7357
43.0	5.1319	5.0876	5.1750	4.8501	4.5405
45.0	5.6446	5.5981	5.5130	5.1264	4.2200
48.0	6.0000	5.9600	6.0117	5.6500	4.7712
50.0	6.0800	6.0620	6.0980	5.8500	5.4000
55.0	6.1224	6.1224	6.1224	6.0650	5.9920
60.0	6.1224	6.1224	6.1224	6.1125	6.0900
70.0	6.1224	6.1224	6.1224	6.1224	6.1224
80.0	6.1224	6.1224	6.1224	6.1224	6.1224
90.0	6.1224	6.1224	6.1224	6.1224	6.1224

Figure 32.: Plots of S1B, S6A and S1A FHH D_e Values

Surface S1B: ————— ; S6A: - - - - - ; S1A:

Where S1A is not visible it is identical to S1B. (a) 180° surfaces.

Figure 32. (contd.): Plots of S1B, S6A and S1A FHH D_e Values

(b) 150° surfaces (c) 120° surfaces

Figure 32. (contd.): Plots of S1B, S6A and S1A FHH D_e Values

(d) 90° surfaces (e) 60° surfaces

Table 14.: Results of Series S6 Calculations

Surface	Collinear Barrier Ht. / kcal mol ⁻¹	σ_r / Å ²	$F(v' = 0)$	$F(v' = 1)$	$F(v' = 2)$	$F(v' = 3)$
6 ₋	0.00	5.55 ± 0.18	0.046 ± 0.008	0.269 ± 0.017	0.478 ± 0.019	0.207 ± 0.016
6B	0.250	5.19 ± 0.17	0.051 ± 0.009	0.276 ± 0.018	0.465 ± 0.020	0.208 ± 0.016
6A	0.500	4.79 ± 0.15	0.076 ± 0.011	0.234 ± 0.017	0.447 ± 0.020	0.243 ± 0.017
6C	0.750	4.28 ± 0.14	0.073 ± 0.010	0.284 ± 0.018	0.470 ± 0.020	0.173 ± 0.015
6D	1.000	4.00 ± 0.13	0.064 ± 0.010	0.300 ± 0.018	0.432 ± 0.020	0.203 ± 0.016
6E	1.250	3.76 ± 0.13	0.070 ± 0.010	0.317 ± 0.019	0.444 ± 0.020	0.169 ± 0.015
6F	1.500	3.36 ± 0.12	0.099 ± 0.013	0.290 ± 0.020	0.440 ± 0.021	0.170 ± 0.016
6G	1.750	3.00 ± 0.12	0.084 ± 0.013	0.289 ± 0.021	0.459 ± 0.023	0.168 ± 0.017
6H	2.000	2.76 ± 0.11	0.111 ± 0.015	0.305 ± 0.022	0.436 ± 0.024	0.148 ± 0.017
6J	2.500	2.48 ± 0.10	0.089 ± 0.014	0.345 ± 0.023	0.429 ± 0.024	0.137 ± 0.016
6I	3.000	2.00 ± 0.10	0.153 ± 0.019	0.324 ± 0.025	0.372 ± 0.026	0.151 ± 0.019

Table 14 gives the numerical results of the Series 6 calculations; Figure 33 shows a plot of the product population distributions as a function of collinear barrier height.

As Table 14 shows, the reaction cross-section followed the expected pattern by decreasing steadily with increasing collinear barrier height. The product vibrational distribution, however, did not behave as expected; instead of becoming sharper, which would have meant an increase in the fraction $F(v' = 2)$, the distribution shifted to lower vibrational states: $F(v' = 0, 1)$ increased, and $F(v' = 2, 3)$

Figure 33.: Product Distribution *vs.* 180° Barrier Height

Results of Series 6 calculations; all trajectories calculated with collision energy of 3.000 kcal mol⁻¹ with H₂ initially in (0,1) state.

decreased. The actual trajectory results show that the fraction of all trajectories (reactive and non-reactive) that end in ($v' = 0$) remains fairly constant, and the fraction ending in ($v' = 1$) actually decreases slightly. However, the fractions ending in ($v' = 2, 3$) decrease very sharply. In other words, the state-to-state rate constants for the two higher product vibrational states decrease much more than the rate constants for the two lower states, with increased barrier height. This means that the reactive paths that lead into the higher vibrational states are being selectively excluded by a higher barrier. The result is an increase in the fraction of reactive trajectories that end in the lower states. Since a particular range of reaction paths is being eliminated, one would expect the distribution to be sharpened. Over the range of barriers studied, however, the eliminated paths were those that gave the most common product state, causing an apparent broadening.

Had the barrier been increased further, it is likely that the distribution would have sharpened again, into the lower vibrational states. A trajectory passing over the highest barrier possible for reaction with a collision energy of $3.0 \text{ kcal mol}^{-1}$ would probably end in ($v' = 0$) or ($v' = 1$). In other words, a trajectory starting out at the saddle point of the barrier with almost no kinetic energy will likely roll down the product side of the barrier, initially following the minimum-energy reaction path until it acquires kinetic energy and momentum, and end up following a path that leads to a ($v' = 0$) or ($v' = 1$) product. In contrast, Table 5 shows that the M5 surface, with a collinear barrier of $1.064 \text{ kcal mol}^{-1}$, has a distribution less peaked in $F(v' = 2)$ than Polanyi and Schreiber's surface SE1 [6], with a collinear barrier of $2.16 \text{ kcal mol}^{-1}$ and a product vibrational distribution of $[F(v' = 0, 1, 2, 3) = 0, 0.15, 0.68, 0.18]$. Of course, the surfaces differ in other ways, and the effects of the barrier height alone cannot be separated from the effects of the other surface features.

Although Muckerman's surfaces M2 through M4 [36] also differ in several ways, they are more comparable with each other. The M2, M5, M3 and M4 surfaces have collinear reaction barriers of 0.89, 1.064, 1.43 and $2.55 \text{ kcal mol}^{-1}$, respectively, and the fraction cross-sections decrease steadily: 3.54 ± 0.25 , 3.26 ± 0.05 , 2.69 ± 0.23 ,

and $1.68 \pm 0.19 \text{ \AA}^2$. The average fractions of total energy ending in vibration for trajectories run on these series of surfaces, with a collision energy of 3 kcal mol^{-1} for $\text{F} + \text{H}_2$ (0.1), are 0.78 ± 0.12 , 0.713 , 0.63 ± 0.13 , and 0.49 ± 0.13 . This suggests that the vibrational distribution is shifting to lower states, as was found in the present study, although the actual distributions are not given.

From the S5 series of calculations, it appears that a decrease in barrier height will shift the population distribution to higher vibrational states; of course, this effect can be taken only to the limiting case of a 0 kcal mol^{-1} collinear reaction barrier, which is in fact much too low. Ungemach *et al.* [53] predicted that the collinear barrier height was not more than 1 kcal mol^{-1} under $3.35 \text{ kcal mol}^{-1}$, from *ab initio* calculations. Schwenke *et al.* [38] calculated the collinear barrier height to be about $3.7 \text{ kcal mol}^{-1}$. Berry's experimental value for the activation energy was $1.60 \text{ kcal mol}^{-1}$ [27], which would be expected to be less than the barrier because of the contribution of the H_2 zero-point energy.

3.6 Trajectory Series 6H: Collision Energy

Trajectories in this series were run to determine the effects of changing the collision energy on the product states when the surface itself was the same. The results of this series were expected to be similar to those of the previous series. As the collision energy increased, a greater proportion of trajectories would react successfully in a wider range of reaction paths, causing a regular increase in collision cross-section and a broadening of the product distribution. In addition, the increase in total system energy would tend to populate higher product vibrational states, leading to a slight shift in the distribution. The energy difference between the ($v = 0$) and ($v = 1$) states of HF is $12.6 \text{ kcal mol}^{-1}$ [49], which is much larger than the additional collision energy, and only a fraction of the increased collision energy will appear as vibrational excitation. However, even a slight shift of this sort should have significant effects because a moderate number of trajectories end up just below the division between ($v' = 2$) and ($v' = 3$); a bit more vibrational energy should cause a noticeable upwards shift in the distribution. The opposite effects

Table 15.: Results of Series S6H Calculations

Surface	Collision Energy / kcal mol ⁻¹	σ_r / Å ²	$F(v' = 0)$	$F(v' = 1)$	$F(v' = 2)$	$F(v' = 3)$
6H_1	1.000	0.453 ± 0.046	0.0155 ± 0.009	0.332 ± 0.034	0.544 ± 0.036	0.109 ± 0.022
6H_1_5	1.500	0.735 ± 0.055	0.043 ± 0.016	0.327 ± 0.037	0.531 ± 0.039	0.099 ± 0.023
6H_2	2.000	1.80 ± 0.09	0.069 ± 0.014	0.315 ± 0.026	0.470 ± 0.028	0.145 ± 0.020
6H_2_5	2.500	2.51 ± 0.11	0.104 ± 0.014	0.341 ± 0.023	0.381 ± 0.023	0.174 ± 0.018
6H	3.000	2.76 ± 0.11	0.111 ± 0.015	0.305 ± 0.022	0.436 ± 0.024	0.148 ± 0.017
6H_3_5	3.500	3.15 ± 0.12	0.134 ± 0.015	0.301 ± 0.021	0.399 ± 0.022	0.166 ± 0.017
6H_4	4.000	3.44 ± 0.13	0.107 ± 0.014	0.302 ± 0.021	0.431 ± 0.022	0.161 ± 0.016
6H_4_5	4.500	3.54 ± 0.12	0.149 ± 0.016	0.260 ± 0.019	0.432 ± 0.022	0.159 ± 0.016
6H_5	5.000	3.87 ± 0.14	0.141 ± 0.015	0.283 ± 0.019	0.363 ± 0.020	0.213 ± 0.017

were expected from low collision energies: smaller cross-sections and sharply-peaked distributions were the anticipated results. It would be expected that for very large collision energies the cross-section would again decrease because the colliding atom would be moving too quickly to interact significantly with the molecule. A direct collision might result in the total dissociation of the three atoms. However, this range of energies was not studied in this project. The numerical results of the Series 6H calculations are shown in Table 15, and a plot of the product vibrational distributions versus the collision energy is shown in Figure 34.

The expected patterns are actually followed. It was found that the reaction cross-section increases with collision energy. The product vibrational distribution

Figure 34.: Product Distribution vs. Collision Energy

Results of Series 6H calculations. All trajectories computed on the 6H surface, which has no reagent or product wells and a 2.000 kcal mol⁻¹ barrier, with H₂ initially in the (0,1) state.

does broaden with increased collision energy, with the ($v' = 2$) fraction dropping sharply and the ($v' = 1$) fraction decreasing slightly, and the ($v' = 0, 3$) fractions increasing steadily. The actual fractions of total trajectories that successfully react to go into the ($v' = 1, 2$) states do increase with collision energy, but the fractions going into the other states increase much more quickly, shifting the fraction of products towards the other states.

This leads to an obvious question: why are the results from this series so different from those of the last series, when both series involve essentially the same change: a variation in collision energy *vs.* barrier height? A possibility is that changing the barrier causes a fundamental change in the surface, such that the trajectories that are just able to cross a $2.00 \text{ kcal mol}^{-1}$ barrier tend to go into the ($v' = 2$) state, but those with $3.00 \text{ kcal mol}^{-1}$ of collision energy barely passing over a high barrier go into ($v' = 1$). This suggests that more work should be done with series similar to this one, testing the effects of changing collision energy on surfaces with collinear reaction barriers of different heights.

3.7 "Diagonal" Trajectory Series: Constant Difference Between Collision Energy and Barrier Height

It was expected that the reaction cross-section would decrease slightly with increasing barrier height, even though the collision energy was increased equally, since a significant part of the zero-point vibrational energy of the H_2 molecule contributes to passing over the reaction barrier and this amount would not change. The increased barrier would work against both. The effect on the product vibrational distribution could not be predicted with certainty. With both the barrier height and the collision energy increasing, no particular range of trajectories would be excluded, and the effects of having extra energy in the system could be separated from the broadening effect of a wider possible range of reactive trajectories. An increase in overall vibrational energy was expected, especially an increase in $F(v' = 3)$ at the expense of $F(v' = 2)$. The actual results of this series are shown in Table 16 and Figure 35.

Table 16.: Results of 'Diagonal' Series Calculations

Surface	Collision Energy / kcal mol ⁻¹	σ_r / Å ²	$F(v' = 0)$	$F(v' = 1)$	$F(v' = 2)$	$F(v' = 3)$
6_2	2.000	5.87 ± 0.18	0.040 ± 0.007	0.248 ± 0.016	0.528 ± 0.019	0.184 ± 0.015
6A_2_5	2.500	4.46 ± 0.15	0.048 ± 0.009	0.295 ± 0.019	0.462 ± 0.021	0.195 ± 0.016
6D	3.000	4.00 ± 0.13	0.064 ± 0.010	0.300 ± 0.018	0.432 ± 0.020	0.203 ± 0.016
6F_3_5	3.500	3.62 ± 0.13	0.094 ± 0.012	0.281 ± 0.019	0.462 ± 0.021	0.163 ± 0.015
6H_4	4.000	3.44 ± 0.13	0.107 ± 0.014	0.302 ± 0.021	0.431 ± 0.022	0.161 ± 0.016
6J_4_5	4.500	3.29 ± 0.13	0.156 ± 0.017	0.312 ± 0.021	0.368 ± 0.022	0.164 ± 0.017
6I_5	5.000	2.83 ± 0.12	0.138 ± 0.016	0.318 ± 0.022	0.371 ± 0.023	0.173 ± 0.018

The effect on the reaction cross-section was considerably stronger than was expected. In fact, the 6_2 calculation (no barrier, collision energy = 2.000 kcal mol⁻¹) had an anomalously large cross-section compared to the 6_ calculation of Series S6 (no barrier, collision energy = 3.000 kcal mol⁻¹); the higher energy should have caused a higher reactivity, since these trajectories were running well below the high-energy range where the cross-section begins to decrease. All of the other comparable calculations in S6 and this series follow the expected pattern that higher collision energy allows more reactivity for surfaces with the same collinear barrier height.

The pattern of the product distributions was not as expected: although the fraction in ($v' = 2$) did decrease sharply, there was not a corresponding increase in ($v' = 3$). Most of the apparent effects were due to a drastic decrease in the actual number of trajectories going into ($v' = 2$); the numbers going into ($v' = 1, 3$)

Figure 35.: Product Distribution vs. 180° Barrier Height

Results of the 'Diagonal' Series calculations on Series 6 surfaces. For this series, (collision energy) - (barrier height) is a constant 2.000 kcal mol⁻¹. All trajectories run with H₂ initially in (0,1) state.

decreased slightly and moderately, and the number going into ($v' = 0$) increased slightly with the higher barrier. These changes were transformed into moderate increases in $F(v' = 0, 1)$ and little change in $F(v' = 3)$.

No simple explanation of these effects is immediately obvious. For the reactive trajectories yielding ($v' = 2, 3$) to decrease in number with increasing collision energy makes little sense. Again, some sort of fundamental change in the surface with varying barrier heights seems to be implicated.

3.8 Other Surface Features

Of the three surface features examined in detail in this study, none was significantly useful with regard to causing the results of trajectory calculations to approximate experimental results. In other words, whatever the differences are between the S0 and S1 surfaces and the "true" potential energy surface of the $F + H_2$ reaction, the significant differences in terms of effects on the product vibrational distribution do *not* seem to involve the features studied. As may be seen in Table 5, the S0 and S1 surfaces assign too many trajectories to the ($v' = 0, 1$) states, as compared with the M5 surface and with experiment. The minimum possible reagent well (*i.e.* no well at all) produces the highest possible fraction of trajectories in ($v' = 2$), a fraction which is not high enough; too few go into ($v' = 3$), and too many into ($v' = 0, 1$). The optimal product well depth of about $0.5 \text{ kcal mol}^{-1}$ puts about the right fraction into ($v' = 2$) but too few in ($v' = 3$) and too many in ($v' = 0, 1$). The minimum possible collinear barrier — none at all — gives the same sort of distribution, and all others are worse. How does surface M5, for example, differ from the S0-based surfaces, and why are its product distributions so much closer to the experimental values?

In the first place, it should be pointed out that the M5 surface is less perfect than it sounds. Although it gives the correct product vibrational distributions when quasi-classical trajectory calculations are performed on it, the reaction cross-sections obtained are much too small. Table 5 shows the cross-sections for the M5, S0 and S1 surfaces; the M5 value is only about 60% of the other two. The thermal

rate constant at 300 K for the reaction $F + H_2 \rightarrow HF + H$ on M5 is only about 0.2 times the experimental value [40]; a rough calculation from the results of S1 gave it a reactivity about 2.5 times too large.

Ashton, Muckerman and Schubert suggest that the quasi-classical trajectory approach is itself flawed [54]. They show that the method tends to give incorrect results near the reaction threshold, for example when the collision energy is close to the activation energy. This range of calculations is very important for determination of the thermal rate constant. In particular, the state-to-state rate constants for $F + H_2 (0,1) \rightarrow HF (3, J) + H$ are overestimated by the QCT method. In other words, if the potential energy surface is correct, QCT calculations will show a $F(v' = 3)$ value somewhat higher than the experimental. This means that the M5 surface does not channel as many trajectories into $(v' = 3)$ as it should. The results from the S0 family of surfaces are then even worse by comparison, since they chronically give low $F(v' = 3)$ values.

There are several ways in which the M5 surface is fundamentally different from the S0- and S1-type surfaces. One is that the LEPS-type M5 surface has very broad reaction barriers, which extend to much greater atomic-diatomic distances than the GMF5 surfaces studied in this project. Figure 36 shows an interpolated plot of the M5, S0 and S1 collinear FHH D_c values as functions of θ . It may be seen that although the S1 and M5 surfaces have the same collinear barrier height, the M5 surface comes much more gradually to that height than the S1.

With a more extended barrier, an incoming atom encounters a repulsive force at a much greater distance. In the case of a direct collision, this would probably make little difference. However, in the case of a grazing collision, if the atom encounters a tangential repulsive force, an early encounter is much more effective at deflecting the atom than a late encounter since the tangential force has more time to operate. The result would be a lower proportion of reactive trajectories, a smaller cross-section, and a more restricted range of reactive trajectory paths. The first two effects are definitely observed; whether a restricted range of paths necessarily leads

Figure 36.: Plots of M5, S0 and S1 FHH 180° D_e Values *vs.* θ

M5: ——— ; S1: - - - - - ; S0:

Table 17.: Barrier Characteristics *vs.* Bond Angle

Energy is in units of kcal mol⁻¹ relative to reagents F + H₂; distances are in Å. M5 data was determined by Williams [19].

Bond Angle/°	Surface M5			Surface S1A		
	E [‡]	R _{FH} [‡]	R _{HH} [‡]	E [‡]	R _{FH} [‡]	R _{HH} [‡]
180	1.06	1.54	0.76	0.993	1.44	0.77
150	1.70	1.45	0.77	1.120	1.42	0.77
120	5.22	1.30	0.82	3.406	1.87	0.75
90	20.0	1.25	0.93	9.094	1.94	0.75
60	38.9	1.32	1.03	9.645	2.22	0.75

to a sharply-peaked product distribution has been brought into question by the Series 6 calculations in this study.

A related difference between the M5 and S0 types of surface is the actual location of the top of the barrier, the saddle point. As Table 17 shows, the two are rather different. For the two largest bond angles, whose barriers are arguably the most important since they are the lowest, the M5 surface has the barriers at larger F-H distances. As described above, this could lead to decreased reactivity and possibly a sharper product distribution.

Another noteworthy difference between M5 and the S0-type surface is the variation of the barrier height with the bond angle γ . All of the specific barrier variations studied for this project were with respect to the collinear (180°) reaction barrier, and the barriers for all other angles were computed by assuming that as the collinear barrier was altered, the barriers for the other fixed bond angles would change by the same amount; the global barrier would thus be raised or lowered. As Table 17 and Figure 37 show, the reaction barrier heights for M5 and S1A are very different at all angles other than 180°.

Similarly, it was assumed for this study that the reagent and product wells would have the same depths for all bond angles. This is not a very realistic assumption;

Figure 37.: M5 and S1A FHH Barriers *vs.* γ

M5: ————— ; S1A: - - - - - ; no barrier: - . - . - .

there is no reason for all the wells to be the same. It is difficult to predict just what the variation of well depth with bond angle should be like, although *ab initio* studies might give some idea.

For bond angles on the FHH surfaces, the M5 surface has consistently greater reaction barriers than the S0-type surfaces. This would tend to discourage non-collinear approaches by the F atom, and would thus again give a lower reactivity and a more restricted set of reactive paths. The M5 barriers are relatively close to the S1A values for the three most linear angles but rise sharply for the other two; the effects of this sharp change are uncertain. It is suggested that this sharp increase tends to funnel the incoming F atom down a potential energy tunnel with more rigid boundaries than are found with the S0 surfaces, once the atom gets into a relatively linear configuration with the rotating H₂ molecule.

On the other hand, the M5 HFH barriers are much too small. The pattern exhibited is similar to that for the FHH barriers: there is a minimum for collinear HFH of 1.30 kcal mol⁻¹, which rises fairly gradually through the 120° value of 6.40 kcal mol⁻¹ and then increases sharply to a 52.8 kcal mol⁻¹ barrier for HFH 60° [19]. *Ab initio* studies have shown that the barriers are in the range of 42 to 49 kcal mol⁻¹, most likely at the higher end [55]; Table 6 shows that the S1A barriers range between 43.9 and 47.7 kcal mol⁻¹. This problem is characteristic of LEPS surfaces that have been fitted to a specific reaction; their characteristics are generally not correct for the other possible reactions for the same atoms [40]. The low barriers would promote the insertion of F into the H₂ molecule, except that to achieve this configuration some higher barriers would have to be overcome. The effects of this feature on the product distribution are unpredictable.

Another difference between the LEPS-type and GMF5 surfaces is that the GMF5 surfaces tend to be less smooth and continuous. Where the LEPS and related surfaces have a simple functional form that of necessity gives a continuous potential energy function, the GMF5 surfaces are assembled from *ab initio* calculations at discrete geometries, which are estimated to have r.m.s. energy deviations of

less than 0.015 eV for most points on S0. Not only are the nodal points' parameter values fitted independently along each ray, but even if the curves are smoothed or adjusted manually along the swing angle θ , they do not necessarily fit well together along the bond angle γ . Adjusting the parameters in the two (θ, γ) dimensions at once is not within the scope of the programs currently available. An example of the problem is shown in Figure 38, which shows contour plots of the STA FHH D_e and λ_2 values against the swing angle θ and the bond angle γ .

As the plot of D_e shows, the separate curves for the different bond angles are joined fairly smoothly across γ . The small valleys on either side, close to $(\gamma = 60^\circ, 300^\circ; \theta = 40^\circ)$, which correspond to the well between the two barriers at $\gamma = 60^\circ$, join continuously with the reagent plateau. The early barriers for the least collinear bond angles do extend a bit farther into the global surface than might be expected from inspection of the fixed-bond-angle curves alone, however. The two small contour loops at $\theta = 40^\circ$ for $150^\circ < \gamma < 210^\circ$ suggest that the reaction barrier is less regular after two-dimensional spline interpolation than might be desired.

The problem becomes much more apparent on inspection of the λ_2 plot. Even when plotted only as a function of θ , the one-dimensionally interpolated curves show a great deal of fine structure and some discontinuity. When interpolated in two dimensions, the erratic behaviour of the parameter becomes far more pronounced; the strange curves and contour loops indicate a high incidence of spline oscillations. It is fortunate that this parameter, which exhibits the most structure of this sort, is the high-order correction term which does not greatly affect the potential energy values when it is within reasonable limits.

The result of this problem is that the GMF5 surfaces can contain some odd features or structures which can remain hidden unless the final interpolated values of the parameters are examined. Elimination of these features may be difficult because of the multidimensional nature of the problem. The effects on trajectories might be insignificant or severe, depending on precisely what features were affected, and could affect the product distributions in almost any way.

Figure 38.: Contour Plot of S1A FHH D_e vs. γ , θ

Contours are 4.3, 4.5, 4.7, 4.8, 5.0, 5.5, 6.0 and 6.1 eV.

Figure 38. (contd.): Contour Plot of S1A FHH λ_2 vs. γ , θ

Contours are 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, 0.055, 0.06, and 0.065 bohr⁻².

This problem can be avoided by careful inspection of contour plots of the two-dimensionally-interpolated parameters, to ensure that no new features arise from the joining of the fixed-bond-angle surfaces. This being done, the procedures followed in this study seem able to provide good insights into the effects of specific potential energy surface features on trajectory product properties.

4. Conclusions

The comparison of trajectory calculations performed by programs both with and without blending functions indicates that some form of blending is necessary for energy to be conserved consistently in trajectory calculations in the RMCS coordinate system. A linear ramp blending function which does not give continuous blending over the whole global surface is inadequate. A cosine blending function gives smooth, continuous blending over the global surface, and improves the energy conservation by an order of magnitude compared with trajectories with no blending.

The depth of the reagent well for the $F + H_2 \rightarrow HF + H$ reaction was found to have no significant effect on the reaction cross-section. A deep reagent well tends to cause a shift of the product distribution from the ($v' = 2$) state to the ($v' = 1$) state. Since experimental results indicate a $F(v' = 2)$ value higher than those obtained in this study, it is suggested that the potential energy surface for $F + H_2$ should have only a very small reagent well or none at all.

Product well depth had no significant effect on the reaction cross-section. The effect on the product vibrational distributions was also very small, giving a small local maximum in the sharpness of the product distribution for product wells with a depth of about $0.5 \text{ kcal mol}^{-1}$. This gives the maximum possible fraction of reactive trajectories going into ($v' = 2$).

A higher collinear reaction barrier gave a lower reaction cross-section. It also selectively decreased the number of reactive trajectories ending in the higher product vibrational states, resulting in a broadened product distribution shifted to a lower average vibrational energy level. The collinear reaction barrier would have to be as low as possible to maximize the fractions of reactive trajectories ending in ($v' = 2, 3$).

An increased collision energy enlarged the reaction cross-section and broadened the product distribution. Greater numbers of reactive trajectories ended up in the

($v' = 0, 3$) states, which have the lowest fractions of the product populations, to cause this broadening.

Equal increases in both collinear reaction barrier and the collision energy resulted in a decrease in reaction cross-section and a broadening of the distribution as the ($v' = 2$) trajectories were selectively reduced.

Appendix A .

3-D RMCS Quasiclassical Trajectory Program

This version of the trajectory program is only slightly modified from that used by Williams [19], itself a modification of the program written by Muckerman [52] and based on the derivations of Karplus, Porter and Sharma [56]. Current changes to Williams' version involve modifications to file input-output procedures to meet the requirements of FPS-64 FORTRAN, and a reduction in the amount of information being printed about each trajectory to reduce the amount of output. The cosine blending function (unnormalized weight of surface x , $c_x = -2 + 1/\cos \gamma_x$ where γ_x is the bond angle on that surface, for $60^\circ < \gamma_x < 90^\circ$) has been added, and the derivatives of the potential energy with respect to the three bond distances are determined analytically. A change to the program wherein the spline parameters were stored in COMMON in four large ($9 \times 21 \times 3 \times 5$) matrices instead of being passed through subroutine arguments resulted in a simplification of the code by taking advantage of the similarity in structure of the data, and a decrease in running time of about 8% by eliminating unnecessary data transfers; this modification, however, was not used in the current version. The major change in Williams' version of the program, as compared to the original, was for the conversion of the potential energy routine to the five-parameter generalized Morse function (GMF5) and use of that coordinate system.

The main program, RWTRAJ1B, reads the fixed values of the maximum and minimum impact parameter, initial (v,J) state of the reactant molecule, collision energy, integration time step and the number of trajectories; it then calls the various subroutines. For each trajectory, the impact parameter and initial coordinates and momenta are Monte Carlo selected in MONTE/JW6E (subroutine MONTE

in program section JW6E). From these data, initial values of the angular momenta (FMOM/SG4E), velocity (ANGLST/JW6E), and total and internal energies (FENGY/SG4E) are determined. The actual trajectory calculations are performed by MASTER/SG3E which integrates Hamilton's equations of motion with a fourth-order Adams-Bashforth predictor-corrector algorithm, beginning with a three-step Runge-Kutta integrator. The criterion used to determine the end of a trajectory is that one atom is separated from the other two by a distance greater than the reaction shell ρ . This is large enough that all such configurations are in the non-interaction region of the PES. Final values for the internal and total energies and angular momenta, and relative velocity and scattering angle (ANGLE/JW6E), are computed. The internal energy is resolved into its vibrational and rotational components by RESOLVE/JPCI5T2, from which the final integral quantum states are determined.

The RMCS potential energy routines are contained in the JPCI5T2 and JWC17T program sections. As discussed in section 1.2, the potential and its derivatives with respect to bond distance are calculated from the surface defined by the largest bond angle and the two smaller of the three internuclear distances. When that largest angle is less than 90° and one of the other angles is greater than 60° , the potential and derivatives from the second surface are also determined and blended with the first values. DFPOT1/JPCI5T2 reads the cubic interpolatory spline coefficients which describe the potential surface to the program, which were calculated from GMF5 data. FPOT3N/JPCI5T2 then uses the three internuclear distances to assign the geometry to one of the three partial surfaces, and then calls VSPLINE/JWC17T which computes the actual interpolated potential energy using the spline evaluator routines contained in JW8E.

A.1 FPSTRAJ7A (RWTRAJ1B)

Contains:

- The main program (default name is MAIN):

```
C  RUNNING VERSION OF RWTRAJ1B,JWC15T2,JW6E,JWC17T,JW8E,SG3E,SG4E
C  MONTE CARLO QUASI-CLASSICAL TRAJECTORY PROGRAM WRITTEN BY
C  J.T. MUCKERMAN...METHOD BASED ON FORMULATION OF KARPLUS,
C  PORTER & SHARMA, J. CHEM. PHYS. 43, 3259 (1965), WITH SOME
C  MODIFICATIONS.
C
C  THIS VERSION OF THE PROGRAM IS APPROPRIATE FOR THREE-ATOM
C  SYSTEMS WHOSE POTENTIAL ENERGY SURFACES ARE GENERATED BY
C  ROTATED MORSE CURVE-CUBIC INTERPOLATORY SPLINE TECHNIQUES
C
C  IN ADDITION, A  FILE IS CREATED CONTAINING A RECORD OF EACH
C  TRAJECTORY FOR SUBSEQUENT ANALYSIS.....
C
C  C.G.S. UNITS ARE USED THROUGHOUT UNLESS OTHERWISE SPECIFIED.....
C
C  -----
C
C  UNIT ASSIGNMENTS ARE AS FOLLOWS :
C
C  UNIT  2 : SCRATCH FILE
C      5 : INPUT DATA
C      6 : OUTPUT
C     10 : SEED NUMBER FOR RANDOM NUMBER GENERATOR
C     20 : BCA SURFACE PARAMETERS
C     21 : BAC SURFACE PARAMETERS
C     22 : ABC SURFACE PARAMETERS
C
C
C
C
REAL*8 VRANN
COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
1FF(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IREACT,VREL,RHO,HO,AVV,ANG,NEQ,
2KQDQ,IDEX,AMINT,AMTOT,XTER,ENFIN,ENTOT,T,H,EVIB,EROT,BMAX,
3IE,TAD,DIST,BMN,P4(3),P5(3)
COMMON/XPRIN3/IANG,ANGL,XSP,YSP,ZSP,EPOT
COMMON/BLEND1/NBLAB,NBLAG,NBLBA,NBLBG,NBLGA,NBLGB,NSKIP
```

```

COMMON/CONST/RAD,HBAR,PI
COMMON/IMPACT/BPM
COMMON/CRAWN/VRANN,IX,INT
INTEGER NUMVIB(0:10)
CHARACTER*3 CHRCHN(0:3)
DIMENSION TITLE(30),EM(3),NDIFF1(18),NDIFF2(18),NDIFF3(18),
1NIMPAC(20),NREAC1(20),NREAC2(20),NREAC3(20),NVBRT1(20,20),
2NVBRT2(20,20),NDFVL1(18,20),NDFVL2(18,20),NDFVL3(18,20),
3YORG(12)
DATA NUMVIB/11*0/,CHRCHN/' ',' ->',' ->',' #' /
RAD=57.29578
HBAR=1.0544E-27
PI=3.1415927
EFACT=1.6021E-12
ANO=6.02252E+23

C
OPEN(2,FILE='SCRATCH')
OPEN(5,FILE='CONTROL')
OPEN(6,FILE='OUTPUT')
OPEN(10,FILE='SEED')
OPEN(20,FILE='SURF1')
OPEN(21,FILE='SURF2')
OPEN(22,FILE='SURF3')
C NEQ IS THE NUMBER OF SIMULTANEOUS DIFFERENTIAL EQUATIONS TO BE
C SOLVED.
C
NEQ=12
C
C READ AND WRITE TITLE TO IDENTIFY SYSTEM AND ENERGY
C
READ(5,500) (TITLE(I),I=1,30)
WRITE(6,600) (TITLE(I),I=1,30)
C
C -----
C
C BMN IS THE MINIMUM VALUE OF B . THIS HAS BEEN ADDED TO THE PROGRAM
C TO ALLOW FOR STRATIFIED SAMPLING . BMAX IS AS IN THE KPS PAPER...
C RHO IS THE DISTANCE FROM ATOM A TO THE CENTRE OF MASS OF BC.....
C HO IS THE STEP SIZE TO BE USED IN NUMERICAL INTEGRATION.....NTOT
C IS THE NUMBER OF TRAJECTORIES TO BE COMPUTED.....NV AND NJ ARE THE
C INITIAL VIBRATIONAL AND ROTATIONAL QUANTUM NUMBERS OF THE REACTANT
C DIATOMIC MOLECULE.....IE DENOTES CHOICE OF CONTROL OPTION.....
C
C 0 NORMAL (NO BACK INTEGRATION)
C 2 BACK INTEGRATION OF EACH TRAJECTORY

```

```

C      1  CREATES DATA FILE (PUNCHED OUTPUT) CONSISTING OF CARTESIAN
C      COORDINATES OF EACH OF THE THREE PARTICLES (IN INTEGER
C      FORMAT).
C      AT EVERY FIFTEENTH POINT IN THE INTEGRATION AND ALSO BACK-
C      INTEGRATES EACH TRAJECTORY. THIS OPTION HAS BEEN USED TO
C      PRODUCE COMPUTER ANIMATED MOVIES OF SELECTED TRAJECTORIES.
C
C  READ AND WRITE THIS GROUP OF PARAMETERS
C
C  -----
C
C      READ(5,501)RHO,BMN,BMAX,HO,NTOT,IE,NV,NJ,IFLAG
C      WRITE(6,601) RHO,BMN,BMAX,HO,NTOT,IE,NV,NJ
C
C  -----
C
C  EM(1), EM(2), AND EM(3) ARE THE MASSES OF ATOMS A,B, AND C,
C  RESPECTIVELY.....ECOL IS THE CENTER-OF-MASS COLLISION ENERGY IN
C  UNITS OF KCAL/MOLE (NOTE NON-C.G.S. UNITS).
C
C  READ AND WRITE THIS GROUP OF PARAMETERS
C
C  IN THIS VERSION ECOL IS READ IN EV
C
C  -----
C
C      READ(5,504) ECOL,(EM(I),I=1,3)
C      WRITE(6,620)ECOL, (EM(I), I=1,3)
C      DO 3 I=1,3
C      3 EM(I)=EM(I)/ANO
C
C  RLO AND RHI ARE THE INNER AND OUTER TURNING POINTS OF THE REACTANT
C  DIATOMIC MOLECULE APPROPRIATE FOR THE (NV,NJ) STATE....TAU IS THE
C  CLASSICAL HALF-PERIOD OF VIBRATION. THESE THREE QUANTITIES ARE
C  ASSUMED TO BE KNOWN PRIOR TO THIS CALCULATION
C
C
C  READ AND WRITE THIS GROUP OF PARAMETERS
C
C  -----
C
C      READ(5,502) RLO,RHI,TAU
C      WRITE(6,606) RLO,RHI,TAU
C
C  -----

```

```

C
C -----
C
C ORANST IS THE REAL RANDOM NUMBER SEED USED TO RESTART THE
C RANDOM NUMBER GENERATOR BY CALL RANST(ORANST).....
C ORANST MAY BE ANY REAL NUMBER LESS THAN 67101323.  FOR THE FIRST
C RUN THE APPROPRIATE VALUE FOR SUBSEQUENT RUNS IS THE LAST VALUE
C INDICATED IN THE OUTPUT FROM THE PREVIOUS RUN...THE LATTER HAS
C BEEN OBTAINED BY CALL RANRE
C
C READ AND WRITE ORANST
C -----
C
      READ(10,503) ORANST
      WRITE(6,621) ORANST
      CALL RANST(ORANST)
503  FORMAT(F10.0)
621  FORMAT(2X,'INITIAL SEED. NUMBER IS: ',F10.0/1X,70(' ')/1X,
      , ' #      SEED          BPM          ENTOT I CHANNEL ANG      EN',
      , 'TOT F          E VIB          E ROT          ECONS      DIFF      NV NJ')
C
C SET UP MASS RATIO ARRAYS
C
      XM=EM(1)+EM(2)+EM(3)
      DO 10 'I=1,3
      S(1,I)=EM(I)/(EM(1)+EM(2))
      S(2,I)=EM(I)/(EM(1)+EM(3))
      S(3,I)=EM(I)/(EM(2)+EM(3))
      S(4,I)=EM(I)/XM
10  CONTINUE
      RME=XM*S(4,1)*(1.-S(4,1))
      ECOL=ECOL*EFACT
      VREL=SQRT(2.*ECOL/RME)
C
C -----
C
C DEFINITIONS OF ARRAYS.....
C NDIFFN IS NUMBER OF EVENTS IN CHANNEL N WITH SCATTERING ANGLE IN
C EACH TEN-DEGREE BIN.
C NIMPAC IS THE NUMBER OF TRAJECTORIES WITH IMPACT PARAMETER IN EACH
C OF TWENTY BINS.
C NREACTN IS THE NUMBER OF EVENTS IN CHANNEL N WITH IMPACT PARAMETER
C IN EACH OF TWENTY BINS.
C NDFVLN IS THE NUMBER OF EVENTS CHANNEL N WITH SCATTERING ANGLE IN

```

C IN EACH TEN-DEGREE BIN AND FINAL RELATIVE VELOCITY IN EACH OF
C TWENTY BINS.

C NVBRTN IS THE NUMBER OF EVENTS IN CHANNEL N WITH PRODUCT
C VIBRATIONAL ENERGY IN EACH OF TWENTY BINS AND PRODUCT
C ROTATIONAL ENERGY IN EACH OF TWENTY BINS.

C

C CHANNEL NUMBERS ARE ASSIGNED AS FOLLOWS.....

C 0 NO REACTION (PRODUCT BC)

C 1 PRODUCT AB

C 2 PRODUCT AC

C 3 DISSOCIATION

C

C INITIALIZE ALL ELEMENTS OF THESE ARRAYS TO ZERO

C

C

C

```

DO 12 J=1,20
  IF(J.GT.18) GO TO 5
  NDIFF1(J)=0
  NDIFF2(J)=0
  NDIFF3(J)=0
5 CONTINUE
  NIMPAC(J)=0
  NREAC1(J)=0
  NREAC2(J)=0
  NREAC3(J)=0
DO 11 K=1,18
  NDFVL1(K,J)=0
  NDFVL2(K,J)=0
  NDFVL3(K,J)=0

```

11 CONTINUE

```

DO 12 K=1,20
  NVBRT1(K,J)=0
  NVBRT2(K,J)=0

```

12 CONTINUE

```

NVS1=0
NVS2=0
NVS3=0
NIES1=0
NIES2=0
SV1=0.
SR1=0.
SV2=0.
SR2=0.
TOTEV=0.

```



```

      TOTER=0.
      TOTET=0.
      TOTB=0.
      TOTANG=0.

C
C   THE FOLLOWING CALLS TO SUBROUTINES INITIALIZE CONSTANTS  IN THESE
C   ROUTINES OR ALLOW DATA TO BE READ BY THESE ROUTINES.....ALL
C   ARGUMENTS ARE TRANSFERRED THROUGH BLANK COMMON.
C
      CALL DFPOTI
      CALL RSOLVI
      CALL MONTIN
      CALL ANGLIN
      CALL DIFFEQ
C   IF(IE.EQ.1) THEN
C       READ(85,85) TV,PV,RV,AV
C 85   FORMAT(2F,1E,F)
C       CALL CINEMA(0.,0.,0.,TV,PV,RV,AV,2,5,6)
C   END IF
      CALL FSTART
      CALL FMOMIN
      CALL FENGIN
      BSORT=(BMAX-BMN)/20.
C   SORT BINS NOW DEPEND ON BMIN
C
C   TRAJECTORIES ARE COMPUTED IN THE FOLLOWING LOOP
C
      DO 300 ITRAJ=1,NTOT
C       WRITE(6,673)
      673 FORMAT( 70(' ') )
C       WRITE(6,614) ITRAJ
      T=0.
      IREACT=0
C
C   INITIALIZE POTENTIAL BLENDING ROUTINE COUNTERS
C   FOR USE WITH RWCI5T1,RWCI7T AND RWSG3E.
C
      NBLAB=0
      NBLBA=0
      NBLAG=0
      NBLGA=0
      NBLBG=0
      NBLGB=0
      NSKIP=0
C

```

```

C
C  INITIALIZE COORDINATES AND MOMENTA
C
      CALL MONTE
      BIN=Y(5)
      DO 13 J=1,12
        YORG(J)=Y(J)
      13 CONTINUE
C
C  RECORD INITIAL RELATIVE VELOCITY VECTOR
C
      CALL ANGLST
C
C  COMPUTE INITIAL ANGULAR MOMENTA
C
      CALL FMOM
C
C  COMPUTE INITIAL ENERGIES
C
      CALL FENGY
      EMIN=ENTOT-ENFIN
C
      WRITE(6,260) IANG,ANGL,XSP,YSP,ZSP,EPOT
C
C  -----
C
C  WRITE INITIAL VALUES OF TOTAL ENERGY (ENTOT), TOTAL ANGULAR
C  MOMENTUM (AMTOT), INTERNAL ENERGY (ENFIN), INTERNAL ANGULAR
C  MOMENTUM (AMINT) AND RELATIVE VELOCITY (VREL).
C
C  -----
C
C      WRITE(6,602) ENTOT,AMTOT,ENFIN,AMINT,VREL
      ENTOTI=ENTOT
C
C  CALL TRAJECTORY CONTROL ROUTINE MASTER
C
      CALL MASTER
C
C  COMPUTE FINAL ENERGIES IN FENGY
C
      CALL FENGY
C
      WRITE(6,260) IANG,ANGL,XSP,YSP,ZSP,EPOT
C
C  COMPUTE FINAL ANGULAR MOMENTA IN FMOM
C

```

```

      CALL FMOM
C
C  COMPUTE FINAL RELATIVE VELOCITY AND SCATTERING ANGLE IN ANGLE
C
      CALL ANGLE
      ANG=ANG*RAD
C
C  -----
C
C  WRITE COLLISION TIME (T), REACTION CHANNEL (IREACT), SCATTERING
C  ANGLE (ANG), AND FINAL VALUES OF RELATIVE VELOCITY (AVV), TOTAL
C  ENERGY, TOTAL ANGULAR MOMENTUM, INTERNAL ENERGY AND INTERNAL
C  ANGULAR MOMENTUM.
C
C  -----
C
      ENTOTF=ENTOT
      DIFF=(ENTOTI-ENTOTF)/EFACT
      ECONS=(ENTOTF/ENTOTI)*100.
C      WRITE(6,603) T,IREACT,ANG,AVV,ENTOT,AMTOT,ENFIN,
C      1ECONS,AMINT,DIFF
C
C  CONTROL OPTION (IE) DETERMINES IF BACK-INTEGRATION IS TO BE
C  PERFORMED.
C
      IF(IE.EQ.0) GO TO 15
C
C  BACK INTEGRATION CONTROLLED BY REMAST
C
      CALL REMAST
15 CONTINUE
C  REGENERATE SEED NUMBER FOR SUBSEQUENT RUNS
      RANNUM=ORANST
      CALL RANRE(ORANST)
C      WRITE(6,641) ORANST
641 FORMAT(F10.0)
      REWIND 10
      WRITE(10,641) ORANST
C
C  BOOKKEEPING SECTION....APPROPRIATE COUNTERS ARE INCREMENTED.
C
      NANG=ANG/10.+1.
      NBIN=(YORG(5)-BMN)/BSORT + 1
      NIMPAC(NBIN)=NIMPAC(NBIN)+1
      IF(IREACT.EQ.0) GO TO 298

```

```

IF(IReact.EQ.3) GO TO 30
IF(IReact.EQ.2) GO TO 20
NREAC1(NBIN)=NREAC1(NBIN)+1
NDIFF1(NANG)=NDIFF1(NANG)+1
ENCM=C(1)-C(2)+Ekin
ENDV=ENCM/20.
NVEL=20.*AVV/SQRT(2.*ENCM/(XM*S(4,3)*(S(4,1)+S(4,2))))+1
IF(NVEL.GT.20) GO TO 18.
NDFVL1(NANG,NVEL)=NDFVL1(NANG,NVEL)+1
16 CONTINUE
C
C INTERNAL ENERGY IS RESOLVED INTO VIBRATIONAL AND ROTATIONAL
C COMPONENTS IN RESOLVE
C
CALL RSOLVE
NVIB=EVIB/ENDV+1
NROT=EROT/ENDV+1
IF(NVIB.GT.20) GO TO 19
IF(NROT.GT.20) GO TO 19
NVBRT1(NVIB,NROT)=NVBRT1(NVIB,NROT)+1
17 CONTINUE
SV1=SV1+EVIB
SR1=SR1+EROT
C
C FINAL STATE QUANTUM NUMBERS (NV,NJ) ARE ROUNDED TO NEAREST INTEGERS
C FROM THE CONTINUOUS CLASSICAL VALUES.....
C WRITE FINAL VIBRATIONAL AND ROTATIONAL ENERGIES AND FINAL STATE
C QUANTUM NUMBERS
C
C WRITE(6,618) EVIB,EROT,NV,NJ
GO TO 299
18 CONTINUE
NVS1=NVS1+1
GO TO 16
19 CONTINUE
NIES1=NIES1+1
GO TO 17
20 CONTINUE
NREAC2(NBIN)=NREAC2(NBIN)+1
NDIFF2(NANG)=NDIFF2(NANG)+1
ENCM=C(3)-C(2)+Ekin
ENDV=ENCM/20.
NVEL=20.*AVV/SQRT(2.*ENCM/(XM*S(4,2)*(S(4,1)+S(4,3))))+1
IF(NVEL.GT.20) GO TO 23
NDFVL2(NANG,NVEL)=NDFVL2(NANG,NVEL)+1

```

```

21 CONTINUE
  CALL RSOLVE
  NVIB=EVIB/ENDV+1
  NROT=EROT/ENDV+1
  IF(NVIB.GT.20) GO TO 24
  IF(NROT.GT.20) GO TO 24
  NVBRT2(NVIB,NROT)=NVBRT2(NVIB,NROT)+1
22 CONTINUE
  SV2=SV2+EVIB
  SR2=SR2+EROT
C  WRITE(6,618) EVIB,EROT,NV,NJ
  GO TO 299
23 CONTINUE
  NVS2=NVS2+1
  GO TO 21
24 CONTINUE
  NIES2=NIES2+1
  GO TO 22
30 CONTINUE
  NV=1000
  NJ=1000
  NREAC3(NBIN)=NREAC3(NBIN)+1
  NDIFF3(NANG)=NDIFF3(NANG)+1
  ENCM=-C(2)+EKIN
  NVEL=20.*AVV/SQRT(2.*ENCM/(XM*S(4,1)*(S(4,2)+S(4,3))))+1
  IF(NVEL.GT.20) GO TO 31
  NDFVL3(NANG,NVEL)=NDFVL3(NANG,NVEL)+1
  GO TO 299
31 CONTINUE
  NVS3=NVS3+1
  GO TO 299
298 CONTINUE
  CALL RSOLVE
C  WRITE(6,618) EVIB,EROT,NV,NJ
299 CONTINUE
C
  IF(IReact.NE.0) THEN
    TOTEV=TOTEV+EVIB
    TOTER=TOTER+EROT
    TOTET=TOTET+ENTOTF
    TOTB=TOTB+BPM
    TOTANG=TOTANG+ANG
    IF(NV.LE.9) NUMVIB(NV)=NUMVIB(NV)+1
    IF(NV.GT.9) NUMVIB(10)=NUMVIB(10)+1
  END IF

```

```

C  WRITE REACTION CHANNEL (IREACT), FINAL STATE QUANTUM NUMBERS
C  (NV,NJ), INITIAL COORDINATES AND MOMENTA (YORG), AND FINAL
C  COORDINATES AND MOMENTA (Y) ON BINARY FILE (TAPE2).
C
C      WRITE(2) IREACT,NV,NJ,(YORG(J), J=1,12),(Y(J), J=1,12)
      REWIND 10
      WRITE(6,650) ITRAJ,RANNUM,BPM,ENTOTI,IREACT,ANG,ENTOTF,
      , EVIB,EROT,ECONS,DIFF,CHRCHN(IREACT),NV,NJ
650  FORMAT(I5,F11.0,E11.4,E13.6,I2,F11.6,3E13.6,F9.4,F9.5,A3,I2,I3)
300  CONTINUE
      KWRITE=1
      MWRITE=2
      NWRITE=3
      NT1=0
      NT2=0
      NT3=0
      DO 310  J=1,20
      NT1=NT1+NREAC1(J)
      NT2=NT2+NREAC2(J)
      NT3=NT3+NREAC3(J)
310  CONTINUE
C
C  PRINT CONTROL: DO NOT COMPUTE AVERAGES IF BINS ARE
C  EMPTY (NT1 OR NT2 = 0).  SKIP BIN LISTS IF IFLAG = 1.
C
      IF(NT1.GT.0) GO TO 312
      AVVB1=0.
      AVRT1=0.
      GO TO 315
312  AVVB1=SV1/NT1
      AVRT1=SR1/NT1
315  IF(NT2.GT.0)GO TO 314
      AVVB2=0.
      AVRT2=0.
      GO TO 316
314  AVVB2=SV2/NT2
      AVRT2=SR2/NT2
316  IF(IFLAG.NE.0) GO TO 999
C
C  WRITE BOOKKEEPING ARRAYS ON THE OUTPUT FILE
C
      WRITE(6,607)
      WRITE(6,608) (NIMPAC(J), J=1,20),NTOT
      WRITE(6,609) KWRITE
      WRITE(6,608) (NREAC1(J), J=1,20),NT1

```

```

WRITE(6,609) MWRITE
WRITE(6,608) (NREAC2(J), J=1,20),NT2
WRITE(6,609) MWRITE
WRITE(6,608) (NREAC3(J), J=1,20),NT3
WRITE(6,610)
WRITE(6,611) KWRITE
WRITE(6,612) (NDIFF1(J), J=1,18),NT1
WRITE(6,611) MWRITE
WRITE(6,612) (NDIFF2(J), J=1,18),NT2
WRITE(6,611) MWRITE
WRITE(6,612) (NDIFF3(J), J=1,18),NT3
WRITE(6,613) KWRITE
WRITE(6,616) ((NDFVL1(19-J,K), K=1,20), J=1,18)
WRITE(6,619) NVS1
WRITE(6,613) MWRITE
WRITE(6,616) ((NDFVL2(19-J,K), K=1,20), J=1,18)
WRITE(6,619) NVS2
WRITE(6,613) MWRITE
WRITE(6,616) ((NDFVL3(19-J,K), K=1,20), J=1,18)
WRITE(6,619) NVS3
WRITE(6,615) KWRITE
WRITE(6,616) ((NVBRT1(21-J,K), K=1,20), J=1,20)
WRITE(6,619) NIES1
WRITE(6,615) MWRITE
WRITE(6,616) ((NVBRT2(21-J,K), K=1,20), J=1,20)
WRITE(6,619) NIES2
WRITE(6,617) KWRITE,NT1,AVVB1,AVRT1,MWRITE,NT2,AVVB2,AVRT2
WRITE(6,631) TOTEV,TOTER,TOTET,TOTB,TOTANG
631 FORMAT(' TOTALS: EVIB',E15.6,' EROT',E15.6,' ETOT',
, E15.6,/, ' IMPACT PARAMETER',E15.6,' SCAT ANGLE',E15.6)
WRITE(6,632) (I,I=0,9),(NUMVIB(I),I=0,10)
632 FORMAT(' V=',10I5,' OVER'/' #: ',11I5)
999 -CONTINUE
CLOSE(2)
CLOSE(5)
CLOSE(6)
CLOSE(10)
CLOSE(20)
CLOSE(21)
CLOSE(22)
STOP
500 FORMAT(15A4/15A4)
501 FORMAT(2E9.2,2E8.1,I4,4I2)
502 FORMAT(3E11.5)
504 FORMAT(F8.6,F10.6,2F6.3)

```

```

600 FORMAT(1H1,5X,15A4/6X,15A4)
601 FORMAT( 3X,'INPUT DATA:',/,5X,'RHO = ',E15.6/,5X,
1 'BMIN = ',E15.6/,5X,'BMAX = ',E15.6/,5X,
2 'HO = ',E15.6/,5X,'NTOT = ',I5/,5X,'IE = ',I5/,5X,'NV = ',I5,
3 /,5X,'NJ = ',I5)
602 FORMAT( 5X,'INITIAL ENERGY AND MOMENTA.....',/,6X,
1'TOTAL ENERGY = ',E15.6/,6X,'TOTAL ANGULAR MOMENTUM = '
2,E15.6/6X,'INTERNAL ENERGY = ', E15.6/6X,
3'INTERNAL ANGULAR MOMENTUM = ', E15.6/6X,
4'RELATIVE VELOCITY = ', E15.6)
603 FORMAT( 5X,'FINAL CONDITIONS.....'/6X,
1'COLLISION TIME = ',E15.6/6X,
2'REACTION CHANNEL = ',I5/6X,
3'SCATTERING ANGLE = ',F10.6/6X,
4'RELATIVE VELOCITY = ',E15.6/6X,
5'TOTAL ENERGY = ',E15.6,25X,'ENERGY',/,6X,
6'TOTAL ANGULAR MOMENTUM = ',E15.6,12X,'CONSERVATION',/,6X,
7'INTERNAL ENERGY = ',E15.6,20X,F8.4,'% ',/,6X,
8'INTERNAL ANGULAR MOMENTUM = ',E15.6,9X,F8.5,' EV')
606 FORMAT( 4X,'RLO = ', E12.6,5X,'RHI = ',E12.6,5X,'TAU = ',E12.6)
607 FORMAT(1H1,43H TOTAL COLLISIONS VS. IMPACT PARAMETER.....///)
608 FORMAT(20I5,5H-----,I5)
609 FORMAT(1H0,8H CHANNEL,I2,31H REACTIONS VS. IMPACT PARAMETER//)
610 FORMAT(1H0,35H PRODUCT ANGULAR DISTRIBUTIONS.....///)
611 FORMAT(1H0,8H CHANNEL,I2,31H REACTIONS VS. SCATTERING ANGLE//)
612 FORMAT(18I5,5H-----,I5)
613 FORMAT(1H0,8H CHANNEL,I2,30H SCATTERING ANGLE VS. VELOCITY//)
614 FORMAT(20X,'TRAJECTORY NO.',I5)
615 FORMAT(2X,'CHANNEL',I2,'VIBRATIONAL ENERGY VS. ROTATIONAL
1' ENERGY',/ )
616 FORMAT(20I5/)
617 FORMAT(2X,'AVERAGE PRODUCT VIBRATIONAL AND ROTATIONAL',
1' ENERGIES',////,10X,'CHANNEL',I2,' (',I3,'REACTIONS)',//,
215X,'AVERAGE VIBRATIONAL ENERGY = ',E15.6,/,15X,
3'AVERAGE ROTATIONAL ENERGY = ',E15.6,/,10X,'CHANNEL',
4I2,' (',I3,'REACTIONS)',//,15X,'AVERAGE VIBRATIONAL ENERGY = ',
5E15.6,/,15X,'AVERAGE ROTATIONAL ENERGY = ',E15.6)
618 FORMAT(6X,'VIBRATIONAL ENERGY = ',E15.6/,6X,
1'ROTATIONAL ENERGY = ',E15.6/,21X,'NV = ',I3/,21X,'NJ = ',I3)
619 FORMAT(1H ,////20X,I3,21H ENTRIES OUT OF RANGE)
620 FORMAT(3X,5HECOL=,F10.6/3X,3HMA=,F10.6/3X,3HMB=,F10.6/3X,
13HMC=,F10.6)
260 FORMAT(/,I3,2X,F7.3,2X,F7.4,2X,F7.4,2X,F7.4,2X,F8.4)
END

```


A.2 FPSTRAJ2 (JW6E)

Contains:

- Subroutine MONTIN, which calculates constants and reads the choice of inner/outer turning point for the first trajectory;
 - Entry MONTE, which initializes the Monte Carlo variables;
- Subroutine ANGLIN, which initializes constants;
 - Entry ANGLST, which stores the initial relative velocity vector for the later determination of the scattering angle;
 - Entry ANGLE, which calculates the scattering angle.

SUBROUTINE MONTIN

```
C
C -----
C
C VARIABLE INITIALIZATION ROUTINE.....TWO ENTRY POINTS.....MONTIN
C CALCULATES CONSTANTS AND READS CHOICE OF DIATOMIC TURNING POINT
C FOR FIRST TRAJECTORY..MONTE INITIALIZES ALL MONTE CARLO VARIABLES
C
C -----
C
C      COMMON/IMPACT/BPM
C      COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
C      1FF(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IReact,VREL,RHO,RO,AVV,ANG,
C      2NEQ,KDQ,IDEX,AMINT,AMTOT,XTER,ENFIN,ENTOT,T,H,EVIB,EROT,BMAX,
C      3IE,TAD,DIST,BMN,P4(3),P5(3)
C      COMMON/CONST/RAD,HBAR,PI
C      D=XM*S(4,1)*(1.-S(4,1))*VREL
C
C IF IR=1 THE FIRST TRAJECTORY STARTS WITH MOLECULE BC AT THE INNER
C TURNING POINT. IF IR=2 THE FIRST TRAJECTORY BEGINS WITH BC AT THE
C OUTER TURNING POINT.....INITIAL TURNING POINT ALTERNATES BETWEEN
C INNER AND OUTER ON SUBSEQUENT TRAJECTORIES
C
C      READ(5,501) IR
```

```

      TJSQ=NJ*(NJ+1)
      TUF=0.
100  RETURN
      ENTRY MONTE
C
C  RANDOMLY SELECTS INITIAL VALUES OF MONTE CARLO VARIABLES FROM
C  PROPER DISTRIBUTION FUNCTIONS.....CALCULATES INITIAL VALUES OF
C  COORDINATES AND MOMENTA
C
C      INITIALIZE Q4
      Y(4)=0.
C      INITIALIZE P4
      Y(10)=0.
C      INITIALIZE P5
      Y(11)=0.
C      INITIALIZE P6
      Y(12)=D
      CALL RANN(X)
      BPM=SQRT(BMN**2+X*(BMAX**2-BMN**2))
C      WRITE(6,400) X,BPM
400  FORMAT(2X,'X = ',F12.8,7X,'BPM = ',E10.4)
C      INITIALIZE Q6
      CALL RANN(X)
      DIST=TAU*VREL*X
      Y(6)=-SQRT(RHO*RHO-BPM*BPM)-DIST
C      INITIALIZE Q5
      Y(5)=BPM
      GO TO (200,250) IR
200  CONTINUE
      RR=RLO
      IR=2
C      WRITE(6,401) X,RR
401  FORMAT(2X,'X = ',F12.8,9X,'R = ',E10.4)
      GO TO 300
250  CONTINUE
      RR=RHI
      IR=1
C      WRITE(6,401) X,RR
300  CONTINUE
      CALL RANN(X)
      XX=2.*X-1.
      THETA=ACOS(XX)
C      WRITE(6,402) X,THETA
402  FORMAT(2X,'X = ',F12.8,5X,'THETA = ',E10.4)
      CALL RANN(X)

```

```

      PHI=2.*PI*X
C     WRITE(6,403) X,PHI
      403 FORMAT(2X,'X = ',F12.8,7X,'PHI = ',E10.4)
      CALL RANH(X)
      ETA=2.*PI*X
C     WRITE(6,404) X,ETA
      404 FORMAT(2X,'X = ',F12.8,7X,'ETA = ',E10.4)
C     INITIALIZE Q1
      Y(1)=RR*SIN(THETA)*COS(PHI)
C     INITIALIZE Q2
      Y(2)=RR*SIN(THETA)*SIN(PHI)
C     INITIALIZE Q3
      Y(3)=RR*COS(THETA)
      PSQ=TJSQ*HBAR*HBAR/(RR*RR)
      PAB=SQRT(PSQ)
C     INITIALIZE P1
      Y(7)=-PAB*(SIN(PHI)*COS(ETA)+COS(PHI)*COS(THETA)*SIN(ETA))
C     INITIALIZE P2
      Y(8)=PAB*(COS(PHI)*COS(ETA)-SIN(PHI)*COS(THETA)*SIN(ETA))
C     INITIALIZE P3
      Y(9)=PAB*SIN(THETA)*SIN(ETA)
C
C     WRITE INITIAL VALUES OF COORDINATES AND MOMENTA
C
C     WRITE(6,500) TUF, (Y(J), J=1,12)
      GO TO 100
C 500 FORMAT(1H0,4X,E10.4,2(/6E10.4))
      501 FORMAT(I5)
      END
      SUBROUTINE ANGLIN
C
C -----
C
C     ROUTINE CALCULATES SCATTERING ANGLE AND FINAL RELATIVE VELOCITY..
C     THREE ENTRY POINTS....ANGLIN INITIALIZES CONSTANTS....ANGLST
C     STORES INITIAL RELATIVE VELOCITY VECTOR....ANGLE PERFORMS
C     CALCULATION.
C
C -----
C
      COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
      1FF(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IREACT,VREL,RHO,HO,AVV,ANG,
      2NEQ,KDQ,IDEX,AMINT,AMTOT,XTER,ENFIN,ENTOT,T,H,EVIB,EROT,BMAX,
      3IE,TAD,DIST,BMW,P4(3),P5(3)
      DIMENSION VO(3),V(3)

```

```

      RM1=XM*S(4,1)*(1.-S(4,1))
      RM2=XM*S(4,3)*(1.-S(4,3))
      RM3=XM*(1.-S(4,3))*(1.-S(4,1))
      RM4=XM*S(4,2)*(1.-S(4,2))
      RM5=XM*(1.-S(4,2))*(1.-S(4,1))
100  RETURN
      ENTRY ANGLST
C
C  STORE RELATIVE VELOCITY VECTOR IN VO(3) AND ITS MAGNITUDE IN AVVO
C
      DO 110  I=1,3
      VO(I)=Y(I+9)/RM1
110  CONTINUE
      AVVO=VREL
      GO TO 100
      ENTRY ANGLE
C
C  CALCULATES FINAL RELATIVE VELOCITY AND SCATTERING ANGLE USING
C  INITIAL AND FINAL RELATIVE VELOCITY VECTORS
C
      DOTPR=0.
      AVV=0.
      DO 600  I=1,3
      NN=IREACT+1
      GO TO(200,300,400,500) NN
200  CONTINUE
      V(I)=Y(I+9)/RM1
      GO TO 500
300  CONTINUE
      V(I)=Y(I+9)/RM3-Y(I+6)/RM2
      GO TO 500
400  CONTINUE
      V(I)=Y(I+6)/RM4+Y(I+9)/RM5
500  CONTINUE
      DOTPR=DOTPR+V(I)*VO(I)
      AVV=AVV+V(I)*V(I)
600  CONTINUE
      AVV=SQRT(AVV)
      ANG=ACOS(DOTPR/(AVVO*AVV))
      GO TO 100
      END

```

A.3 FPSTRAJ3 (JW8E)

Contains:

- Subroutine GRAEVU, which evaluates a two-dimensional spline;
- Function SPLINE, which evaluates a one-dimensional spline;
- Subroutine SPCOEF, which fits data to and calculates parameters for a one-dimensional spline.

```
      SUBROUTINE GRAEVU(X,NX,Y,NY,F,SX2,SY2,SX2Y2,XX,YY,LX,LY
1,SS,DSDX,DSDY)
C
C -----
C
C EVALUATES A 2-D SPLINE FOR A POINT (XX,YY)
C
C INPUT :
C -----
C
C      X : VECTOR OF LENGTH NX
C      Y : VECTOR OF LENGTH NY
C      F : NX BY NY MATRIX
C      SX2,SY2,SX2Y2 : NX BY NY MATRICES OF SPLINE COEFF.
C      (XX,YY) : THE POINT TO BE SPLINE-EVALUATED
C
C OUTPUT :
C -----
C
C      SS : THE SPLINE APPROXIMATION TO F(XX,YY)
C -----
C
C      DIMENSION X(NX),Y(NY),SX2(NX,NY),SY2(NX,NY),SX2Y2(NX,NY),
1F(NX,NY),PXP(4),PYP(4),C(4,4),PX(4),PY(4)
C
C      LXP1=LX+1
C      LYP1=LY+1
C
```

```

C(1,1)=SX2Y2(LXP1,LYP1)
C(3,1)=SX2(LXP1,LYP1)
C(1,3)=SY2(LXP1,LYP1)
C(3,3)=F(LXP1,LYP1)

```

C

```

C(2,1)=SX2Y2(LXP1,LY)
C(4,1)=SX2(LXP1,LY)
C(2,3)=SY2(LXP1,LY)
C(4,3)=F(LXP1,LY)

```

C

```

C(1,2)=SX2Y2(LX,LYP1)
C(3,2)=SX2(LX,LYP1)
C(1,4)=SY2(LX,LYP1)
C(3,4)=F(LX,LYP1)

```

C

```

C(2,2)=SX2Y2(LX,LY)
C(4,2)=SX2(LX,LY)
C(2,4)=SY2(LX,LY)
C(4,4)=F(LX,LY)

```

C

```

HX01=XX-X(LX)
HX10=X(LXP1)-XX
HY01=YY-Y(LY)
HY10=Y(LYP1)-YY
HX11=X(LXP1)-X(LX)
HY11=Y(LYP1)-Y(LY)

```

C

```

PX(1)=(HX01**3/(6.*HX11))-(HX01*HX11/6.)
PX(2)=(HX10**3/(6.*HX11))-(HX10*HX11/6.)
PX(3)=HX01/HX11
PX(4)=HX10/HX11
PY(1)=(HY01**3/(6.*HY11))-(HY01*HY11/6.)
PY(2)=(HY10**3/(6.*HY11))-(HY10*HY11/6.)
PY(3)=HY01/HY11
PY(4)=HY10/HY11
PXP(1)=(.5*HX01**2/HX11)-(HX11/6.)
PXP(2)=-(.5*HX10**2/HX11)+(HX11/6.)
PXP(3)=(1./HX11)
PXP(4)=- (1./HX11)
PYP(1)=(.5*HY01**2/HY11)-(HY11/6.)
PYP(2)=-(.5*HY10**2/HY11)+(HY11/6.)
PYP(3)=(1./HY11)
PYP(4)=- (1./HY11)

```

C

```

SUM2=0.

```

```

      DO 70 I=1,4
      SUM1=0.
      DO 80 J=1,4
80    SUM1=SUM1+C(I,J)*PX(J)
70    SUM2=SUM2+(SUM1*PY(I))
      SS=SUM2
C
      SUM2=0.
      DO 71 I=1,4
      SUM1=0.
      DO 81 J=1,4
81    SUM1=SUM1+C(I,J)*PXP(J)
71    SUM2=SUM2+(SUM1*PY(I))
      DSDX=SUM2
      SUM2=0.
      DO 72 I=1,4
      SUM1=0.
      DO 82 J=1,4
82    SUM1=SUM1+C(I,J)*PX(J)
72    SUM2=SUM2+(SUM1*PYP(I))
      DSDY=SUM2
      RETURN
      END
      SUBROUTINE SPCOEF(N,XN,FN,S)
C
C -----
C
C 1-D SPLINE FITTING ROUTINE .
C -----
C
      DIMENSION XN(N),FN(N),S(N),RHO(201),TAU(201)
      NM1=N-1
      NM2=N-2
      RHO(2)=0.
      TAU(2)=0.
      DO 4 I=2,NM1
      IIM1=I-1
      II=I
      IIP1=I+1
      HIM1=XN(II)-XN(IIM1)
      HI=XN(IIP1)-XN(II)
      TEMP=(HIM1/HI)*(RHO(I)+2.)+2.
      RHO(I+1)=-1./TEMP
      D=6.*((FN(IIP1)-FN(II))/HI-(FN(II)-FN(IIM1))/HIM1)/HI

```

```

4   TAU(I+1)=(D-HIM1*TAU(I)/HI)/TEMP
    S(1)=0.
    S(N)=0.
    DO 5 I=1,NM2
      IB=N-I
5   S(IB)=RHO(IB+1)*S(IB+1)+TAU(IB+1)
    RETURN
    END
    FUNCTION SPLINE(N,XN,FN,S,X)

```

C

C

C

C 1-D SPLINE EVALUATOR .

C

C

C

```

    DIMENSION XN(N),FN(N),S(N)
    I1=1
    IF(X.GE.XN(I1)) GO TO 1
    I2=2
    H1=XN(I2)-XN(I1)
    SPLINE=FN(I1)+(X-XN(I1))*((FN(I2)-FN(I1))/H1-H1*S(2)/6.)
    RETURN
1   IN=N
    IF(X.LE.XN(IN)) GO TO 2
    INM1=N-1
    HNM1=XN(IN)-XN(INM1)
    SPLINE=FN(IN)+(X-XN(IN))*((FN(IN)-FN(INM1))/HNM1+
2HNM1*S(N-1)/6.)
    RETURN
2   DO 3 I=2,N
    II=I
    IF(X.LE.XN(II)) GO TO 4
3   CONTINUE
4   L=I-1
    IL=L
    ILP1=L+1
    A=XN(ILP1)-X
    B=X-XN(IL)
    HL=XN(ILP1)-XN(IL)
    SPLINE=A*S(L)*(A**2/HL-HL)/6.+B*S(L+1)*(B**2/HL-HL)/6.
2+(A*FN(IL)+B*FN(ILP1))/HL
    RETURN
    END

```


A.4 FPSTRAJ4 (JWCI7T)

Contains:

- Subroutine VSPLIN, which determines the potential energy and its derivatives with respect to the three internuclear distances for a specific surface;
- Subroutine GRA2DS, which fits data to and calculates parameters for a two-dimensional spline.

```
      SUBROUTINE VSPLIN(X,Y,Z,ANG,IANG,EPOT,DRAB,DRBC,DRAC)
C
C -----
C
C THIS ROUTINE HAS BEEN MODIFIED TO HANDLE THE 5-PARAMETER
C GENERALIZED MORSE FUNCTION . IN PARTICULAR ALL OF THE
C PARTIAL DERIVATIVES HAVE BEEN RE-DEFINED .
C
C R.J.WILLIAMS OCTOBER 11-1984 .
C
C -----
C
      COMMON /SURFA/THETA(21),GAMA(9),DA(9,21),SX2DA(9,21),
      1SY2DA(9,21),SKY2DA(9,21),BOA(9,21),SX2BOA(9,21),SY2BOA(9,21),
      2SXY2BA(9,21),RA(9,21),SX2RA(9,21),SY2RA(9,21),
      3SXY2RA(9,21),P4A(9,21),SX2P4A(9,21),SY2P4A(9,21),
      4SXY24A(9,21),P5A(9,21),SX2P5A(9,21),SY2P5A(9,21),
      5SXY25A(9,21)
      COMMON /SURFB/THETB(19),GAMB(9),DB(9,19),SX2DB(9,19),
      1SY2DB(9,19),SKY2DB(9,19),BOB(9,19),SX2BOB(9,19),SY2BOB(9,19),
      2SXY2BB(9,19),RB(9,19),SX2RB(9,19),SY2RB(9,19),
      3SXY2RB(9,19),P4B(9,19),SX2P4B(9,19),SY2P4B(9,19),
      4SXY24B(9,19),P5B(9,19),SX2P5B(9,19),SY2P5B(9,19),
      5SXY25B(9,19)
      COMMON /SURFC/THETC(21),GAMC(9),DC(9,21),SX2DC(9,21),
      1SY2DC(9,21),SKY2DC(9,21),BOC(9,21),SX2BOC(9,21),SY2BOC(9,21),
      2SXY2BC(9,21),RC(9,21),SX2RC(9,21),SY2RC(9,21),
      3SXY2RC(9,21),P4C(9,21),SX2P4C(9,21),SY2P4C(9,21),
      4SXY24C(9,21),P5C(9,21),SX2P5C(9,21),SY2P5C(9,21),
      5SXY25C(9,21)
```

```

      RAD=.01745329
C
C SPECIFY THE SWING POINT COORDINATES
C
      XS=10.
      YS=10.
C
      IF(IANG.EQ.1)GO TO 100
      IF(IANG.EQ.2)GO TO 200
      IF(IANG.EQ.3)GO TO 300
C
C -----
C
C THIS IS SURFA I.E. THE ACB SURFACE (FHH HERE) . THIS SURFACE WAS
C SET ON UNIT 20 .
C
100 IF(X.LT.XS.AND.Y.LT.YS)GO TO 1
      THTA=90.
      IF(XS-X)3,3,4
3      THTA=0.
      RL=YS-Y
      GO TO 5
4      THTA=90.
      RL=XS-X
      GO TO 5
1      ARG=(XS-X)/(YS-Y)
      THTA=ATAN(ARG)/.01745329252
      ARG1=(X-XS)**2
      ARG2=(Y-YS)**2
      ARG3=ARG1+ARG2
      RL=SQRT(ARG3)
5      I=0
10     I=I+1
      IF(I.GT.9)GO TO 11
      IF(ANG.LE.GAMA(I))GO TO 11
      GO TO 10
11     IF(I.EQ.1)I=2
      LY=I-1
      J=0
20     J=J+1
      IF(J.GE.23)GO TO 21
      IF(THTA.LE.THETA(J))GO TO 21
      GO TO 20
21     IF(J.EQ.1)J=2
      LX=J-1

```

```

      CALL GRAEVU(GAMA,9,THETA,21,DA,SX2DA,SY2DA,SXY2DA,ANG,
1THTA,LY,LX,SD,DDANG,DDT)
      CALL GRAEVU(GAMA,9,THETA,21,BOA,SX2BOA,SY2BOA,SXY2BA,ANG,
1THTA,LY,LX,SBO,DBOANG,DBOT)
      CALL GRAEVU(GAMA,9,THETA,21,RA,SX2RA,SY2RA,SXY2RA,ANG,
1THTA,LY,LX,SR,DLANG,DLT)
      CALL GRAEVU(GAMA,9,THETA,21,P4A,SX2P4A,SY2P4A,SXY24A,ANG,
1THTA,LY,LX,SP4,DP4ANG,DP4T)
      CALL GRAEVU(GAMA,9,THETA,21,P5A,SX2P5A,SY2P5A,SXY25A,ANG,
1THTA,LY,LX,SP5,DP5ANG,DP5T)
      XX=RL-GR

```

```

2      GO TO 500

```

```

C

```

```

C

```

```

C

```

```

C THIS IS SURFB I.E. THE BAC SURFACE (HFH HERE) .THIS SURFACE WAS
C SET ON UNIT 21 .

```

```

C

```

```

200 IF(X.LT.XS.AND.Y.LT.YS)GO TO 25

```

```

      THTA=90.

```

```

      IF(XS-X)13,13,14

```

```

13      THTA=0.

```

```

      RL=YS-Y

```

```

      GO TO 15

```

```

14      THTA=90.

```

```

      RL=XS-X

```

```

      GO TO 15

```

```

25      ARG=(XS-X)/(YS-Y)

```

```

      THTA=ATAN(ARG)/.01745329252

```

```

      ARG1=(X-XS)**2

```

```

      ARG2=(Y-YS)**2

```

```

      ARG3=ARG1+ARG2

```

```

      RL=SQRT(ARG3)

```

```

15      I=0

```

```

22      I=I+1

```

```

      IF(I.GE.9)GO TO 23

```

```

      IF(ANG.LE.GAMB(I))GO TO 23

```

```

      GO TO 22

```

```

23      IF(I.EQ.1)I=2

```

```

      LY=I-1

```

```

      J=0

```

```

30      J=J+1

```

```

      IF(J.GE.19)GO TO 31

```

```

      IF(THTA.LE.THETB(J))GO TO 31

```

```

      GO TO 30

```

```

31  IF(J.EQ.1)J=2
    LX=J-1
    CALL GRAEVU(GAMB,9,THETB,19,DB,SX2DB,SY2DB,SXY2DB,ANG,
1THTA,LY,LX,SD,DDANG,DDT)
    CALL GRAEVU(GAMB,9,THETB,19,BOB,SX2BOB,SY2BOB,SXY2BB,ANG,
1THTA,LY,LX,SBO,DBOANG,DBOT)
    CALL GRAEVU(GAMB,9,THETB,19,RB,SX2RB,SY2RB,SXY2RB,ANG,
1THTA,LY,LX,SR,DLANG,DLT)
    CALL GRAEVU(GAMB,9,THETB,19,P4B,SX2P4B,SY2P4B,SXY24B,ANG,
1THTA,LY,LX,SP4,DP4ANG,DP4T)
    CALL GRAEVU(GAMB,9,THETB,19,P5B,SX2P5B,SY2P5B,SXY25B,ANG,
1THTA,LY,LX,SP5,DP5ANG,DP5T)
    XX=RL-SR
12  GO TO 500
C
C -----
C
C THIS IS SURFC I.E. THE ABC SURFACE (FHH HERE) .THIS SURFACE WAS
C SET ON UNIT 22 .
C
300 IF(X.LT.XS AND.Y.LT.YS)GO TO 61
    THTA=90.
    IF(XS-X)43,43,44
43  THTA=0.
    RL=YS-Y
    GO TO 45
44  THTA=90.
    RL=XS-X
    GO TO 45
61  ARG=(XS-X)/(YS-Y)
    THTA=ATAN(ARG)/.01745329252
    ARG1=(X-XS)**2
    ARG2=(Y-YS)**2
    ARG3=ARG1+ARG2
    RL=SQRT(ARG3)
45  I=0
40  I=I+1
    IF(I.GE.9)GO TO 41
    IF(ANG.LE.GAMC(I))GO TO 41
    GO TO 40
41  IF(I.EQ.1)I=2
    LY=I-1
    J=0
50  J=J+1
    IF(J.GE.23)GO TO 51

```

```

      IF(THTA.LE.THETC(J))GO TO 51
      GO TO 50
51    IF(J.EQ.1)J=2
      LX=J-1
      CALL GRAEVU(GAMC,9,THETC,21,DC,SX2DC,SY2DC,SXY2DC,ANG,
1THTA,LY,LX,SD,DDANG,DDT)
      CALL GRAEVU(GAMC,9,THETC,21,BOC,SX2BOC,SY2BOC,SXY2BC,ANG,
1THTA,LY,LX,SBO,DBOANG,DBOT)
      CALL GRAEVU(GAMC,9,THETC,21,RC,SX2RC,SY2RC,SXY2RC,ANG,
1THTA,LY,LX,SR,DLANG,DLT)
      CALL GRAEVU(GAMC,9,THETC,21,P4C,SX2P4C,SY2P4C,SXY24C,ANG,
1THTA,LY,LX,SP4,DP4ANG,DP4T)
      CALL GRAEVU(GAMC,9,THETC,21,P5C,SX2P5C,SY2P5C,SXY25C,ANG,
1THTA,LY,LX,SP5,DP5ANG,DP5T)
      XX=RL-SR
C
C -----
C
C EVALUATE THE POTENTIAL ENERGY
C
500  SB=SBO*(1.+(SP4*XX)+(SP5*((XX)**2)))
      EPOT=SD*((1.-EXP(SB*XX))**2-1.)
C
C NOW EVALUATE DX,DY,DZ AND THEN SORT INTO DRAB,DRBC,DRAC
C
C THE VARIOUS PARTIAL DERIVATIVES ARE DEFINED AS :
C
C   DX=DV/DX  Y,Z CONSTANT
C   DY=DV/DY  X,Z CONSTANT
C   DZ=DV/DZ  X,Y CONSTANT
C   DANGX=DGAMMA/DX  Y,Z CONSTANT
C   DANGY=DGAMMA/DY  X,Z CONSTANT
C   DANGZ=DGAMMA/DZ  X,Y CONSTANT
C   DVT=DV/DTHETA  L,GAMMA CONSTANT
C   DVL=DV/DL  THETA,GAMMA CONSTANT
C   DVANG=DV/DGAMMA  THETA,L CONSTANT
C   DTX=DTHETA/DX  Y,Z CONSTANT
C   DTY=DTHETA/DY  X,Z CONSTANT
C   DLX=DL/DX  Y,Z CONSTANT
C   DLY=DL/DY  X,Z CONSTANT
C   DVD=DV/DDE  (BETA*A) CONSTANT
C   DVBA=DV/D(BETA*A)  DE CONSTANT
C   DDT=DDE/DTHETA  GAMMA CONSTANT
C   DBAT=D(BETA*A)/DTHETA  GAMMA CONSTANT
C   DBOT=DBETA0/DTHETA  GAMMA CONSTANT

```

```

C   DLT=DLE/DTHETA  GAMMA CONSTANT
C   DP4T=DLAMBDA1/DTHETA  GAMMA CONSTANT
C   DP5T=DLAMBDA2/DTHETA  GAMMA CONSTANT
C   DBABO=D(BETA*A)/DBETAO  LE,LAMBDA1,LAMBDA2 CONSTANT
C   DBAL=D(BETA*A)/DLE  BETAO,LAMBDA1,LAMBDA2 CONSTANT
C   DBAP4=D(BETA*A)/DLAMBDA1  LAMBDA2,BETAO,LE CONSTANT
C   DBAP5=D(BETA*A)/DLAMBDA2  LAMBDA1,BETAO,LE CONSTANT
C   DDANG=DDE/DGAMMA  THETA CONSTANT
C   DBAANG=D(BETA*A)/DGAMMA  THETA CONSTANT
C   DBOANG=DBETAO/DGAMMA  THETA CONSTANT
C   DLANG=DLE/DGAMMA  THETA CONSTANT
C   DP4ANG=DLAMBDA1/DGAMMA  THETA CONSTANT
C   DP5ANG=DLAMBDA2/DGAMMA  THETA CONSTANT
C
C   DBOT=DBOT/RAD
C   DDT=DDT/RAD
C   DLT=DLT/RAD
C   DP4T=DP4T/RAD
C   DP5T=DP5T/RAD
C   DBOANG=DBOANG/RAD
C   DDANG=DDANG/RAD
C   DLANG=DLANG/RAD
C   DP4ANG=DP4ANG/RAD
C   DP5ANG=DP5ANG/RAD
C   U=(X*X+Y*Y-Z*Z)/(2.*X*Y)
C   COEF=1./SQRT(1.-U*U)
C   DANGX=-COEF*((1./Y)-(U/X))
C   DANGY=-COEF*((1./X)-(U/Y))
C   DANGZ=-COEF*(Z/(X*Y))
C   EXPBX=EXP(SB*XX)
C   EXPBM=1.-EXPBX
C   EXPBX2=EXPBX**2
C   DTX=-(YS-Y)/(RL*RL)
C   DTY=(XS-X)/(RL*RL)
C   DTZ=0.0
C   DLX=-(XS-X)/RL
C   DLY=-(YS-Y)/RL
C   DLZ=0.0
C   CALCULATE DVT
C
C   DVDE=-2.*EXPBX + EXPBX2
C   DVBO=-2.*SD*XX*EXPBX*EXPBM*(1.+SP4*XX+SP5*XX**2)
C   DVLE=2.*SD*SBO*EXPBX*EXPBM*(1.+2.*SP4*XX+3.*SP5*XX**2)

```

```

DVP4=-2.*SD*SB0*XX*XX*EXPBX*EXPBM
DVP5=DVP4*XX
DVT=DVDE*DDT+DVBO*DBOT+DVLE*DLT+DVP4*DP4T+DVP5*DP5T
C
C  CALCULATE DVANG
C
    DVANG=DVDE*DDANG+DVBO*DBOANG+DVLE*DLANG+DVP4*DP4ANG
1    +DVP5*DP5ANG
C
C
    DVL=-2.*SD*SB0*EXPBX*EXPBM*(1.+2.*SP4*XX+3.*SP5*XX**2)
C
C
    DY=DVT*DTY+DVL*DLY+DVANG*DANGY
    DX=DVT*DTX+DVL*DLX+DVANG*DANGX
    DZ=DVANG*DANGZ
C
C  SORT OUT
C
    IF(IANG.EQ.1) THEN
        DRAB=DZ
        DRBC=DY
        DRAC=DX
        GO TO 600
    END IF
    IF(IANG.EQ.2) THEN
        DRAB=DX
        DRBC=DZ
        DRAC=DY
        GO TO 600
    END IF
    IF(IANG.EQ.3) THEN
        DRAB=DX
        DRBC=DY
        DRAC=DZ
        GO TO 600
    END IF
600 CONTINUE
    RETURN
    END
    SUBROUTINE GRA2DS(X,NX,Y,NY,F,SX2,SY2,SX2Y2)
C
C -----
C
C  2-D SPLINE ROUTINE . FITS A 2-D SPLINE TO A SET OF F(X,Y)

```

```

C DATA .
C ----- INPUT -----
C
C X : VECTOR OF LENGTH NX
C Y : VECTOR OF LENGTH NY
C F : NX BY NY MATRIX
C
C ----- OUTPUT -----
C
C SX2,SY2,SX2Y2 : ALL NX BY NY MATRICES OF COEFFICIENTS
C
C USE GRAEVU TO OBTAIN A SPLINE EVALUATION OF A POINT (XX,YY).
C
C -----
C
      DIMENSION X(NX),Y(NY),F(NX,NY),DUMMY(50),S(50),
      1SX2(NX,NY),SY2(NX,NY),SX2Y2(NX,NY)
C
      DO 10 I=1,NY
      DO 20 J=1,NX
20    DUMMY(J)=F(J,I)
      CALL SPCOEF(NX,X,DUMMY,S)
      DO 30 JJ=1,NX
30    SX2(JJ,I)=S(JJ)
10    CONTINUE
C
      DO 11 J=1,NX
      DO 21 I=1,NY
21    DUMMY(I)=F(J,I)
      CALL SPCOEF(NY,Y,DUMMY,S)
      DO 31 II=1,NY
31    SY2(J,II)=S(II)
11    CONTINUE
C
      DO 13 I=1,NY
      DO 23 J=1,NX
23    DUMMY(J)=SY2(J,I)
      CALL SPCOEF(NX,X,DUMMY,S)
      DO 33 JJ=1,NX
33    SX2Y2(JJ,I)=S(JJ)
13    CONTINUE
C
      RETURN
      END

```


A.5 FPSTRAJ5 (SG3E)

Contains:

- Subroutine MASTER, which runs a single trajectory;
 - Entry REMAST, which allows back-calculation of a trajectory to ensure numerical accuracy of results;
- Subroutine MODAMS, a numerical integrator with a three-step Runge-Kutta startup and a fourth-order Adams-Bashforth predictor-corrector;
- Subroutine DIFFEQ, which is a dummy retained to maintain compatibility with the original main program.

```

SUBROUTINE MASTER
C
C -----
C
C ROUTINE CONTROLS CALCULATION OF TRAJECTORY...TWO ENTRY POINTS...
C MASTER CALCULATES STANDARD TRAJECTORY...REMAST CONTROLS BACK-
C INTEGRATION OF EACH TRAJECTORY IF IE=1 OR 2...IF IE=1 MASTER
C CREATES PUNCHED OUTPUT FILE CONSISTING OF CARTESIAN COORDINATES
C OF EACH ATOM AT EACH FIFTEENTH POINT IN THE TRAJECTORY...ONE CARD
C IN INTEGER FORMAT AT EACH POINT PUNCHED
C
C -----
C
COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
1FF(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IReact,VREL,RHO,HO,AVV,ANG,
2NEQ,KDQ,INDEX,AMINT,AMTOT,XTER,ENFIN,ENTOT,T,H,EVIB,EROT,BMAX,
3IE,TAD,DIST,BMN,P4(3),P5(3)
COMMON/BASH/ARRAY(4,12),DIFF(12),XA
C COMMON/XPRINT2/IANG1,ANG1,EPOT1
C COMMON/XPRINT2/IANG1,ANG1,XSP1,YSP1,ZSP1,DRAB1,DRBC1,DRAC1,
C 1 EPOT1
C COMMON/XPRINT4/BRANCH,XSPG,YSPG,ZSPG,GAMMA1,EPOTG1,DRABG1,
C 1 DRBCG1,DRACG1,XSPA,YSPA,ZSPA,ALPHA1,EPOTA1,DRABA1,DRBCA1,
C 2 DRACA1,XSPB,YSPB,ZSPB,BETA1,EPOTB1,DRABB1,DRBCB1,DRACB1,
C 3 EPOTF,DRABF,DRBCF,DRACF

```

```

      DIMENSION COORD(9)
C      WRITE(6,207)
C 207 FORMAT(/,5X,'ENTOT,TIME,IANG,ANG,XSP,YSP,ZSP,EPOT',/,5X,
C      1 'DRAB,DRBC,DRAC')
      TF1=S(4,1)/S(3,1)
      TF2=-S(3,3)
      TF3=-S(4,1)
      TF4=S(3,2)
      H=HO
      KDQ=1
      NP=0

C
C  CALCULATE QUANTITIES USED IN END TEST OF TRAJECTORY
C
      DENOM=-Y(6)-DIST
      NMAX=50
      RTEST=RHO+.5*RHI
100 CONTINUE
C
C  TEST TO SEE IF COORDINATES SHOULD BE PUNCHED OUT
C
      IF(IE.EQ.1) GO TO 130
110 CONTINUE
C
C  CHECK FOR END OF TRAJECTORY ONLY AFTER TAKING NMAX STEPS
C
      IF(KDQ.LT.NMAX) GO TO 120
      IF(KDQ.GT.10000) GO TO 800
C
C  CHECK FOR END OF TRAJECTORY...IS ONE INTERNUCLEAR DISTANCE GREATER
C  THAN RTEST
C
      IF(R(1).GT.RTEST) GO TO 200
      IF(R(2).GT.RTEST) GO TO 300
120 CONTINUE
C
C  INTEGRATE EQUATIONS OF MOTION ONE STEP
C
      CALL MODAMS
C      IF(R(1).LT.R(2)) GO TO 88
C      IF(R(2).LT.R(3)) GO TO 92
C      GO TO 94
C 88 IF(R(1).LT.R(3)) GO TO 93
C      GO TO 94
C 92 IREACT=0

```

```

C      GO TO 95
C 93 IREACT = 1
C      GO TO 95
C 94 IREACT=2
C 95 CONTINUE
C      CALL FENGY
C      CALL FMOM
C      IF(BRANCH.EQ.1) WRITE(6,206) T,IANG1,ANG1,XSP1,YSP1,ZSP1,
C 1 EPOT1,DRAB1,DRBC1,DRAC1,ENTOT
C      IF(BRANCH.EQ.2) WRITE(6,208) T,XSPG,YSPG,ZSPG,GAMMA1,EPOTG1,
C 1 DRABG1,DRBCG1,DRACG1,XSPA,YSPA,ZSPA,ALPHA1,EPOTA1,DRABA1,
C 2 DRBCA1,DRACA1,EPOTF,DRABF,DRBCF,DRACF,ENTOT
C      IF(BRANCH.EQ.3) WRITE(6,209) T,XSPG,YSPG,ZSPG,GAMMA1,EPOTG1,
C 1 DRABG1,DRBCG1,DRACG1,XSPB,YSPB,ZSPB,BETA1,EPOTB1,DRABB1,
C 2 DRBCB1,DRACB1,EPOTF,DRABF,DRBCF,DRACF,ENTOT
C      IF(BRANCH.EQ.4) WRITE(6,210) T,XSPA,YSPA,ZSPA,ALPHA1,EPOTA1,
C 1 DRABA1,DRBCA1,DRACA1,XSPG,YSPG,ZSPG,GAMMA1,EPOTG1,DRABG1,
C 2 DRBCG1,DRACG1,EPOTF,DRABF,DRBCF,DRACF,ENTOT
C      IF(BRANCH.EQ.5) WRITE(6,211) T,XSPA,YSPA,ZSPA,ALPHA1,EPOTA1,
C 1 DRABA1,DRBCA1,DRACA1,XSPB,YSPB,ZSPB,BETA1,EPOTB1,DRABB1,
C 2 DRBCB1,DRACB1,EPOTF,DRABF,DRBCF,DRACF,ENTOT
C      IF(BRANCH.EQ.6) WRITE(6,212) T,XSPB,YSPB,ZSPB,BETA1,EPOTB1,
C 1 DRABB1,DRBCB1,DRACB1,XSPA,YSPA,ZSPA,ALPHA1,EPOTA1,DRABA1,
C 2 DRBCA1,DRACA1,EPOTF,DRABF,DRBCF,DRACF,ENTOT
C      IF(BRANCH.EQ.7) WRITE(6,213) T,XSPB,YSPB,ZSPB,BETA1,EPOTB1,
C 1 DRABB1,DRBCB1,DRACB1,XSPG,YSPG,ZSPG,GAMMA1,EPOTG1,DRABG1,
C 2 DRBCG1,DRACG1,EPOTF,DRABF,DRBCF,DRACF,ENTOT
C      KDQ=KDQ+1
C      WRITE(6,40) T,(R(J),J=1,3)
C      WRITE(6,38) IANG1,ANG1,XTER
C 38 FORMAT(1X,'IANG,ANG,XTER= ',I3,F9.2,E10.3)
C      WRITE(6,39)(DD(J),J=1,3)
C 39 FORMAT(1X,'DD= ',3E11.3)
C      GO TO 100
C 130 CONTINUE
C
C      TEST FOR EACH FIFTEENTH STEP AND PRINT
C
C      IF(MOD(KDQ,15).EQ.1) GO TO 150
C      GO TO 110
C 150 CONTINUE
C
C      TRANSFORM GENERALIZED COORDINATES TO CARTESIAN COORDINATES
C      AND PUNCH.
C

```

```

      NP=NP+1
      DO 160 J=1,3
      COORD(J)=TF1*Y(J+3)
      COORD(J+3)=TF2*Y(J)+TF3*Y(J+3)
      COORD(J+6)=TF4*Y(J)+TF3*Y(J+3)
160  CONTINUE
      WRITE(6,40) T,(R(J),J=1,3)
      GO TO 110
200  CONTINUE
C
C  TEST FOR A SECOND INTERNUCLEAR DISTANCE GREATER THAN RTEST...
C  ASSIGN CHANNEL NUMBER (IREACT)
C
      IF(R(2).GT.RTEST) GO TO 310
      IF(R(3).GT.RTEST) GO TO 320
      GO TO 120
300  CONTINUE
      IF(R(3).GT.RTEST) GO TO 330
      GO TO 120
310  CONTINUE
      IREACT=2
      GO TO 500
320  CONTINUE
      IREACT=0
      GO TO 500
330  CONTINUE
      IREACT=1
500  CONTINUE
      KNG=KDQ-1
C
C  WRITE NUMBER OF INTEGRATION STEPS TAKEN AND REAL ELAPSED TIME FOR
C  COMPUTATION OF TRAJECTORY
C
C      WRITE(6,10) KNG
C
C  WRITE SIMULATED TIME FOR COLLISION PROCESS AND FINAL VALUES OF THE
C  COORDINATES AND MOMENTA
C
C      WRITE(6,20) T,(Y(J),J=1,12)
      GO TO 700
800  WRITE(6,50)
700  RETURN
      ENTRY REMAST
C
C  BEGIN BACK-INTEGRATION

```

```

C
      H=-H0
      DO 600 KDQ=1,KNG
      CALL MODAMS
600  CONTINUE
C
C  WRITE FINAL SIMULATED TIME AND COORDINATES AND MOMENTA FROM BACK-
C  INTEGRATION.....THESE SHOULD BE IDENTICAL TO THE INITIAL VALUES
C
C      WRITE(6,20) T,(Y(J), J=1,12)
      GO TO 700
      10 FORMAT(19H NUMBER OF STEPS = ,I10)
      20 FORMAT(1H0,4X,E10.4,2(/6E10.4))
      40 FORMAT(4E10.4)
      50 FORMAT(4X,'TRAJECTORY STOPPED AT 10000 STEPS')
C 206 FORMAT(5X,E10.5,2X,I3,2X,F7.3,2X,F8.5,2X,F8.5,2X,F8.5,
C      1 2X,F8.4,/,5X,E12.6,2X,E12.6,2X,E12.6,2X,E12.6)
C 208 FORMAT(2X,'SURFACE 1 BLENDED WITH 2',/,2X,
C      1 'X,Y,Z,GAMMA,EPOTG,DRABG,DRBCG,DRACG = ',/,2X,
C      2 E10.5,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,F8.5,/,2X,
C      3 E12.6,2X,E12.6,2X,E12.6,/,2X,'X,Y,Z,ALPHA,EPOTA,DRABA',
C      4 ',DRBCA,DRACA = ',/,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,
C      5 F8.5,/,2X,E12.6,2X,E12.6,2X,E12.6,/,2X,
C      6 'BLENDED EPOT,DRAB,DRBC,DRAC = ',/,2X,F8.5,2X,E12.6,2X,
C      7 E12.6,2X,E12.6)
C 209 FORMAT(' SURFACE 1 BLENDED WITH 3',/,2X,
C      1 'X,Y,Z,GAMMA,EPOTG,DRABG,DRBCG,DRACG = ',/,2X,
C      2 E10.5,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,F8.5,/,2X,
C      3 E12.6,2X,E12.6,2X,E12.6,/,2X,'X,Y,Z,BETA,EPOTB,DRABB',
C      4 ',DRBCB,DRACB = ',/,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,
C      5 F8.5,/,2X,E12.6,2X,E12.6,2X,E12.6,/,2X,
C      6 'BLENDED EPOT,DRAB,DRBC,DRAC = ',/,2X,F8.5,2X,E12.6,2X,
C      7 E12.6,2X,E12.6,2X,E12.6)
C 210 FORMAT(' SURFACE 2 BLENDED WITH 1',/,2X,
C      1 'X,Y,Z,ALPHA,EPOTA,DRABA,DRBCA,DRACA = ',/,2X,
C      2 E10.5,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,F8.5,/,2X,
C      3 E12.6,2X,E12.6,2X,E12.6,/,2X,'X,Y,Z,GAMMA,EPOTG,DRABG',
C      4 ',DRBCG,DRACG = ',/,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,
C      5 F8.5,/,2X,E12.6,2X,E12.6,2X,E12.6,/,2X,
C      6 'BLENDED EPOT,DRAB,DRBC,DRAC = ',/,2X,F8.5,2X,E12.6,2X,
C      7 E12.6,2X,E12.6,2X,E12.6)
C 211 FORMAT(' SURFACE 2 BLENDED WITH 3',/,2X,
C      1 'X,Y,Z,ALPHA,EPOTA,DRABA,DRBCA,DRACA = ',/,2X,
C      2 E10.5,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,F8.5,/,2X,
C      3 E12.6,2X,E12.6,2X,E12.6,/,2X,'X,Y,Z,BETA,EPOTB,DRABB',

```

```

C   4  ',DRBCB,DRACB = ',/,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,
C   5  F8.5,/,2X,E12.6,2X,E12.6,2X,E12.6,/,2X,
C   6  'BLENDED EPOT,DRAB,DRBC,DRAC = ',/,2X,F8.5,2X,E12.6,2X,
C   7  E12.6,2X,E12.6,2X,E12.6)
C 212 FORMAT(' SURFACE 3 BLENDED WITH 2',/,2X,
C   1  'X,Y,Z,BETA,EPOTB,DRABB,DRBCB,DRACB = ',/,2X,
C   2  E10.5,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,F8.5,/,2X,
C   3  E12.6,2X,E12.6,2X,E12.6,/,2X,'X,Y,Z,ALPHA,EPOTA,DRABA',
C   4  ',DRBCA,DRACA = ',/,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,
C   5  F8.5,/,2X,E12.6,2X,E12.6,2X,E12.6,/,2X,
C   6  'BLENDED EPOT,DRAB,DRBC,DRAC = ',/,2X,F8.5,2X,E12.6,2X,
C   7  E12.6,2X,E12.6,2X,E12.6)
C 213 FORMAT(' SURFACE 3 BLENDED WITH 1',/,2X,
C   1  'X,Y,Z,BETA,EPOTB,DRABB,DRBCB,DRACB = ',/,2X,
C   2  E10.5,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,F8.5,/,2X,
C   3  E12.6,2X,E12.6,2X,E12.6,/,2X,'X,Y,Z,GAMMA,EPOTG,DRABG',
C   4  ',DRBCG,DRACG = ',/,2X,F8.5,2X,F8.5,2X,F8.5,2X,F8.4,2X,
C   5  F8.5,/,2X,E12.6,2X,E12.6,2X,E12.6,/,2X,
C   6  'BLENDED EPOT,DRAB,DRBC,DRAC = ',/,2X,F8.5,2X,E12.6,2X,
C   7  E12.6,2X,E12.6,2X,E12.6)

```

END

SUBROUTINE MODAMS

```

C
C -----
C
C NUMERICAL INTEGRATION ROUTINE...BASED ON ADAMS-BASHFORTH
C FOURTH-ORDER PREDICTOR-CORRECTOR ALGORITHM .
C
C -----
C
COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
1DY(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IReact,VREL,RHO,HO,AVV,ANG,NE,
2KDQ>IDEX,AMINT,AMTOT,XTER,ENFIN,ENTOT,X,DX,EVIB,EROT,BMAX,IE,
3TAD,DIST,BMN,P4(3),P5(3)
COMMON/BASH/ARRAY(4,12),DIFF(12),XA
NSTEP=KDQ-1

C
IF(NSTEP.LT.3) GOTO 5

C
C PREDICTOR - CORRECTOR INTEGRATION
C
XA = XA + DX
TEMP = X + XA
XA = (X - TEMP) + XA
X = TEMP

```

```

DO 1 J = 1,NE
  YPC = ARRAY(4,J)+DX*(2.29166667*DY(J)-2.45833333*
1ARRAY(3,J)+1.54166667*ARRAY(2,J)-.375*ARRAY(1,J))
  ARRAY(1,J) = ARRAY(2,J)
  ARRAY(2,J) = ARRAY(3,J)
  ARRAY(3,J) = DY(J)
  Y(J) = YPC-.92962963*DIFF(J)
1 DIFF(J) = YPC
  CALL F
DO 2 J = 1,NE
  YPC = ARRAY(4,J)+DX*(.375*DY(J)+.79166667*ARRAY(3,J)
1-.208333333*ARRAY(2,J)+.04166667*ARRAY(1,J))
  DIFF(J) = DIFF(J) - YPC
2 Y(J) = YPC + .07037037*DIFF(J)
  CALL F
3 DO 4 J = 1,NE
4 ARRAY(4,J) = Y(J)
  RETURN
C
C   RUNGE KUTTA INTEGRATION
C
5 IF(NSTEP.NE.0) GOTO 7
  XA = 0.
  CALL F
DO 6 J = 1,NE
6 ARRAY(1,J) = DY(J)
7 DO 16 I = 1,4
  DO 14 J = 1,NE
  GOTO(8,9,9,10),I
8 DIFF(J) = Y(J)
  ARRAY(4,J) = -DY(J)
9 YPC = 2.
10 ARRAY(4,J) = ARRAY(4,J) + YPC*DY(J)
  GOTO(13,13,12,11),I
11 Y(J) = DIFF(J) + DX*ARRAY(4,J)/6.
  GOTO 14
12 YPC = 1.
13 Y(J) = DIFF(J) + DX*DY(J)/YPC
14 CONTINUE
  GOTO(15,16,15,16),I
C
C   STEP SIZE FOR RUNGE KUTTA STARTUP (3 STEPS) IS H/2
C
15 XA = XA + DX/2.
  TEMP = X + XA

```

```
XA = (X - TEMP) + XA
X = TEMP
16 CALL F
  NSTEP = NSTEP + 1
  DO 17 J = 1,NE
    ARRAY(NSTEP+1,J) = DY(J)
17 DIFF(J) = 0.
  IF(NSTEP.LT.3) RETURN
  GOTO 3
END
SUBROUTINE DIFFEQ
```

C

C -----

C

C DUMMY SUBROUTINE FOR COMPATIBILITY WITH MAIN (TRAJ1B)

C

C -----

C

RETURN

END

A.6 FPSTRAJ6 (SG4E)

Contains:

- Subroutine FSTART, which initializes constants for calculations of Hamilton's equations of motion;
 - Entry F, which calculates the time derivatives of the atomic coordinates and momenta;
- Subroutine RVECT, which calculates the interatomic distances from generalized coordinates;
- Subroutine FMOMIN, which initializes constants for the calculation of total and internal momenta;
 - Entry FMOM, which performs those calculations;
- Subroutine FENGIN, which initializes constants for the calculation of total and internal energies;
 - Entry FENGY, which performs those calculations;
- Subroutine RANST, the initializer for a machine-independent random number generator;
 - Entry RANN, which yields a random number between 0 and 1;
 - Entry RANRE, which returns a new seed for continuation of the sequence.

SUBROUTINE FSTART

```
C
C -----
C
C ROUTINE FOR HAMILTON'S EQUATIONS OF MOTION...TWO ENTRY POINTS...
C FSTART INITIALIZES CONSTANTS.....F CALCULATES TIME DERIVATIVES OF
C COORDINATES AND MOMENTA
C -----
C
C
```

```

COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
1FF(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IREACT,VREL,RHO,HO,AVV,ANG,
2NEQ,KDQ,IDEX,AMINT,AMTOT,XTER,ENFIN,ENTOT,T,H,EVIB,EROT,BMAX,
3IE,TAD,DIST,BMN,P4(3),P5(3)
W=1./S(3,2)/S(4,3)/XM
Z=1./S(4,1)/(1.-S(4,1))/XM
W1=S(3,2)
W2=S(3,3)
100 RETURN
ENTRY F

C
C TIME DERIVATIVES OF COORDINATES & MOMENTA ARE CALCULATED AT POINT
C SPECIFIED BY Y(12) AND ARE STORED IN FF(12)
C
150 CONTINUE
DO 200 J=1,3
FF(J)=W*Y(J+6)
FF(J+3)=Z*Y(J+9)
200 CONTINUE
CALL RVECT
CALL FPOT3M
DO 300 I=1,3
DD(I)=DD(I)/R(I)
300 CONTINUE
DO 400 I=1,3
PAR1=(W2*Y(I)+Y(I+3))*DD(1)
PAR2=(W1*Y(I)-Y(I+3))*DD(3)
FF(I+6)=-W2*PAR1-DD(2)*Y(I)-W1*PAR2
FF(I+9)=PAR2-PAR1
400 CONTINUE
GO TO 100
END
SUBROUTINE RVECT
C
C -----
C
C INTERNUCLEAR DISTANCES ARE CALCULATED FROM GENERALIZED COORDINATES
C (FIRST SIX ELEMENTS IN Y(12)) AND ARE STORED IN R(3)
C
C -----
C
COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
1FF(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IREACT,VREL,RHO,HO,AVV,ANG,
2NEQ,KDQ,IDEX,AMINT,AMTOT,XTER,ENFIN,ENTOT,T,H,EVIB,EROT,BMAX,
3IE,TAD,DIST,BMN,P4(3),P5(3)

```

```

W1=S(3,3)
W2=S(3,2)
W3=W1*Y(1)+Y(4)
W4=W1*Y(2)+Y(5)
R1=W1*Y(3)+Y(6)
R1=SQRT(R1*R1+W3*W3+W4*W4)
R2=SQRT(Y(1)*Y(1)+Y(2)*Y(2)+Y(3)*Y(3))
W3=W2*Y(1)-Y(4)
W4=W2*Y(2)-Y(5)
R3=W2*Y(3)-Y(6)
R3=SQRT(W3*W3+W4*W4+R3*R3)
R(1)=R1
R(2)=R2
R(3)=R3
RETURN
END
SUBROUTINE FMOMIN

```

```

C
C -----
C
C ROUTINE FOR CALCULATING TOTAL AND INTERNAL ANGULAR MOMENTA.....TWO
C ENTRY POINTS....FMOMIN INITIALIZES CONSTANTS.....FMOM PERFORMS
C CALCULATION
C
C -----
C

```

```

COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
*F(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IReact,VREL,RHO,HO,AVV,ANG,
2NEQ,KDQ,IDX,AMINT,AMTOT,XTER,ENFIN,ENTOT,T,H,EVIB,EROT,BMAX,
3IE,TAD,DIST,BMN,P4(3),P5(3)

```

```

C1=S(1,2)/(1.-S(4,1))
C2=S(1,2)*S(3,3)/(1.-S(4,1))
C3=S(1,1)*S(3,3)
C4=S(1,1)
C5=S(2,3)/(1.-S(4,1))
C6=-S(2,2)*S(3,3)/(1.-S(4,1))
C7=S(2,1)*S(3,2)
C8=-S(2,1)

```

```
100 RETURN
```

```
ENTRY FMOM
```

```

C
C TOTAL ANGULAR MOMENTUM (AMTOT) & INTERNAL ANGULAR MOMENTUM (AMINT)
C IN CHANNEL DESIGNATED BY IReact ARE CALCULATED
C

```

```
NN=IReact+1
```

```

GO TO(200,300,300,200) NN
200 CONTINUE
  AX=Y(2)*Y(9)-Y(3)*Y(8)
  AY=Y(3)*Y(7)-Y(1)*Y(9)
  AZ=Y(1)*Y(8)-Y(2)*Y(7)
  AXT=AX+Y(5)*Y(12)-Y(6)*Y(11)
  AYT=AY+Y(6)*Y(10)-Y(4)*Y(12)
  AZT=AZ+Y(4)*Y(11)-Y(5)*Y(10)
  AMINT=SQRT(AX*AX+AY*AY+AZ*AZ)
  AMTOT=SQRT(AXT*AXT+AYT*AYT+AZT*AZT)
  IF(IREACT.EQ.3) GO TO 500
  GO TO 100
300 CONTINUE
  AX1=Y(5)*Y(12)-Y(6)*Y(11)
  AY1=Y(6)*Y(10)-Y(4)*Y(12)
  AZ1=Y(4)*Y(11)-Y(5)*Y(10)
  AX2=Y(2)*Y(12)-Y(3)*Y(11)
  AY2=Y(3)*Y(10)-Y(1)*Y(12)
  AZ2=Y(1)*Y(11)-Y(2)*Y(10)
  AX3=Y(2)*Y(9)-Y(3)*Y(8)
  AY3=Y(3)*Y(7)-Y(1)*Y(9)
  AZ3=Y(1)*Y(8)-Y(2)*Y(7)
  AX4=Y(5)*Y(9)-Y(6)*Y(8)
  AY4=Y(6)*Y(7)-Y(4)*Y(9)
  AZ4=Y(4)*Y(8)-Y(5)*Y(7)
  IREACT.EQ.2) GO TO 400
  AX=C1*AX1+C2*AX2+C3*AX3+C4*AX4
  AY=C1*AY1+C2*AY2+C3*AY3+C4*AY4
  AZ=C1*AZ1+C2*AZ2+C3*AZ3+C4*AZ4
350 CONTINUE
  AMINT=SQRT(AX*AX+AY*AY+AZ*AZ)
  AXT=AX3+AX1
  AYT=AY3+AY1
  AZT=AZ3+AZ1
  AMTOT=SQRT(AXT*AXT+AYT*AYT+AZT*AZT)
  GO TO 100
400 CONTINUE
  AX=C5*AX1+C6*AX2+C7*AX3+C8*AX4
  AY=C5*AY1+C6*AY2+C7*AY3+C8*AY4
  AZ=C5*AZ1+C6*AZ2+C7*AZ3+C8*AZ4
  GO TO 350
500 CONTINUE
  AMINT=0.
  GO TO 100
END

```

3 of/de 3

SUBROUTINE FENGIN

```

C
C -----
C
C ROUTINE FOR CALCULATING TOTAL AND INTERNAL ENERGIES.....TWQ ENTRY
C POINTS.....FENGIN INITIALIZES CONSTANTS. ...FENGY PERFORMS
C CALCULATION
C
C -----
C
C      COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
C      1FF(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IREACT,VREL,RHO,HO,AVV,ANG,
C      2NEQ,KDQ>IDEX,AMINT,AMTOT,XTER,ENFIN,ENTOT,T,H,EVIB,EROT,BMAX,
C      3IE,TAD,DIST,BMN,P4(3),P5(3)
C      RED1=1./(2.*XM*S(3,2)*S(4,3))
C      RED2=S(1,1)/(2.*XM*S(4,2))
C      RED3=S(1,2)/(2.*XM*S(4,1)*(1.-S(4,1))**2)
C      RED4=1./(XM*(1.-S(4,3))*(1.-S(4,1)))
C      RED5=S(2,1)/(2.*XM*S(4,3))
C      RED6=S(2,3)/(2.*XM*S(4,1)*(1.-S(4,1))**2)
C      RED7=-1./(XM*(1.-S(4,2))*(1.-S(4,1)))
C      RED8=RED1
C      RED9=1./(2.*XM*S(4,1)*(1.-S(4,1)))
10 RETURN
C      ENTRY FENGY
C
C CALCULATE TOTAL ENERGY (ENTOT) AND INTERNAL ENERGY (ENFIN) IN
C CHANNEL DESIGNATED BY IREACT
C
C      CALL RVECT
C      CALL FPOTN
C      CALL FPOT3N
C      PP1=Y(7)*Y(7)+Y(8)*Y(8)+Y(9)*Y(9)
C      PP2=Y(10)*Y(10)+Y(11)*Y(11)+Y(12)*Y(12)
C      PP3=Y(7)*Y(10)+Y(8)*Y(11)+Y(9)*Y(12)
C      ENKT=RED8*PP1+RED9*PP2
C      NN=IREACT+1
C      GO TO(30,40,50,30) NN
30 CONTINUE
C      TINTF=RED1*PP1
C      ENFIN=TINTF+TERM
C      IF(ENFIN.GE.C(2)) GO TO 60
C      ENTOT=ENKT+XTER
C      WRITE(6,70) ENTOT
C      GO TO 10

```

```

40 CONTINUE
   TINTF=RED2*PP1+RED3*PP2+RED4*PP3
   ENFIN=TINTF+TERM
   IF(ENFIN.GE.C(1)) GO TO 60
   ENTOT=ENKT+XTER
C   WRITE(6,70) ENTOT
   GO TO 10
50 CONTINUE
   TINTF=RED5*PP1+RED6*PP2+RED7*PP3
   ENFIN=TINTF+TERM
   IF(ENFIN.GE.C(3)) GO TO 60
   ENTOT=ENKT+XTER
C   WRITE(6,70) ENTOT
   GO TO 10
60 CONTINUE
   IREACT=3
   ENFIN=0.
   ENTOT=ENKT+XTER
C   WRITE(6,70) ENTOT
C 70 FORMAT(/,5X,'ENTOT = ',E12.6)
   GO TO 10
   END
   SUBROUTINE RANST(X)
C   ROUTINE OBTAINED FROM J. T. MUCKERMAN...MACHINE INDEPENDENT RANDOM
C   NUMBER GENERATOR...THREE ENTRY POINTS...RANST(X) INITIALIZES THE
C   GENERATOR USING THE SEED IX=X...RANN(X) GENERATES UNIFORMLY
C   DISTRIBUTED RANDOM NUMBERS X IN THE OPEN INTERVAL (0,1) .....
C   RANRE(X) RETURNS THE SEED X=IX TO CONTINUE THE SEQUENCE.
   REAL*8 X,V,IT
   INTEGER*4 INT,IX
   COMMON/CRANN/V,IX,INT
   INT=67101323
   IX=X
   V=1.DO/DFLOAT(INT)
   RETURN
   ENTRY RANN(X)
   IT=DFLOAT(IX)*8192.DO
   X=INT
   X=DMOD(IT,X)
   IX=X
   X=V*X
   RETURN
   ENTRY RANRE(X)
   X=IX
   RETURN
   END

```

A.7 FPSTRAJ1A (JPCI5T2)

Contains:

- Subroutine DFPOTI, which initializes constants for the interpolator:
 - Entry FPOTN, which evaluates the energy of the Morse oscillator;
 - Entry FPOT3N, which calculates the potential energy and its derivatives for a possibly-blended surface;
- Subroutine DERIVS, which calculates the derivatives of the blending-function weights with respect to the internuclear distances:
 - Entries CALPHA, CBETA and CGAMMA, which perform the calculations for specific surfaces
- Subroutine RSOLVI, which initializes the spectroscopic constants for the resolution of the diatomic's internal energy into its vibrational and rotational components:
 - Entry RSOLVE, which performs that calculation.

```

SUBROUTINE DFPQTI
C
C -----
C
C  POTENTIAL ENERGY ROUTINE FOR RMC-CUBIC SPLINE METHOD.
C  TWO ENTRY POINTS....DFPOTI INITIALIZES SPLINE CONSTANTS AND
C  MORSE DIATOMIC FRAGMENT CONSTANTS....FPOTN EVALUATES THE ENERGY
C  OF THE MORSE OSCILLATOR....FPOT3N EVALUATES THE POTENTIAL
C  ENERGY AND ITS DERIVATIVES .
C
C -----
C
C  THIS ROUTINE HAS BEEN MODIFIED TO HANDLE THE 5-PARAMETER
C  GENERALIZED MORSE FUNCTION . IN PARTICULAR ALL OF THE
C  PARTIAL DERIVATIVES HAVE BEEN RE-DEFINED .
C
```


C R.J.WILLIAMS OCTOBER 11-1984

C

C

C

COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
1FF(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IReact,VREL,RHO,HO,AVV,ANG,
2NEQ,KDQ,INDEX,AMINT,AMTOT,XTER,ENFIN,ENTOT,T,H,EVIB,EROT,BMAX,
3IE,TAD;DIST,BMN,P4(3),P5(3)

DIMENSION BO(3)

COMMON /SURFA/THETA(21),GAMA(9),DA(9,21),SX2DA(9,21),
1SY2DA(9,21),SXY2DA(9,21),BOA(9,21),SX2BOA(9,21),SY2BOA(9,21),
2SXY2BA(9,21),RA(9,21),SX2RA(9,21),SY2RA(9,21),
3SXY2RA(9,21),P4A(9,21),SX2P4A(9,21),SY2P4A(9,21),
4SXY24A(9,21),P5A(9,21),SX2P5A(9,21),SY2P5A(9,21),
5SXY25A(9,21)

COMMON /SURFB/THETB(19),GAMB(9),DB(9,19),SX2DB(9,19),
1SY2DB(9,19),SXY2DB(9,19),BOB(9,19),SX2BOB(9,19),SY2BOB(9,19),
2SXY2BB(9,19),RB(9,19),SX2RB(9,19),SY2RB(9,19),
3SXY2RB(9,19),P4B(9,19),SX2P4B(9,19),SY2P4B(9,19),
4SXY24B(9,19),P5B(9,19),SX2P5B(9,19),SY2P5B(9,19),
5SXY25B(9,19)

COMMON /SURFC/THETC(21),GAMC(9),DC(9,21),SX2DC(9,21),
1SY2DC(9,21),SXY2DC(9,21),BOC(9,21),SX2BOC(9,21),SY2BOC(9,21),
2SXY2BC(9,21),RC(9,21),SX2RC(9,21),SY2RC(9,21),
3SXY2RC(9,21),P4C(9,21),SX2P4C(9,21),SY2P4C(9,21),
4SXY24C(9,21),P5C(9,21),SX2P5C(9,21),SY2P5C(9,21),
5SXY25C(9,21)

COMMON/RVAL/R1,R2,R3

COMMON/XPRIN3/IANG,ANGL,XSP,YSP,ZSP,EPOT

COMMON/BLEND1/NBLAB,NBLAG,NBLBA,NBLBG,NBLGA,NBLGB,NSKIP

C

C

C

GAM = 180 IS THE LINEAR CONFIGURATION

DATA DEL,RAD/.001E-08,.01745329/

DATA RFACT,EFACT/.529167E-08,1.6021E-12/

C

20 FORMAT (4E16.9)

DO 888 I=1,9

DO 777 J=1,21

READ(20,20) RA(I,J),SX2RA(I,J),SY2RA(I,J),SXY2RA(I,J)

READ(20,20) DA(I,J),SX2DA(I,J),SY2DA(I,J),SXY2DA(I,J)

READ(20,20) BOA(I,J),SX2BOA(I,J),SY2BOA(I,J),SXY2BA(I,J)

READ(20,20) P4A(I,J),SX2P4A(I,J),SY2P4A(I,J),SXY24A(I,J)

READ(20,20) P5A(I,J),SX2P5A(I,J),SY2P5A(I,J),SXY25A(I,J)

READ(22,20) RC(I,J),SX2RC(I,J),SY2RC(I,J),SXY2RC(I,J)

```

READ(22,20) DC(I,J),SX2DC(I,J),SY2DC(I,J),SXY2DC(I,J)
READ(22,20) BOC(I,J),SX2BOC(I,J),SY2BOC(I,J),SXY2BC(I,J)
READ(22,20) P4C(I,J),SX2P4C(I,J),SY2P4C(I,J),SXY24C(I,J)
READ(22,20) P5C(I,J),SX2P5C(I,J),SY2P5C(I,J),SXY25C(I,J)
777 CONTINUE
DO 666 J=1,19
READ(21,20) RB(I,J),SX2RB(I,J),SY2RB(I,J),SXY2RB(I,J)
READ(21,20) DB(I,J),SX2DB(I,J),SY2DB(I,J),SXY2DB(I,J)
READ(21,20) BOB(I,J),SX2BOB(I,J),SY2BOB(I,J),SXY2BB(I,J)
READ(21,20) P4B(I,J),SX2P4B(I,J),SY2P4B(I,J),SXY24B(I,J)
READ(21,20) P5B(I,J),SX2P5B(I,J),SY2P5B(I,J),SXY25B(I,J)
666 CONTINUE
888 CONTINUE

```

```

C
C C(I) IS MORSE DISSOCIATION ENERGY FOR DIATOMIC FRAGMENT I,
C B(I) IS MORSE BETA,RO(I) IS MORSE RE,BO(I) IS MORSE BETA0,
C P4(I) IS MORSE LAMBDA1,P5(I) IS MORSE LAMBDA2.
C 1 IS BOND AB, 2 IS BOND BC, 3 IS BOND AC . THE REACTION
C IS A + BC - ( NOTE NEGATIVE VALUE OF LAMBDA1 )
C

```

```

C(1)=6.1250
C(2)=4.7478
C(3)=6.1250
BO(1)=1.1741
BO(2)=1.0276
BO(3)=1.1741
RO(1)=1.7329
RO(2)=1.4016
RO(3)=1.7329
RA(1)=-0.000066
P4(2)=-0.000132
P4(3)=-0.000066
P5(1)=0.000049
P5(2)=0.000098
P5(3)=0.000049

```

```

C
C CONVERT TO CGS UNITS
C

```

```

DO 10 I=1,3
C(I)=C(I)*EFACT
RO(I)=RO(I)*RFACT
BO(I)=BO(I)/RFACT
P4(I)=P4(I)/RFACT
P5(I)=P5(I)/(RFACT**2)
10 CONTINUE

```

100 RETURN

ENTRY FPOTM

C

C

C

C EVALUATE ENERGY OF DIATOMIC FRAGMENT INDICATED BY IREACT

C

C

C

C FIRST CALCULATE BETA FROM BETA0,P4,P5 WHICH ARE PASSED

C FROM DFPOTI . NOW BETA CAN BE PASSED THROUGH BLANK COMMON

C TO RSOLVI TO CALCULATE SPECTROSCOPIC CONSTANTS

C

B(1)=BO(1)*(1.+(P4(1)*(R(1)-RO(1)))+(P5(1)*((R(1)-RO(1))
1**2)))

B(2)=BO(2)*(1.+(P4(2)*(R(2)-RO(2)))+(P5(2)*((R(2)-RO(2))
1**2)))

B(3)=BO(3)*(1.+(P4(3)*(R(3)-RO(3)))+(P5(3)*((R(3)-RO(3))
1**2)))

C

NN=IREACT +1

GO TO(60,70,80,90) NN

60 CONTINUE

ZE=EXP(-B(2)*(R(2)-RO(2)))

ZC=C(2)

TERM=ZC*(1.-ZE)**2

GO TO 100

70 CONTINUE

ZE=EXP(-B(1)*(R(1)-RO(1)))

ZC=C(1)

TERM=ZC*(1.-ZE)**2

GO TO 100

80 CONTINUE

ZE=EXP(-B(3)*(R(3)-RO(3)))

ZC=C(3)

TERM=ZC*(1.-ZE)**2

GO TO 100

90 CONTINUE

TERM=0.

C

C ENERGY OF SYSTEM WHEN ALL R'S ARE LARGE IS ZERO.

C

GO TO 100

ENTRY FPOT3M

C

```

C -----
C
C THE POTENTIAL ENERGY OF THE 3-ATOM SYSTEM IS EVALUATED AT
C R(1),R(2),R(3) AND RETURNED IN XTER. DETERMINE WHICH ANGLE
C OF TRIANGLE ABC IS LARGEST AND CALL APPROPRIATE SPLINE PROGRAM
C -----
C
C THIS SUBROUTINE NOW INCORPORATES BLENDING FUNCTION BY
C J. POLOWIN WHEREIN WT(ANGLE)=SEC(ANGLE)-.5, YIELDING WT(60)=0,
C WT(90) --> LARGE. WEIGHTS ARE NORMALIZED, AND ENTER RESULTS
C AS:  $V = C1 \cdot V1 + C2 \cdot V2$ 
C  $DV/DR1 = DC1/DR1 \cdot (V1 - V2) + C1 \cdot DV1/DR1 + C2 \cdot DV2/DR1$ 
C DV1/DR1 CALCULATED AS DRABA ETC. BY OLD PROGRAM; DC1/DR1
C AND C(ANGLE) CALCULATED IN SUBROUTINE DERIVS.
C IN ALL CASES, CX REFERS TO LARGER ANGLE, CY TO SMALLER FOR
C NOT-NORMALIZED WEIGHTS; V1, V2 SIMILARLY TO LARGER AND
C SMALLER ANGLES.
C
C REFERENCES TO SUBROUTINES DBLEND AND EBLEND, WHICH
C BLENDED POTENTIALS AND THEIR DERIVATIVES IN THE PREVIOUS
C VERSION OF THIS PROGRAM, HAVE BEEN DELETED ALONG WITH THE
C SUBROUTINES THEMSELVES FROM THIS SET OF FILES.
C
C THIS IS THE SET UP FOR THE FHH SYSTEM WHERE A=F, B=H, C=H ATOM
C THEN THE FOLLOWING MUST APPLY: R(1)=RAB=RFH; R(2)=RBC=RH;
C R(3)=RAC=RFH
C
C
C R1=R(1)/RFACT
C R2=R(2)/RFACT
C R3=R(3)/RFACT
C ARG1=(R(2)**2+R(3)**2-R(1)**2)/(2.0*R(2)*R(3))
C ARG2=(R(1)**2+R(3)**2-R(2)**2)/(2.0*R(1)*R(3))
C ARG3=(R(1)**2+R(2)**2-R(3)**2)/(2.0*R(1)*R(2))
C IF(ARG1.LE.-1.0E0) THEN
C   GAMMA=180.
C   ALPHA=0.
C   BETA=0.
C   GOTO110
C END IF
C IF(ARG2.LE.-1.0E0) THEN
C   ALPHA=180.
C   GAMMA=0.
C   BETA=0.
C   GOTO120

```

```

END IF
IF(ARG3.LE.-1.0E0) THEN
    BETA=180.
    ALPHA=0.
    GAMMA=0
    GOTO130
END IF
GAMMA=ACOS(ARG1)/RAD
ALPHA=ACOS(ARG2)/RAD
BETA =ACOS(ARG3)/RAD
C
C  GAMMA IS ANGLE ACB ; ALPHA IS ANGLE BAC ; BETA IS ANGLE ABC
C  CHOOSE LARGEST ANGLE & ROUTE TO APPROPRIATE SURFACE
C
    ANGLE=AMAX1(GAMMA,ALPHA,BETA)
    IF(ABS(ANGLE-GAMMA).LT.DEL) GOTO 110
    IF(ABS(ANGLE-ALPHA).LT.DEL) GOTO 120
    IF(ABS(ANGLE-BETA).LT.DEL) GOTO 130
C
C  -----
C
C  THIS IS SURFACE ACB WITH X=RAC AND Y=RBC (SET ON UNIT 20)
C  LARGEST ANGLE IS ACB.(GAMMA)
C
110 IANG=1
    XSP=R(3)/RFACT
    YSP=R(2)/RFACT
    ZSP=R(1)/RFACT
    ANGL=GAMMA
    CALL VSPLIN(XSP,YSP,ZSP,ANGL,IANG,EPOTG,DRABG,DRBCG,DRACG)
C
C  NOW TEST FOR A SECOND ANGLE LARGER THAN 60 DEGREES
C
    IF(GAMMA.LT.90.0.AND.(ALPHA.GT.60.0.OR.BETA.GT.60.0)) GOTO 113
    EPOT=EPOTG
    DRAB=DRABG
    DRBC=DRBCG
    DRAC=DRACG
    GOTO 140
113 CALL CGAMMA(CX,DCXR1,DCXR2,DCXR3)
    V1=EPOTG
    DV1R1=DRABG
    DV1R2=DRBCG
    DV1R3=DRACG
    IF(BETA.GT.60.0) GOTO112.

```

```

111 IANG=2
    ANGL=ALPHA
    CALL VSPLIN(ZSP,XSP,YSP,ANGL,IANGL,EPOTA,DRABA,DRBCA,DRACA)
    CALL CALPHA(CY,DCYR1,DCYR2,DCYR3)
    V2=EPOTA
    DV2R1=DRABA
    DV2R2=DRBCA
    DV2R3=DRACA
    GOTO 135

```

```

112 IANG=3
    ANGL=BETA
    CALL VSPLIN(ZSP,YSP,XSP,ANGL,IANGL,EPOTB,DRABB,DRBCB,DRACB)
    CALL CBETA(CY,DCYR1,DCYR2,DCYR3)
    VE=EPOTB
    DV2R1=DRABB
    DV2R2=DRBCB
    DV2R3=DRACB
    GOTO 135

```

C

C

C

C THIS IS SURFACE BAC WITH X=RAB AND Y=RAC (SET ON UNIT 21)

C LARGEST ANGLE IS BAC (ALPHA)

C

```

120 IANG=2
    XSP=R(1)/RFACT
    YSP=R(3)/RFACT
    ZSP=R(2)/RFACT
    ANGL=ALPHA
    CALL VSPLIN(XSP,YSP,ZSP,ANGL,IANGL,EPOTA,DRABA,DRBCA,DRACA)

```

C

C NOW TEST FOR A SECOND ANGLE LARGER THAN 60 DEGREES

C

```

    IF(ALPHA.LT.90.0.AND.(GAMMA.GT.60.0.OR.BETA.GT.60.0)) GOTO 123

```

```

    EPOT=EPOTA

```

```

    DRAB=DRABA

```

```

    DRBC=DRBCA

```

```

    DRAC=DRACA

```

```

    GOTO 140

```

```

123 CALL CALPHA(CX,DCXR1,DCXR2,DCXR3)

```

```

    V1=EPOTA

```

```

    DV1R1=DRABA

```

```

    DV1R2=DRBCA

```

```

    DV1R3=DRACA

```

```

    IF(BETA.GT.60.0) GOTO 122

```

```

121 IANG=1
    ANGL=GAMMA
    CALL VSPLIN(YSP,ZSP,XSP,ANGL,IANGL,EPOTG,DRABG,DRBCG,DRACG)
    CALL CGAMMA(CY,DCYR1,DCYR2,DCYR3)
    V2=EPOTG
    DV2R1=DRABG
    DV2R2=DRBCG
    DV2R3=DRACG
    GOTO 135

```

```

122 IANG=3
    ANGL=BETA
    CALL VSPLIN(XSP,ZSP,YSP,ANGL,IANGL,EPOTB,DRABB,DRBCB,DRACB)
    CALL CBETA(CY,DCYR1,DCYR2,DCYR3)
    V2=EPOTB
    DV2R1=DRABB
    DV2R2=DRBCB
    DV2R3=DRACB
    GOTO 135

```

C

C -----

C

C THIS IS SURFACE ABC WITH X=RAB AND Y=RBC (SET ON UNIT 22)

C LARGEST ANGLE IS ABC (BETA)

C

```

130 IANG=3
    XSP=R(1)/RFACT
    YSP=R(2)/RFACT
    ZSP=R(3)/RFACT
    ANGL=BETA
    CALL VSPLIN(XSP,YSP,ZSP,ANGL,IANGL,EPOTB,DRABB,DRBCB,DRACB)

```

C

C NOW TEST FOR A SECOND ANGLE LARGER THAN 60 DEGREES

C

```

    IF(BETA.LT.90.0.AND.(ALPHA.GT.60.0.OR.GAMMA.GT.60.0)) GOTO 133
    EPOT=EPOTB
    DRAB=DRABB
    DRBC=DRBCB
    DRAC=DRACB
    GOTO 140

```

```

133 CALL CBETA(CX,DCXR1,DCXR2,DCXR3)
    V1=EPOTB
    DV1R1=DRABB
    DV1R2=DRBCB
    DV1R3=DRACB
    IF(GAMMA.GT.60.0) GOTO 132

```

```

131 IANG=2
    ANGL=ALPHA
    CALL VSPLIN(XSP,ZSP,YSP,ANGL,IANGL,EPOTA,DRABA,DRBCA,DRACA)
    CALL CALPHA(CY,DCYR1,DCYR2,DCYR3)
    V2=EPOTA
    DV2R1=DRABA
    DV2R2=DRBCA
    DV2R3=DRACA
    GOTO 135

132 IANG=1
    ANGL=GAMMA
    CALL VSPLIN(ZSP,YSP,XSP,ANGL,IANGL,EPOTG,DRABG,DRBCG,DRACG)
    CALL CGAMMA(CY,DCYR1,DCYR2,DCYR3)
    V2=EPOTG
    DV2R1=DRABG
    DV2R2=DRBCG
    DV2R3=DRACG

135 C1=CX/(CX+CY)
    C2=1.-C1
    CTERM1=CY/((CX+CY)**2)
    CTERM2=CX/((CX+CY)**2)
    EPOT=C1*V1+C2*V2
    DRAB=(CTERM1*DCXR1-CTERM2*DCYR1)*(V1-V2)+C1*DV1R1+C2*DV2R1
    DRBC=(CTERM1*DCXR2-CTERM2*DCYR2)*(V1-V2)+C1*DV1R2+C2*DV2R2
    DRAC=(CTERM1*DCXR3-CTERM2*DCYR3)*(V1-V2)+C1*DV1R3+C2*DV2R3

C
C -----
C
C CONVERT ENERGY TO EV
C
140 EPOT=EPOT*27.2107
C
C ENERGY OF A + BC IS ZERO FOR XTER
C
    XTER=C(2) + EPOT*EFACT
C
C CONVERT DERIVATIVES FROM AU/AU TO ERG/CM
C
    DD(1)=DRAB*27.2107*EFACT/RFACT
    DD(2)=DRBC*27.2107*EFACT/RFACT
    DD(3)=DRAC*27.2107*EFACT/RFACT
    GO TO 100
    END
    SUBROUTINE DERIVS

```


C ROUTINE BY J. POLOWIN TO CALCULATE ANALYTICALLY DERIVATIVES
 C OF BLENDING-FUNCTION WEIGHTS WRT. INTERATOMIC DISTANCES
 C R1,R2,R3 FOR 3 POSSIBLE CASES.

C
 COMMON/RVAL/R1,R2,R3
 $CANG(X1,X2,X3)=2.*X1*X2/(X1**2+X2**2-X3**2)-2.$
 $DCOPP(X1,X2,X3)=4.*X1*X2*X3/(X1**2+X2**2-X3**2)**2$
 $DCADJ(X1,X2,X3)=2.*X2*(X2**2-X1**2-X3**2)/(X1**2+X2**2-$
 $-X3**2)**2$
 ENTRY CALPHA(C,DCR1,DCR2,DCR3)
 C=CANG(R1,R3,R2)
 DCR1=DCADJ(R1,R3,R2)
 DCR2=DCOPP(R1,R3,R2)
 DCR3=DCADJ(R3,R1,R2)
 RETURN
 ENTRY CBETA(C,DCR1,DCR2,DCR3)
 C=CANG(R1,R2,R3)
 DCR1=DCADJ(R1,R2,R3)
 DCR2=DCADJ(R2,R1,R3)
 DCR3=DCOPP(R1,R2,R3)
 RETURN
 ENTRY CGAMMA(C,DCR1,DCR2,DCR3)
 C=CANG(R2,R3,R1)
 DCR1=DCOPP(R2,R3,R1)
 DCR2=DCADJ(R2,R3,R1)
 DCR3=DCADJ(R3,R2,R1)
 RETURN
 END
 SUBROUTINE RSOLVI

C
 C -----
 C
 C ROUTINE RESOLVES THE FINAL INTERNAL ENERGY INTO ITS VIBRATIONAL &
 C ROTATIONAL COMPONENTS... ALSO CALCULATES NEAREST INTEGER VALUES FOR
 C THE VIBRATIONAL AND ROTATIONAL QUANTUM NUMBERS... TWO ENTRY POINTS
 CRSOLVI INITIALIZES SPECTROSCOPIC CONSTANTS.....RESOLVE USES
 C METHOD DESCRIBED BY J. T. MUCKERMAN, J.C.P. 54, 1155 (1971) AND
 C J.C.P. 56, 2997 (1972) TO DO CALCULATION
 C
 C -----
 C

COMMON XM,S(4,3),C(3),B(3),RO(3),NV,NJ,RLO,RHI,TAU,Y(12),R(3),
 1FF(12),DD(3),ZE,ZC,ZB,ZS,ZF,TERM,IReact,VREL,RHO,HO,AVV,ANG,
 2NEQ,KDQ,IDEX,AMINT,AMTOT,XTER,ENFIN,ENTOT,T,H,EVIB,EROT,BMAX,
 3IE,TAD,DIST,P4(3),P5(3)

```

COMMON/CONST/RAD,HBAR,PI
C  EMU0=XM*S(4,2)*S(3,3)
C  EMU1=XM*S(4,2)*S(1,1)
C  EMU2=XM*S(4,1)*S(2,3)
C  OEO=B(2)*HBAR*SQRT(2.*C(2)/EMU0)
C  OE1=B(1)*HBAR*SQRT(2.*C(1)/EMU1)
C  OE2=B(3)*HBAR*SQRT(2.*C(3)/EMU2)
C  OEXEO=(HBAR*B(2))**2/(2.*EMU0)
C  OEXE1=(HBAR*B(1))**2/(2.*EMU1)
C  OEXE2=(HBAR*B(3))**2/(2.*EMU2)
C  BEO=HBAR**2/(2.*EMU0*RO(2)**2)
C  BE1=HBAR**2/(2.*EMU1*RO(1)**2)
C  BE2=HBAR**2/(2.*EMU2*RO(3)**2)
C  AEO=6.*(SQRT(OEXEO*BEO**3)-BEO**2)/OEO
C  AE1=6.*(SQRT(OEXE1*BE1**3)-BE1**2)/OE1
C  AE2=6.*(SQRT(OEXE2*BE2**3)-BE2**2)/OE2
C  DEO=4.*BEO**3/OEO**2
C  DE1=4.*BE1**3/OE1**2
C  DE2=4.*BE2**3/OE2**2
C
C  ABOVE EQUATIONS ARE NOT CORRECT FOR GMF-5 MORSE FUNCTION.
C  NUMEROV-COOLEY METHOD (RWVIBLM.) WAS USED TO CALCULATE
C  THE EVJ LINES FOR THE DIATOMIC SURFACE ASYMPTOTES
C  REPRESENTING HF & H2 WHERE THESE POTENTIALS WERE DESCRIBED
C  BY GMF-5. A SERIES OF 45 EVJ LINES OF HF SPANNING (0,0) TO
C  (4,18) & A SERIES OF 50 EVJ LINES OF H2 SPANNING (0,0) TO (5,4)
C  WERE THEN FIT BY LEAST SQUARES TO GIVE NUMERICAL VALUES OF THE
C  SPECTROSCOPIC CONSTANTS. (MUST CONVERT FROM CM-1 TO ERGS).
C
C  ERGFCT=1.98630E-16
C  OEO=4442.21 * ERGFCT
C  OE1=4242.60 * ERGFCT
C  OE2=4242.60 * ERGFCT
C  OEXEO=118.60 * ERGFCT
C  OEXE1=87.59 * ERGFCT
C  OEXE2=87.59 * ERGFCT
C  BEO=61.259 * ERGFCT
C  BE1=20.985 *ERGFCT
C  BE2=20.985 *ERGFCT
C  AEO=3.022 * ERGFCT
C  AE1=0.7409 * ERGFCT
C  AE2=0.7409 * ERGFCT
C  DEO=0.0429 * ERGFCT
C  DE1=0.001879 * ERGFCT
C  DE2=0.001879 * ERGFCT

```

10 RETURN

ENTRY RSOLVE

C

C RESOLVES INTERNAL ENERGY (ENFIN) AND INTERNAL ANGULAR MOMENTUM

C (AMINT) IN CHANNEL DESIGNATED BY IREACT INTO VIBRATIONAL ENERGY

C (EVIB), ROTATIONAL ENERGY (EROT), VIBRATIONAL QUANTUM NUMBER (NV),

C AND ROTATIONAL QUANTUM NUMBER (NJ)

C

TJ=(AMINT/HBAR)**2

NJ=SQRT(TJ)

NN=IREACT+1

GO TO (1,4,7,11) NN

1 CONTINUE

MM=0

EROT=TJ*BEO

EVIB=ENFIN-EROT

TER=0.

TEV=0.

2 CONTINUE

ARG=(OEO/OEXEO)**2-4.*EVIB/OEXEO

IF(ARG) 21,22,22

21 CONTINUE

ARG=0.

WRITE(6,61)

22 CONTINUE

TV=(OEO/OEXEO-SQRT(ARG))/2.

BV=BEO-TV*AEO

EROT=TJ*BV-TJ*TJ*DEO

EVIB=ENFIN-EROT

IF(ABS((EROT-TER)/EROT).GT.1.E-03) GO TO 3

IF(ABS((EVIB-TEV)/EVIB).GT.1.E-03) GO TO 3

NV=TV

GO TO 10

3 CONTINUE

IF(MM.GT.50) GO TO 12

TER=EROT

TEV=EVIB

MM=MM+1

GO TO 2

4 CONTINUE

MM=0

EROT=TJ*BE1

EVIB=ENFIN-EROT

TER=0.

TEV=0.

```
5 CONTINUE
  ARG=(OE1/OEXE1)**2-4.*EVIB/OEXE1
  IF(ARG) 51,52,52
51 CONTINUE
  ARG=0.
  WRITE(6,61)
52 CONTINUE
  TV=(OE1/OEXE1-SQRT(ARG))/2.
  BV=BE1-TV*AE1
  EROT=TJ*BV-TJ*TJ*DE1
  EVIB=ENFIN-EROT
  IF(ABS((EROT-TER)/EROT).GT.1.E-03) GO TO 6
  IF(ABS((EVIB-TEV)/EVIB).GT.1.E-03) GO TO 6
  NV=TV
  GO TO 10
6 CONTINUE
  IF(MM.GT.50) GO TO 12
  TER=EROT
  TEV=EVIB
  MM=MM+1
  GO TO 5
7 CONTINUE
  MM=0
  EROT=TJ*BE2
  EVIB=ENFIN-EROT
  TER=0.
  TEV=0.
8 CONTINUE
  ARG=(OE2/OEXE2)**2-4.*EVIB/OEXE2
  IF(ARG) 81,82,82
81 CONTINUE
  ARG=0.
  WRITE(6,61)
82 CONTINUE
  TV=(OE2/OEXE2-SQRT(ARG))/2.
  BV=BE2-TV*AE2
  EROT=TJ*BV-TJ*TJ*DE2
  EVIB=ENFIN-EROT
  IF(ABS((EROT-TER)/EROT).GT.1.E-03) GO TO 9
  IF(ABS((EVIB-TEV)/EVIB).GT.1.E-03) GO TO 9
  NV=TV
  GO TO 10
9 CONTINUE
  IF(MM.GT.50) GO TO 12
  TER=EROT
```

```

      TEV=EVIB
      MM=MM+1
      GO TO 8
11  CONTINUE
      EROT=0.
      EVIB=0.
      GO TO 10
12  CONTINUE
      WRITE( 6,60)
      EROT=0.
      EVIB=0.
      GO TO 10
60  FORMAT(50H ITERATIVE DECONVOLUTION OF INTERNAL ENERGY FAILED)
61  FORMAT(20H ARG WAS SET TO ZERO)
      END

```

BLOCK DATA PARAMS

```

      COMMON /SURFA/THETA(21),GAMA(9),DA(9,21),SX2DA(9,21),
1SY2DA(9,21),SXY2DA(9,21),BOA(9,21),SX2BOA(9,21),SY2BOA(9,21),
2SXY2BA(9,21),RA(9,21),SX2RA(9,21),SY2RA(9,21),
3SXY2RA(9,21),P4A(9,21),SX2P4A(9,21),SY2P4A(9,21),
4SXY24A(9,21),P5A(9,21),SX2P5A(9,21),SY2P5A(9,21),
5SXY25A(9,21)
      COMMON /SURFB/THETB(19),GAMB(9),DB(9,19),SX2DB(9,19),
1SY2DB(9,19),SXY2DB(9,19),BOB(9,19),SX2BOB(9,19),SY2BOB(9,19),
2SXY2BB(9,19),RB(9,19),SX2RB(9,19),SY2RB(9,19),
3SXY2RB(9,19),P4B(9,19),SX2P4B(9,19),SY2P4B(9,19),
4SXY24B(9,19),P5B(9,19),SX2P5B(9,19),SY2P5B(9,19),
5SXY25B(9,19)
      COMMON /SURFC/THETC(21),GAMC(9),DC(9,21),SX2DC(9,21),
1SY2DC(9,21),SXY2DC(9,21),BOC(9,21),SX2BOC(9,21),SY2BOC(9,21),
2SXY2BC(9,21),RC(9,21),SX2RC(9,21),SY2RC(9,21),
3SXY2RC(9,21),P4C(9,21),SX2P4C(9,21),SY2P4C(9,21),
4SXY24C(9,21),P5C(9,21),SX2P5C(9,21),SY2P5C(9,21),
5SXY25C(9,21)

```

C

C ASSUMING SAME GRID SIZES FOR ALL THREE SURFACES HERE

C GENERATION OF THET AND GAM GRIDS:

C

```

      DATA THETA/0.,10.,20.,25.,27.5,30.,32.5,35.,37.,39.,
1 40.,41.,43.,45.,48.,50.,55.,60.,70.,80.,90./
      DATA THETB/0.,10.,20.,30.,35.,37.5,40.,42.,44.,
1 45.,46.,48.,50.,52.5,55.,60.,70.,80.,90./
      DATA THETC/0.,10.,20.,25.,27.5,30.,32.5,35.,37.,39.,
1 40.,41.,43.,45.,48.,50.,55.,60.,70.,80.,90./
      DATA GAMA/60.,90.,120.,150.,180.,210.,240.,270.,300./

```

DATA GAMB/60.,90.,120.,150.,180.,210.,240.,270.,300./

DATA GAMC/60.,90.,120.,150.,180.,210.,240.,270.,300./

END

Appendix B

Surface Generation Programs

B.1 JPM5COEF1

This program reads a set of fixed-bond-angle surfaces (for bond angles of 60°, 90°, 120°, 150°, 180°) and uses GRA2DS in JWCI7T to construct a global surface. Note that this version of JPM5COEF1 outputs its files in binary format, which requires little storage but is not suitable for transmission to other systems, nor for use with the FPS version of the trajectory program; for such purposes, a short program which reads the binary file and writes it in standard F and E formats should be used to generate a compatible file.

```

C THIS PROGRAM CALCULATES 2-D SPLINE COEFFICIENTS FROM MORSE
C PARAMETER DATA FOR THE 3 SURFACES REPRESENTING THE GENERAL
C REACTION :      A + BC -> AB + C
C
C -----
C
C R.J.WILLIAMS OCTOBER 6-1983
C
C MODIFIED FOR VARIABLE NUMBER OF POINTS BY J. POLOWIN AUG. 1986
C
C -----
C
C THE INPUT MORSE PARAMETER DATA FILES HAVE THE FOLLOWING
C FORMAT : THETA,DE,BETA0,LE,P4,P5  FORMAT ( 6F )
C WHERE.....
C
C      THETA IN DEGREES
C      DE IN EV
C      BETA0 IN BOHR**-1
C      LE IN BOHR
C      P4 IN BOHR**-1
C      P5 IN BOHR**-2

```

C

C THE UNIT ASSIGNMENTS ARE AS FOLLOWS :

C

C UNIT 1 : GAMMA = 60 DEGREES MORSE PARAMETER DATA SET

C UNIT 2 : GAMMA = 90 DEGREES MORSE PARAMETER DATA SET

C UNIT 3 : GAMMA = 120 DEGREES MORSE PARAMETER DATA SET

C UNIT 4 : GAMMA = 150 DEGREES MORSE PARAMETER DATA SET

C UNIT 5 : GAMMA = 180 DEGREES MORSE PARAMETER DATA SET

C UNIT 7 : BINARY OUTPUT FILE

C

C

C

```

      DIMENSION THET(21),GAM(9),R(9,21),D(9,21),B(9,21),
      1P4(9,21),P5(9,21),RX2(9,21),RY2(9,21),RX2Y2(9,21),
      2DX2(9,21),DY2(9,21),DX2Y2(9,21),BX2(9,21),BY2(9,21),
      3BX2Y2(9,21),P4X2(9,21),P4Y2(9,21),P4X2Y2(9,21),P5X2(9,21),
      4P5Y2(9,21),P5X2Y2(9,21)

```

```

      DATA GAM/60.,90.,120.,150.,180.,210.,240.,270.,300./

```

```

      WRITE(6, '( HOW MANY POINTS? (I) )')

```

```

      READ(9, '(I)') NX

```

```

      NY=9

```

```

      DO 10 I=1,NX

```

```

      READ(1,200) THET(I),D(1,I),B(1,I),R(1,I),P4(1,I),P5(1,I)

```

```

      READ(2,200) THET(I),D(2,I),B(2,I),R(2,I),P4(2,I),P5(2,I)

```

```

      READ(3,200) THET(I),D(3,I),B(3,I),R(3,I),P4(3,I),P5(3,I)

```

```

      READ(4,200) THET(I),D(4,I),B(4,I),R(4,I),P4(4,I),P5(4,I)

```

```

      READ(5,200) THET(I),D(5,I),B(5,I),R(5,I),P4(5,I),P5(5,I)

```

C

C THE GAMMA = 210,240,270 & 300 MORSE DATA SETS ARE

C GENERATED BY SYMMETRY

C

```

      DO 7 L=6,9

```

```

      LL=10-L

```

```

      R(L,I)=R(LL,I)

```

```

      D(L,I)=D(LL,I)

```

```

      B(L,I)=B(LL,I)

```

```

      P4(L,I)=P4(LL,I)

```

```

      P5(L,I)=P5(LL,I)

```

```

      7 CONTINUE

```

```

      10 CONTINUE

```

```

      200 FORMAT(6F)

```

C

C CONVERT DE FROM EV TO AU FOR CALL TO SPLINE

C

```

      DO 300 I=1,NX

```



```
D(1,I)=D(1,I)/27.2107
D(2,I)=D(2,I)/27.2107
D(3,I)=D(3,I)/27.2107
D(4,I)=D(4,I)/27.2107
D(5,I)=D(5,I)/27.2107
D(6,I)=D(6,I)/27.2107
D(7,I)=D(7,I)/27.2107
D(8,I)=D(8,I)/27.2107
D(9,I)=D(9,I)/27.2107
300 CONTINUE
CALL GRA2DS(GAM,NY,THET,NX,R,RX2,RY2,RX2Y2)
CALL GRA2DS(GAM,NY,THET,NX,D,DX2,DY2,DX2Y2)
CALL GRA2DS(GAM,NY,THET,NX,B,BX2,BY2,BX2Y2)
CALL GRA2DS(GAM,NY,THET,NX,P4,P4X2,P4Y2,P4X2Y2)
CALL GRA2DS(GAM,NY,THET,NX,P5,P5X2,P5Y2,P5X2Y2)
DO 20 I=1,NY
DO 20 J=1,NX
WRITE(7) R(I,J),RX2(I,J),RY2(I,J),RX2Y2(I,J)
WRITE(7) D(I,J),DX2(I,J),DY2(I,J),DX2Y2(I,J)
WRITE(7) B(I,J),BX2(I,J),BY2(I,J),BX2Y2(I,J)
WRITE(7) P4(I,J),P4X2(I,J),P4Y2(I,J),P4X2Y2(I,J)
WRITE(7) P5(I,J),P5X2(I,J),P5Y2(I,J),P5X2Y2(I,J)
20 CONTINUE
END
```

B.2 JPSPLINFIT

This program reads a file of GMF5 parameters and, using SPCOEF in JW8E, creates files of spline coefficients. The algorithm for one-dimensional spline fitting and spline interpolation is taken from Shampine and Allen [57].

```
C 1-D spline fitter program by Joel Polowin. Reads file of
C GMF5 parameters from unit 10, creates files of spline coefficients
C as follows: De on 20, B on 21, Le on 22, P4 on 23, P5 on 24. Note
C that these assignments are compatible with the contour-drawing
C program RWGAMMA3/JPGAMMA3, etc.
```

```
C
```

```
REAL ANG(50),DE(50),B(50),LE(50),P4(50),P5(50),S(50)
WRITE(6,('( Enter the number of points (N)'))')
READ(5, '(I)') N
READ(10, '(6F)') (ANG(I),DE(I),B(I),LE(I),P4(I),P5(I),I=1,N)
CALL SPCOEF(N,ANG,DE,S)
WRITE(20, '(3G)') (ANG(I),DE(I),S(I),I=1,N)
CALL SPCOEF(N,ANG,B,S)
WRITE(21, '(3G)') (ANG(I),B(I),S(I),I=1,N)
CALL SPCOEF(N,ANG,LE,S)
WRITE(22, '(3G)') (ANG(I),LE(I),S(I),I=1,N)
CALL SPCOEF(N,ANG,P4,S)
WRITE(23, '(3G)') (ANG(I),P4(I),S(I),I=1,N)
CALL SPCOEF(N,ANG,P5,S)
WRITE(24, '(3G)') (ANG(I),P5(I),S(I),I=1,N)
STOP
END
SUBROUTINE SPCOEF(N,XN,FN,S)
```

```
C
```

```
C
```

```
C
```

```
C 1-D SPLINE FITTING ROUTINE
```

```
C
```

```
C
```

```
C
```

```
  DIMENSION XN(N),FN(N),S(N),RHO(201),TAU(201)
```

```
  NM1=N-1
```

```
  NM2=N-2
```

```
  RHO(2)=0.
```

```

TAU(2)=0.
DO 4 I=2,NM1
IIM1=I-1
II=I
IIP1=I+1
HIM1=XN(II)-XN(IIM1)
HI=XN(IIP1)-XN(II)
TEMP=(HIM1/HI)*(RHO(I)+2.)/2
RHO(I+1)=-1./TEMP
D=6.*((FN(IIP1)-FN(II))/HI-(FN(II)-FN(IIM1))/HIM1)/HI
4 TAU(I+1)=(D-HIM1*TAU(I)/HI)/TEMP
S(1)=0.
S(N)=0.
DO 5 I=1,NM2
IB=N-I
5 S(IB)=RHO(IB+1)*S(IB+1)+TAU(IB+1)
RETURN
END

```

B.3 JPSPLINSHOW

This program reads a set of spline parameters for D_c vs. θ created by the use of SPCOEF in JW8E, and outputs to device 8 (which may be the terminal or a file) the interpolated values of D_c at input intervals of θ . This can be used to determine the location or height of a surface feature by successive refinement of the search range, or to create a file of data for plotting. The program contains coding to compile and link itself.

```
!DONT ECHO
!"
!" THIS IS INSTRUCTIONS, XEQ FILE AND FORTRAN PROGRAM FOR
!" JPSPLINSHOW. CAN BE EXECUTED AS AN XEQ FILE; WHEN COMPILED,
!" XEQ COMMANDS ARE IGNORED AS COMMENTS.
!"
!" THIS PROGRAM OUTPUTS EVALUATIONS OF A 1-D SPLINE, ASSUMED TO BE
!" OF A GMF5-TYPE PARAMETER VS. THETA. OUTPUTS PROMPTS TO DEVICE 5,
!" INPUTS INITIAL THETA, INCREMENTS AND NUMBER OF INCREMENTS FROM
!" 6, AND OUTPUTS THETA AND EVALATED RESULTS TO DEVICE 8. - CAN THUS
!" BE USED TO CREATE A FILE FOR X-Y PLOTTING. TO RUN, REQUIRES A FILE
!" OF SPLINE PARAMETERS (ON DEVICE NUMBER INPUT BY USER). TO HALT,
!" ENTER THETA=0 OR BLANK LINE.
!" J. POLOWIN 861125
!"
!FORTRAN JPSPLINSHOW OVER *SPLINBIN
!LINK *SPLINBIN OVER *SPLINLM
!Q
!"
      DIMENSION THET(50),X(50),SX(50)
      WRITE(6,('( ENTER FILE NUMBER FOR INPUT (I).'))')
      READ(5,'(I)') NUMFIL
      DO 10 I=1,50
      IF(I.GT.1) THEN
        IF(THET(I-1).GE.89.999) GOTO 20
      END IF
10    READ(NUMFIL,'(3G)',END=20) THET(I),X(I),SX(I)
20    NTHET=I-1
25    WRITE(6,30)
```

```

30  FORMAT(' ENTER START THETA, INCREMENT, NO. OF INCREMENTS',
, ' (2F,I)')
    READ(5,'(2F,I)') THST,THINC,NINC
    IF(THST.LT.1.E-6) GOTO 200
    DO 100 I=0,NINC
    THETA=THST+FLOAT(I)*THINC
    Y=SPLINE(NTHET,THET,X,SX,THETA)
100  WRITE(8,'(1X,2G)') THETA,Y.
    GOTO 25
200  STOP
    END

    FUNCTION SPLINE(N,XN,FN,S,X)
    DIMENSION XN(N),FN(N),S(N)
    I1=1
    IF(X.GE.XN(I1)) GO TO 1
    I2=2
    H1=XN(I2)-XN(I1)
    SPLINE=FN(I1)+(X-XN(I1))*((FN(I2)-FN(I1))/H1-H1*S(2)/6.)
    RETURN

1   IN=N
    IF(X.LE.XN(IN)) GO TO 2
    INM1=N-1
    HNM1=XN(IN)-XN(INM1)
    SPLINE=FN(IN)+(X-XN(IN))*((FN(IN)-FN(INM1))/HNM1+
2HNM1*S(N-1)/6.)
    RETURN

2   DO 3 I=2,N
    II=I
    IF(X.LE.XN(II)) GO TO 4
3   CONTINUE
4   L=I-1
    IL=L
    ILP1=L+1
    A=XN(ILP1)-X
    B=X-XN(IL)
    HL=XN(ILP1)-XN(IL)
    SPLINE=A*S(L)*(A**2/HL-HL)/6.+B*S(L+1)*(B**2/HL-HL)/6.
    2+(A*FN(IL)+B*FN(ILP1))/HL
    RETURN
    END

```

B.4 MPXY

This program, written by Michael Porter, was used to examine the plots of D_i vs. θ , to check that the curves were smooth and without spline overshoots, and to help show which nodes required adjustment to produce a desired effect on the surface. It utilizes the NAG graphical supplement subroutines.

```
*      MPXY (X-Y PLOTTER)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION X(10,1000),Y(10,1000),ITYPE(10),KSYM(10),DATA(10),
*ILSTYL(10),NPTS(10),XA(1000),YA(1000)
      INTEGER FLAG0,FLAG1,LI,AN,Font
      CHARACTER*20 TITLE,XLAB,YLAB
      CHARACTER*1 ANS,TYPE(10),DUMMY(1)
      CALL XXXXXX
      CALL JO6WAF
      CALL JO6XFF(2)
      PRINT*,'Font'
      READ*,Font
      PRINT*,'RANGE OF PLOT (Xmin,Xmax,Ymin,Ymax separated by commas)'
      PRINT*,' '
      READ (5,9030) X1,X2,Y1,Y2
      AMIN=X1-(X2-X1)/7.
      BMIN=Y1-(Y2-Y1)/15.
      CALL JO6WBF(AMIN,X2,BMIN,Y2,1)
      PRINT*,'DO YOU WANT A TITLE (Y/N)'
      READ (5,9000) ANS
      IF (ANS.EQ.'Y'.OR.ANS.EQ.'y') THEN
        PRINT*,'ENTER TITLE'
        PRINT*,' '
        READ (5,9000) TITLE
        FLAG0=1
      ELSE
        FLAG0=0
      ENDIF
      PRINT*,'DO YOU WANT AXIS LABELS (Y/N)'
      READ (5,9000) ANS
      IF (ANS.EQ.'Y'.OR.ANS.EQ.'y') THEN
        PRINT*,'ENTER X-AXIS LABEL'
```

```

PRINT*, ' '
READ (5,9000) XLAB
PRINT*, 'ENTER Y-AXIS LABEL'
PRINT*, ' '
READ (5,9000) YLAB
FLAG1=1
ELSE
    FLAG1=0
ENDIF
PRINT*, 'DO YOU WISH TO SPECIFY INTERSECTION OF AXES (Y/N)'
READ (5,9000) ANS.
IF (ANS.EQ.'Y'.OR.ANS.EQ.'y') THEN
    PRINT*, 'ENTER X,Y COORDINATES OF INTERSECTION'
    PRINT*, ' '
    READ (5,9020) THRU1,THRU2
ELSE
    THRU1=X1
    THRU2=Y1
ENDIF
1020 PRINT*, 'HOW MANY LINES WILL YOU BE PLOTTING (UP TO 10)'
READ (5,9010) LI
IF (LI.GT.10.OR.LI.LT.1) THEN
    PRINT*, 'NO. OF LINES MUST BE IN RANGE 1-10...TRY AGAIN'
    GOTO 1020
ENDIF
DO 1030 I=1,LI
    ILSTYL(I)=1
    AN=0
    PRINT*, '*** LINE NUMBER',I,'***'
    PRINT*, 'WHAT UNIT IS YOUR DATA ARRAY ON FOR LINE #',I
    READ (5,9010) DATA(I)
    PRINT*, 'SELECT OPTION:'
    PRINT*, 'STRAIGHT LINES JOINING POINTS:  L'
    PRINT*, 'SMOOTH LINE JOINING POINTS:      C'
    PRINT*, ' '
    READ (5,9000) TYPE(I)
    IF (TYPE(I).EQ.'L'.OR.TYPE(I).EQ.'1') THEN
        PRINT*, 'SELECT OPTION:'
        PRINT*, 'MARKERS ONLY           :  1'
        PRINT*, 'LINE ONLY              :  2'
        PRINT*, 'BOTH MARKERS AND LINE:  3'
        PRINT*, ' '
        READ (5,9010) AN
        ITYPE(I)=AN-1
        IF (ITYPE(I).NE.1) THEN

```

```

      PRINT*, 'SELECT MARKER TYPE:'
      PRINT*, 'X (TYPE 1)'
      PRINT*, 'O (TYPE 2)'
      PRINT*, '+' (TYPE 3)'
      PRINT*, '*' (TYPE 4)'
      PRINT*, ' '
      READ (5,9010) KSYM(I)
    ENDIF
  ENDIF
  IF (AN.NE.1) THEN
    PRINT*, 'SELECT LINSTYLE:'
    PRINT*, 'SOLID   : 1'
    PRINT*, 'DASH    : 2'
    PRINT*, 'DOT     : 3'
    PRINT*, 'DASH-DOT: 4'
    PRINT*, ' '
    READ (5,9010) ILSTYL(I)
  ENDIF
1030  CONTINUE
      DO 1080 I=1,LI
        DO 1040 J=1,1000
          READ (DATA(I),9020,END=1050) X(I,J),Y(I,J)
1040  CONTINUE
          WRITE (6,*) 'ONLY THE FIRST 100 POINTS USED FROM UNIT',DATA(I)
1050  NPTS(I)=J-1
          WRITE (6,*) NPTS(I), 'POINTS READ ON UNIT',DATA(I)
          DO 1070 K=1,NPTS(I)-1
            DO 1060 L=K,NPTS(I)
              IF (X(I,L).LT.X(I,K)) THEN
                XBUFF=X(I,K)
                X(I,K)=X(I,L)
                X(I,L)=XBUFF
                YBUFF=Y(I,K)
                Y(I,K)=Y(I,L)
                Y(I,L)=YBUFF
              ENDIF
            ENDIF
          CONTINUE
1060  CONTINUE
1070  CONTINUE
1080  CONTINUE
          CALL JO6WDF
          DO 1100 I=1,LI
            DO 1090 J=1,NPTS(I)
              XA(J)=X(I,J)
              YA(J)=Y(I,J)
1090  CONTINUE

```



```

      CALL JO6YRF(ILSTYL(I))
      IF (TYPE(I).EQ.'L'.OR.TYPE(I).EQ.'1') THEN
        IFAIL=0
        CALL JO6BAF(XA,YA,NPTS(I),ITYPE(I),KSYM(I),IFAIL)
      ENDIF
      IF (TYPE(I).EQ.'C'.OR.TYPE(I).EQ.'c') THEN
        IFAIL=10
        CALL JO6CAF(XA,YA,NPTS(I),2,IFAIL)
      ENDIF
1100  CONTINUE
      CALL JO6YRF(1)
      CALL JO6XGF(1.DO,1.DO)
      CALL JO6YSF(FONT)
      IF (FLAGO.EQ.1) CALL JO6AHF(TITLE)
      CALL JO6XGF(2.DO,2.DO)
      CALL JO6AGF(1,X1,X2,0,0.DO,0,THRU2,DUMMY,1)
      CALL JO6AGF(2,Y1,Y2,0,0.DO,0,THRU1,DUMMY,1)
      IF (FLAG1.EQ.1) THEN
        CALL JO6AJF(1,XLAB)
        CALL JO6AJF(2,YLAB)
      ENDIF
      CALL JO6WZF
9000  FORMAT(1A)
9010  FORMAT(I)
9020  FORMAT(2F)
9030  FORMAT(4F)
      END

```

B.5 JPFHH_DATA5

This is a sample control file for the trajectory program. Some of its parameters will be changed at time of submission by the batch file JPWELLBATCH, but the file shown below is itself correct for use

```
DATA DECK TO RUN A SET OF 250 TRAJECTORIES ON SURFACE S5  
BLENDING, NO WELLS, .50 KCAL BARRIER; F+H2, V=0 J=1, 3 KCAL  
4.80E-08 0.00E-08 2.0E-08 2.0E-16 250 0 0 1 0  
.130093 18.997999 1.008 1.008  
.62788E-08 .88591E-08 .38800E-14  
00001
```

B.6 JPFPSBATCH

This is the subordinate batch or XEQ file that runs the trajectories.

```
'SJE (ECHO)
ATTACH
COPYIN /B JFPSTRAJLM,TRAJLM
COPYIN JPFHH_DATA5.F65TRAJ,CONTROL
COPYIN JPFPSRAND,SEED
COPYIN JWCIFHH-S6XF.F65TRAJ,SURF1
COPYIN JWCIFHH-S5XF.F65TRAJ,SURF2
COPYIN JWCIFHH-S6XF.F65TRAJ,SURF3
TRAJLM
COPYOUT SEED,JPFPSRAND
COPYOUT OUTPUT,JPOUT1
DELETE OUTPUT
TRAJLM
COPYOUT SEED,JPFPSRAND
COPYOUT OUTPUT,JPOUT2
DELETE OUTPUT
TRAJLM
COPYOUT SEED,JPFPSRAND
COPYOUT OUTPUT,JPOUT3
DELETE OUTPUT
TRAJLM
COPYOUT SEED,JPFPSRAND
COPYOUT OUTPUT,JPOUT4
DETACH
QUIT
'C JPOUT1,JPOUT2,JPOUT3,JPOUT4 TO LP
```

B.7 JPWELLBATCH

This is the main batch file, which submits the trajectory program. Lower-case letters indicate an option which should be changed at time of submission with the CP6 replacement options. This file modifies the control file JPFHH_DATA5 (see next section), generates the new surfaces, and runs the trajectories.

```
'JOB ORDER,PRI0=9,NAME=name,DEFER (defer)
'RES TIME=10,FPS=1
'LIMIT LO=200
'DIR .F65TRAJ
'JPBARRIER_LM.
depth
.001
6X
'SET 1 JWCIFHH60-S6X
'SET 2 JWCIFHH90-S6X
'SET 3 JWCIFHH120-S6X
'SET 4 JWCIFHH150-S6X
'SET 5 JWCIFHH180-S6X
'SET 7 JWCIFHH-S6X
'JPM5COEF1LM.
21
'RESET DCBS
'SET 10 JWCIFHH-S6X
'SET 20 JWCIFHH-S6XF
'JPFORMAT_LM.
'"JPHFWELL_LM.
'"depth,depth,depth,depth,depth
! ".001
'"5X
! "SET 1 JWCIFHH60-S5X
! "SET 2 JWCIFHH90-S5X
! "SET 3 JWCIFHH120-S5X
! "SET 4 JWCIFHH150-S5X
! "SET 5 JWCIFHH180-S5X
! "SET 7 JWCIFHH-S5X
! "JPM5COEF1LM.
! "19
```

```
"RESET DCBS
"SET 10 JWCIFHH-S6X
"SET 20 JWCIFHH-S6XF
J"JPFORMAT_LM.
'E JPFHH_DATA5
SE1;/S6/S/name/;TY
SE2;/3/S/kcal/;/.50/S/depth/;ty
SE3;/2 0/S/bmax/;TY
SE4;/.130093/S/ecol/;TY
Q
'C JWCIFHH?-S6X (TY=DA),JWCIFHH?-S5X (TY=DA) TO LP
'DIR RESET
'XEQ JPFPSBATCH
'XEQ JPFPSBATCH
'E JPFHH_DATA5.F65TRAJ
SE1;/name/S/S6/;TY
SE2;/depth/S/.50/;/kcal/S/3/;TY
SE3;/bmax/S/2.0/;TY
SE4;/ecol/S/.130093/;TY
Q
```

B.8 JPRGTWELLBUILD

This program reads in GMF5 parameter data for two surfaces: surface S1, with no reagent wells, and surface S3A, which features a reagent well of $0.5 \text{ kcal mol}^{-1}$ for the surface at each bond angle. It prompts the user for the desired well depth for each bond angle; then assuming a linear change in the height of a spline maximum with a change in the node values, it calculates an expansion or contraction factor for the difference between the input surfaces' nodes in order to give a surface of the desired well depth. Using this scaling factor, a set of new nodes is determined, then the spline parameters are calculated by SPCOE in JWSE. Using SPLINE in JWSE, the new single-angle surface is scanned in a quinary search to find the new maximum; this is compared against the desired value. If the two are not in agreement within the input tolerance factor, a new scaling factor is calculated from the current well depth and averaged with the previous scaling factor to damp out overshoot/undershoot swings; the program returns to the point where the scaling factor is used to construct new nodes. The resulting surfaces are output to a set of files whose name is specified by the user.

```
C Surface generation program by Joel Polowin. Takes a set of
C data with no well (surface 1) and data with a well (usually
C 0.5 kcal, on surface 3) and interpolates/approximates repet-
C itively until a well of the desired depth is obtained. Prompts
C user for desired well depths, tolerance on result, and name for
C resulting data sets. To run, must be linked with SPCOE and
C SPLINE (as of 870403, found in program set JWSE).
```

```
C
```

```
CHARACTER S1(5)*14/'JWCIFHH60-S1 ','JWCIFHH90-S1A',
, 'JWCIFHH120-S1 ','JWCIFHH150-S1 ','JWCIFHH180-S1 '/
CHARACTER S3(5)*14/'JWCIFHH60-S3A','JWCIFHH90-S3A',
, 'JWCIFHH120-S3A','JWCIFHH150-S3A','JWCIFHH180-S3A'/
CHARACTER SNUM*2,SNEW(5)*14
REAL DEPTH(5),ANG(21),DE1(21),DE3(21),DEX(21),SDEX(21),
, B(21),LE(21),P4(21),P5(21),THBEG(5)/24.,29.,30.,30.,33./
WRITE(6,2)
```

```

2   FORMAT(' Desired reagent well depths, surfaces 60 thru 180',
, ' , in kcal (5F)')
   READ(5,'(5F)') (DEPTH(I),I=1,5)
   WRITE(6,'('' Tolerance, in kcal?''')')
   READ(5,'(F)') TOL
   WRITE(6,'('' Surface number for output (A2)?''')')
   READ(5,'(A2)') SNUM
   SNEW(1)='JWCIFHH60-S'//SNUM
   SNEW(2)='JWCIFHH90-S'//SNUM
   SNEW(3)='JWCIFHH120-S'//SNUM
   SNEW(4)='JWCIFHH150-S'//SNUM
   SNEW(5)='JWCIFHH180-S'//SNUM
   DO 300 I=1,5
   OPEN(1,FILE=S1(I))
   OPEN(3,FILE=S3(I))
   OPEN(10,FILE=SNEW(I))
   READ(1,'(6F)') (ANG(J),DE1(J),B(J),LE(J),P4(J),P5(J),J=1,21)
   READ(3,'(6F)') (ANG(J),DE3(J),B(J),LE(J),P4(J),P5(J),J=1,21)
   FACT=DEPTH(I)*2.
10  THST=THBEG(I)
   THINC=1.
   DO 20 J=1,21
20  DEX(J)=DE1(J)+FACT*(DE3(J)-DE1(J))
   CALL SPCOEF(21,ANG,DEX,SDEX)
40  PREV=SPLINE(21,ANG,DEX,SDEX,THST)
   DO 80 K=1,10
   THETA=THST+THINC*FLOAT(K)
   VAL=SPLINE(21,ANG,DEX,SDEX,THETA)
   IF(VAL.LT.PREV) GOTO 90
   PREV=VAL
80  CONTINUE
90  IF(THINC.LE.2.E-3) GOTO 100
   IF(K.EQ.1.OR.K.EQ.11) THEN
       DEPX=DEPTH(I)*.2
       GOTO 110
   END IF
   THST=THST+THINC*FLOAT(K-2)
   THINC=THINC/5.
   GOTO 40
100 DEPX=(PREV-DE1(1))*23.060468
   IF(ABS(DEPX-DEPTH(I)).LE.TOL) GOTO 200
110 FACT=FACT*(DEPTH(I)/DEPX*.5+.5)
   GOTO 10
200 WRITE(10,210) (ANG(J),DEX(J),B(J),LE(J),P4(J),P5(J),J=1,21)
210 FORMAT(F4.1,',',F6.4,',',F6.4,',',F7.4,',',F9.6,',',F8.6)

```

```
CLOSE(1)
CLOSE(3)
CLOSE(10)
WRITE(6, '( '' Done surface #'',I2)') I
300 CONTINUE
STOP
END
```


B.9 JPPRDWELLBUILD

This program is quite similar to JPRGTWELLBUILD. It reads data from surface S1B, which has no product wells, and surface S5B, which has a product well of $0.5 \text{ kcal mol}^{-1}$ at each bond angle. The range of search for the well depth is different; also, because the proximity to a large steep slope promotes a rapid change in well depth with node change, the damping of expansion factor change is more drastic here than for the reagent well program: the new factor is 90% based on the old factor, and only 10% on the new calculated value.

```
C Surface generation program by Joel Polowin. Takes a set of
C data with no well (surface 1) and data with a well (usually
C 0.5 kcal, on surface 3) and interpolates/approximates repet-
C itively until a well of the desired depth is obtained. Prompts
C user for desired well depths, tolerance on result, and name for
C resulting data sets. To run, must be linked with SPCOEF and
C SPLINE (as of 870403, found in program set JW8E).
```

```
C
      CHARACTER S1(5)*14/'JWCIFHH60-S1B','JWCIFHH90-S1B',
      , 'JWCIFHH120-S1B','JWCIFHH150-S1B','JWCIFHH180-S1B'/
      CHARACTER S3(5)*14/'JWCIFHH60-S5B','JWCIFHH90-S5B',
      , 'JWCIFHH120-S5B','JWCIFHH150-S5B','JWCIFHH180-S5B'/
      CHARACTER SNUM*2,SNEW(5)*14
      REAL DEPTH(5),ANG(21),DE1(21),DE3(21),DEX(21),SDEX(21),
      , B(21),LE(21),P4(21),P5(21),THBEG(5)/54.,54.,48.,48.,48./
      WRITE(6,2)
2  FORMAT(' Desired reagent well depths, surfaces 60 thru 180',
      , ', in kcal (5F)')
      READ(5,'(5F)') (DEPTH(I),I=1,5)
      WRITE(6,(' Tolerance, in kcal?'))
      READ(5,'(F)') TOL
      WRITE(6,(' Surface number for output (A2)?'))
      READ(5,'(A2)') SNUM
      SNEW(1)='JWCIFHH60-S'//SNUM
      SNEW(2)='JWCIFHH90-S'//SNUM
      SNEW(3)='JWCIFHH120-S'//SNUM
      SNEW(4)='JWCIFHH150-S'//SNUM
      SNEW(5)='JWCIFHH180-S'//SNUM
```

```

DO 300 I=1,5
OPEN(1,FILE=S1(I))
OPEN(3,FILE=S3(I))
OPEN(10,FILE=SNEW(I))
READ(1,'(6F)') (ANG(J),DE1(J),B(J),LE(J),P4(J),P5(J),J=1,21)
READ(3,'(6F)') (ANG(J),DE3(J),B(J),LE(J),P4(J),P5(J),J=1,21)
FACT=DEPTH(I)*2.
10 THST=THBEG(I)
THINC=1.
DO 20 J=1,21
20 DEX(J)=DE1(J)+FACT*(DE3(J)-DE1(J))
CALL SPCOEF(21,ANG,DEX,SDEX)
40 PREV=SPLINE(21,ANG,DEX,SDEX,THST)
DO 80 K=1,12
THETA=THST+THINC*FLOAT(K)
VAL=SPLINE(21,ANG,DEX,SDEX,THETA)
IF(VAL.LT.PREV) GOTO 90
PREV=VAL
80 CONTINUE
85 FACT=FACT*1.5
GOTO 10
90 IF(THINC.LE.2.E-3) GOTO 100
THST=THST+THINC*FLOAT(K-2)
THINC=THINC/5.
GOTO 40
100 DEPX=(PREV-DE1(21))*23.060468
IF(ABS(DEPX-DEPTH(I)).LE.TOL) GOTO 200
110 FACT=FACT*(DEPTH(I)/DEPX*.1+.9)
GOTO 10
200 WRITE(10,210) (ANG(J),DEX(J),B(J),LE(J),P4(J),P5(J),J=1,21)
210 FORMAT(F4.1,',',F6.4,',',F6.4,',',F7.4,',',F9.6,',',F8.6)
CLOSE(1)
CLOSE(3)
CLOSE(10)
WRITE(6,'(' Done surface #',I2)') I
300 CONTINUE
STOP
END

```

B.10 JPHFHWELLBUILD

This program is essentially identical to JPPRDWELLBUILD; the data is read from surface S1 (no wells) and surface S3A (.5 kcal mol⁻¹ wells). The HFH wells are broader than the FHH product wells, so the change of interpolated values with node values is less extreme; a simple averaging suffices to damp overshoots.

```

      CHARACTER S1(5)*13/'JWCIFHFH60-S1','JWCIFHFH90-S1',
      , 'JWCIFHFH120-S1','JWCIFHFH150-S1','JWCIFHFH180-S1'/
      CHARACTER S3(5)*14/'JWCIFHFH60-S3A','JWCIFHFH90-S3A',
      , 'JWCIFHFH120-S3A','JWCIFHFH150-S3A','JWCIFHFH180-S3A'/
      CHARACTER SNUM*2,SNEW(5)*14
      REAL DEPTH(5),ANG(19),DE1(19),DE3(19),DEX(19),SDEX(19),
      , B(19),LE(19),P4(19),P5(19),THBEG(5)/26.,29.,29.,29.,29./
      WRITE(6,2)
2    FORMAT(' Desired reagent well depths, surfaces 60 thru 180',
      , ', in kcal (5F)?')
      READ(5,'(5F)') (DEPTH(I),I=1,5)
      WRITE(6,'('' Tolerance, in kcal?''?)')
      READ(5,'(F)') TOL
      WRITE(6,'('' Surface number for output (A2)?''?)')
      READ(5,'(A2)') SNUM
      SNEW(1)='JWCIFHFH60-S'//SNUM
      SNEW(2)='JWCIFHFH90-S'//SNUM
      SNEW(3)='JWCIFHFH120-S'//SNUM
      SNEW(4)='JWCIFHFH150-S'//SNUM
      SNEW(5)='JWCIFHFH180-S'//SNUM
      DO 300 I=1,5
      OPEN(1,FILE=S1(I))
      OPEN(3,FILE=S3(I))
      OPEN(10,FILE=SNEW(I))
      READ(1,'(6F)') (ANG(J),DE1(J),B(J),LE(J),P4(J),P5(J),J=1,19)
      READ(3,'(6F)') (ANG(J),DE3(J),B(J),LE(J),P4(J),P5(J),J=1,19)
      FACT=DEPTH(I)*2.
10   THST=THBEG(I)
      THINC=1.
      DO 20 J=1,19
20   DEX(J)=DE1(J)+FACT*(DE3(J)-DE1(J))
      CALL SPCOEF(19,ANG,DEX,SDEX)

```

```
40  PREV=SPLINE(19,ANG,DEX,SDEX,THST)
    DO 80 K=1,10
      THETA=THST+THINC*FLOAT(K)
      VAL=SPLINE(19,ANG,DEX,SDEX,THETA)
      IF(VAL.LT.PREV) GOTO 90
      PREV=VAL
80  CONTINUE
90  IF(THINC.LE.2.E-3) GOTO 100
      THST=THST+THINC*FLOAT(K-2)
      THINC=THINC/5.
      GOTO 40
100  DEPX=(PREV-DE1(1))*23.060468
      IF(ABS(DEPX-DEPTH(I)).LE.TOL) GOTO 200
      FACT=FACT*(DEPTH(I)/DEPX*.5+.5)
      GOTO 10
200  WRITE(10,210) (ANG(J),DEX(J),B(J),LE(J),P4(J),P5(J),J=1,19)
210  FORMAT(F4.1,',',',',F6.4,',',',',F6.4,',',',',F7.4,',',',',F9.6,',',',',F8.6)
      CLOSE(1)
      CLOSE(3)
      CLOSE(10)
      WRITE(6,'('' Done surface #'',I2)') I
300  CONTINUE
      STOP
      END
```

B.11 JPBARRIERBUILD

This program is similar to the others except that it searches for a spline minimum instead of a maximum. Data is read from surfaces S1B (.99 kcal mol⁻¹ barrier for the collinear [180°] surface) and S6A (no barriers) and extrapolated in the usual manner. A distinction is that the user is prompted only for the desired collinear barrier height; the barriers for the other angles are calculated assuming that the absolute differences in heights for the other angles will be the same as for surface S1B.

```
C Surface generation program by Joel Polowin. Takes a set of
C data with no barrier (surface 3) and data with a barrier (usually
C .99 kcal for 180° surface, on surface 1) and interpolates/approx-
C imates repetitively until a barrier of the desired height is
C obtained. Prompts user for desired 180° barrier height, tolerance
C on result, and name for resulting data sets. To run, must be
C linked with SPCOEF and SPLINE (as of 870403 found in program set
C JW8E).
```

```
C
  CHARACTER S1(5)*14/'JWCIFHH60-S1B','JWCIFHH90-S1B',
, 'JWCIFHH120-S1B','JWCIFHH150-S1B','JWCIFHH180-S1B'/
  CHARACTER S3(5)*14/'JWCIFHH60-S6A','JWCIFHH90-S6A',
, 'JWCIFHH120-S6A','JWCIFHH150-S6A','JWCIFHH180-S6A'/
  CHARACTER SNUM*2,SNEW(5)*14
  REAL ANG(21),DE1(21),DE3(21),DEX(21),SDEX(21),
, B(21),LE(21),P4(21),P5(21),THBEG(5)/31.,33.,34.,37.,37./,
, DEPTH(5)/9.6515,9.1005,3.4083,1.1208,0.9932/
  WRITE(6,2)
2  FORMAT(' Desired 180° surface barrier in kcal (F)?')
  READ(5,'(F)') DEPNEW
  WRITE(6,(' Tolerance, in kcal?'))
  READ(5,'(F)') TOL
  WRITE(6,(' Surface number for output (A2)?'))
  READ(5,'(A2)') SNUM
  SNEW(1)='JWCIFHH60-S'//SNUM
  SNEW(2)='JWCIFHH90-S'//SNUM
  SNEW(3)='JWCIFHH120-S'//SNUM
  SNEW(4)='JWCIFHH150-S'//SNUM
```

```

SNEW(5)='JWCIFHH180-S'//SNUM
DO 300 I=1,5
OPEN(1,FILE=S1(I))
OPEN(3,FILE=S3(I))
OPEN(10,FILE=SNEW(I))
READ(1,'(6F)') (ANG(J),DE1(J),B(J),LE(J),P4(J),P5(J),J=1,21)
READ(3,'(6F)') (ANG(J),DE3(J),B(J),LE(J),P4(J),P5(J),J=1,21)
HGT=DEPTH(I)-DEPTH(5)+DEPNW
FACT=HGT/DEPTH(I)
10 THST=THBEG(I)
THINC=1.
DO 20 J=1,21
20 DEX(J)=DE3(J)+FACT*(DE1(J)-DE3(J))
CALL SPCOEF(21,ANG,DEX,SDEX)
40 PREV=SPLINE(21,ANG,DEX,SDEX,THST)
DO 80 K=1,10
THETA=THST+THINC*FLOAT(K)
VAL=SPLINE(21,ANG,DEX,SDEX,THETA)
IF(VAL.GT.PREV) GOTO 90
PREV=VAL
80 CONTINUE
90 IF(THINC.LE.2.E-3) GOTO 100
THST=THST+THINC*FLOAT(K-2)
THINC=THINC/5.
GOTO 40
100 DEPX=(DE3(1)-PREV)*23.060468
IF(ABS(DEPX-HGT).LE.TOL) GOTO 200
110 FACT=FACT*(HGT/DEPX*.3+.7)
GOTO 10
200 WRITE(10,210) (ANG(J),DEX(J),B(J),LE(J),P4(J),P5(J),J=1,21)
210 FORMAT(F4.1,' ',F6.4,' ',F6.4,' ',F7.4,' ',F9.6,' ',F8.6)
CLOSE(1)
CLOSE(3)
CLOSE(10)
WRITE(6,'(' Done surface #',I2)') I
300 CONTINUE
STOP
END

```

Appendix C

Derivations of Uncertainty Calculations

C.1 Derivation of Monte Carlo Error for Trajectories

Let x be a variable which takes the value 1 if a trajectory yields a reaction, and the value 0 if it does not. Then for N trajectories,

$$\bar{x} = \frac{N_r}{N} = P_r$$

where N_r is the number of reactive trajectories and P_r is the probability of reaction. Then the variance of x , denoted σ_x^2 , is given by

$$\sigma_x^2 = \frac{\sum (x - \bar{x})^2}{N} = \frac{\sum x^2 - N\bar{x}^2}{N}$$

$$\sigma_x^2 = \frac{N_r - NP_r^2}{N}$$

$$= P_r - P_r^2$$

$$= P_r(1 - P_r)$$

$$\sigma_x^2 = \frac{\sigma_x^2}{N}$$

$$\sigma_{P_r}^2 = \frac{P_r(1 - P_r)}{N}$$

Each reactive trajectory may end up in any of several product states $\mathbf{v}$; it is desired to express results in terms of a population fraction f_v , where $f_v = N_v/N_r$, with the associated uncertainty σ_{f_v} . This uncertainty calculation is not straightforward because both the total reactive population and the population in state $\mathbf{v}$ are uncertain values which are related. For example, in the case where one state dominates the products, the uncertainty of that fraction is small, tending to 0 as the population fraction approaches 1. The derivation of the formula for the uncertainty of each population fraction follows.

C.2 Derivation of Standard Deviation for Population Fractions

$$\text{If } r = \frac{u}{v}, \quad \sigma_r^2 = \frac{u^2}{v^2} \left(\frac{\sigma_u^2}{u^2} + \frac{\sigma_v^2}{v^2} - 2 \frac{\sigma_{uv}}{uv} \right)$$

where σ_{uv} is the covariance of u and v . The conditions for validity of the approximation [58] are given below.

$$f_v = \frac{N_v}{N_r} = \frac{P_v}{P_r}$$

$$\sigma_{f_v}^2 = f_v^2 \left(\frac{\sigma_{P_v}^2}{P_v^2} + \frac{\sigma_{P_r}^2}{P_r^2} - 2 \frac{\sigma_{P_v P_r}}{P_v P_r} \right)$$

Let v be a variable which takes the value 1 if a trajectory yields a reaction ending in state y and 0 otherwise; and r a variable which takes the value 1 if a trajectory yields a reaction and 0 if it does not. Then for N trajectories

$$\sum v = N_v \quad \sum r = N_r$$

$$v = \frac{N_v}{N} = P_v \quad r = \frac{N_r}{N} = P_r$$

$$\sigma_{vr} = \frac{\sum (v - \bar{v})(r - \bar{r})}{N} = \frac{\sum vr - N \bar{v} \bar{r}}{N} = \frac{N_v}{N} - P_v P_r$$

$$\sigma_{vr} = P_v(1 - P_r)$$

$$\sigma_{P_v P_r} = \sigma_{vr} = \frac{\sigma_{vr}}{N} = \frac{P_v(1 - P_r)}{N}$$

$$\begin{aligned} \sigma_{f_v}^2 &= f_v^2 \left(\frac{\sigma_{P_v}^2}{P_v^2} + \frac{\sigma_{P_r}^2}{P_r^2} - 2 \frac{P_v(1 - P_r)}{N P_v P_r} \right) \\ &= f_v^2 \left(\frac{\sigma_{P_v}^2}{P_v^2} + \frac{\sigma_{P_r}^2}{P_r^2} - \frac{2}{P_r^2} \cdot \frac{P_r(1 - P_r)}{N} \right) \\ &= f_v^2 \left(\frac{\sigma_{P_v}^2}{P_v^2} + \frac{\sigma_{P_r}^2}{P_r^2} - \frac{2\sigma_{P_r}^2}{P_r^2} \right) \\ &= f_v^2 \left(\frac{\sigma_{P_v}^2}{P_v^2} - \frac{\sigma_{P_r}^2}{P_r^2} \right) \\ \sigma_{f_v} &= f_v \left(\frac{\sigma_{P_v}^2}{P_v^2} - \frac{\sigma_{P_r}^2}{P_r^2} \right)^{\frac{1}{2}} \end{aligned}$$

The above formula for the variance of a ratio $r = \frac{u}{v}$ is valid when

$$V_v \leq .05, \quad \text{or} \quad \rho = \frac{V_v}{V_u} \quad \text{and} \quad V_v \leq .15$$

$$\text{where } V_r = \frac{\sigma_r}{r}, \quad \rho = \frac{S_{uv}}{S_u S_v}, \quad S_{uv} = \frac{N}{N-1} \sigma_{uv}, \quad S_u = \sqrt{\frac{N}{N-1}} \sigma_u^2$$

Here, $r = f_v = \frac{P_v}{P_r}$; conditions on the trajectory results to allow the second part of the validity criterion to be true are determined.

$$\begin{aligned} \rho &= \frac{\frac{N}{N-1} \sigma_{vr}}{\frac{N}{N-1} \sigma_v \sigma_r} = \frac{\frac{P_r(1-P_r)}{N}}{\sqrt{\frac{P_r(1-P_r)}{N}} \sqrt{\frac{P_r(1-P_r)}{N}}} \\ &= \frac{P_v(1-P_r)}{\sqrt{P_v P_r (1-P_v)(1-P_r)}} \\ &= \frac{P_v}{P_r} \sqrt{\frac{P_r(1-P_r)}{P_v(1-P_v)}} \\ &= \frac{P_v}{P_r} \frac{\sqrt{\frac{P_r(1-P_r)}{N}}}{\sqrt{\frac{P_v(1-P_v)}{N}}} \\ &= \frac{P_v}{P_r} \cdot \frac{\sigma_{P_r}}{\sigma_{P_v}} \\ &= \frac{V_{P_r}}{V_{P_v}} \quad \text{as required.} \end{aligned}$$

$$\text{For } V_{P_r} \leq .15, \quad \frac{\sqrt{\frac{P_r(1-P_r)}{N}}}{P_r} \leq 0.15$$

$$\frac{P_r(1-P_r)}{N} \leq .0225 P_r^2$$

$$1 - P_r \leq .0225 P_r N$$

$$\frac{1}{.0225N + 1} \leq P_r$$

For $N = 2000$, $P_r \geq .022$ if the formula is to be accurate.

(References for derivation: [59], [58], [5].)

Appendix D

Derivation of Blending Function Calculations

Choosing a swing point S at (10,10) bohr, the RMCS [10] coordinate system defines θ and ℓ according to

$$\ell = [(10 - R_1)^2 + (10 - R_2)^2]^{\frac{1}{2}}, \quad \theta = \tan^{-1}[(10 - R_2)/(10 - R_1)],$$

where R_1 and R_2 are the bond distances. The potential function is

$$V = D_c(1 - e^{\beta x})^2 - D_c,$$

where $x = \ell - \ell_c$, $\beta = \beta_0(1 + \lambda_1 x + \lambda_2 x^2)$, and ℓ_c is the distance from S to the minimum energy along each ray.

Now $V = V(D_c, \beta, \ell, \ell_c)$, $\beta = \beta(\beta_0, \lambda_1, \lambda_2)$, $D_c = D_c(\gamma, \theta)$ and similarly for ℓ_c , β_0 , λ_1 and λ_2 , $\theta = \theta(R_1, R_2, R_3)$ and similarly for γ and ℓ . Then

$$\begin{aligned} \frac{\partial V}{\partial R_1} = & \left[\left(\frac{\partial V}{\partial D_c} \right) \left(\frac{\partial D_c}{\partial \gamma} \right) + \left(\frac{\partial V}{\partial \beta_0} \right) \left(\frac{\partial \beta_0}{\partial \gamma} \right) + \left(\frac{\partial V}{\partial \lambda_1} \right) \left(\frac{\partial \lambda_1}{\partial \gamma} \right) \right. \\ & \left. + \left(\frac{\partial V}{\partial \lambda_2} \right) \left(\frac{\partial \lambda_2}{\partial \gamma} \right) + \left(\frac{\partial V}{\partial \ell_c} \right) \left(\frac{\partial \ell_c}{\partial \gamma} \right) \right] \frac{\partial \gamma}{\partial R_1} \\ & + \left[\left(\frac{\partial V}{\partial D_c} \right) \left(\frac{\partial D_c}{\partial \theta} \right) + \left(\frac{\partial V}{\partial \beta_0} \right) \left(\frac{\partial \beta_0}{\partial \theta} \right) + \left(\frac{\partial V}{\partial \lambda_1} \right) \left(\frac{\partial \lambda_1}{\partial \theta} \right) \right. \\ & \left. + \left(\frac{\partial V}{\partial \lambda_2} \right) \left(\frac{\partial \lambda_2}{\partial \theta} \right) + \left(\frac{\partial V}{\partial \ell_c} \right) \left(\frac{\partial \ell_c}{\partial \theta} \right) \right] \frac{\partial \theta}{\partial R_1} \\ & + \left(\frac{\partial V}{\partial \ell} \right) \left(\frac{\partial \ell}{\partial R_1} \right), \end{aligned}$$

where

$$\left(\frac{\partial V}{\partial D_c} \right) = e^{2\beta x} - 2e^{\beta x}, \quad \left(\frac{\partial V}{\partial \beta} \right) = 2D_c x (e^{2\beta x} - 2e^{\beta x}),$$

$$\left(\frac{\partial V}{\partial \beta_0}\right) = 2D_e x(\epsilon^{2\beta x} - 2\epsilon^{\beta x})(1 + \lambda_1 x + \lambda_2 x^2),$$

$$\left(\frac{\partial V}{\partial \lambda_1}\right) = 2D_e \beta_0 x^2(\epsilon^{2\beta x} - 2\epsilon^{\beta x}), \quad \left(\frac{\partial V}{\partial \lambda_2}\right) = 2D_e \beta_0 x^3(\epsilon^{2\beta x} - 2\epsilon^{\beta x}),$$

$$\frac{\partial V}{\partial \ell} = \frac{\partial V}{\partial x}, \quad \frac{\partial V}{\partial \ell_e} = -\frac{\partial V}{\partial x}, \quad \frac{\partial V}{\partial x} = 2D_e \beta_0(1 + 2\lambda_1 x + 3\lambda_2 x^2)(\epsilon^{2\beta x} - 2\epsilon^{\beta x})$$

and $\partial D_e/\partial \theta$, $\partial \beta_0/\partial \theta$, $\partial \lambda_1/\partial \theta$, $\partial \lambda_2/\partial \theta$, $\partial \ell_e/\partial \theta$, $\partial D_e/\partial \gamma$, $\partial \beta_0/\partial \gamma$, $\partial \lambda_1/\partial \gamma$, $\partial \lambda_2/\partial \gamma$, $\partial \ell_e/\partial \gamma$ are all obtained from the cubic spline functions.

From the law of cosines we have $\cos \gamma = (R_1^2 + R_2^2 - R_3^2)/2R_1R_2$, so

$$\frac{\partial \gamma}{\partial R_1} = \frac{-1}{(1 - u^2)^{1/2}} \frac{R_1^2 - R_2^2 + R_3^2}{2R_1^2R_2},$$

$$\frac{\partial \gamma}{\partial R_2} = \frac{-1}{(1 - u^2)^{1/2}} \frac{R_2^2 - R_1^2 + R_3^2}{2R_1^2R_2},$$

$$\frac{\partial \gamma}{\partial R_3} = \frac{-1}{(1 - u^2)^{1/2}} \frac{R_3}{R_1R_2},$$

where $u = (R_1^2 + R_2^2 - R_3^2)/2R_1R_2$. From the definition $\theta = \tan^{-1}[(10 - R_2)/(10 - R_1)]$ we obtain

$$\frac{\partial \theta}{\partial R_1} = \frac{R_2}{\ell^2}, \quad \frac{\partial \theta}{\partial R_2} = \frac{R_1 - 10}{\ell^2}, \quad \frac{\partial \theta}{\partial R_3} = 0.$$

Finally from $\ell = [(10 - R_1)^2 + (10 - R_2)^2]^{1/2}$ we obtain

$$\frac{\partial \ell}{\partial R_1} = \frac{R_1 - 10}{\ell}, \quad \frac{\partial \ell}{\partial R_2} = \frac{R_2 - 10}{\ell}, \quad \frac{\partial \ell}{\partial R_3} = 0.$$

For the case of blending two surfaces with bond angles γ_1 and γ_2 , the corresponding formulae apply with $V = c_1V_1 + c_2V_2$. For the derivatives $\partial V/\partial R_i$, blending gives

$$\frac{\partial V}{\partial R_i} = c_1 \frac{\partial V_1}{\partial R_i} + c_2 \frac{\partial V_2}{\partial R_i} + V_1 \frac{\partial c_1}{\partial R_i} + V_2 \frac{\partial c_2}{\partial R_i},$$

where R_1 , R_2 , and R_3 are the three bond distances. Since $c_1 + c_2 = 1$, $\partial c_2/\partial R_i = -\partial c_1/\partial R_i$ and thus

$$\frac{\partial V}{\partial R_i} = \frac{\partial c_1}{\partial R_i}(V_1 - V_2) + c_1 \frac{\partial V_1}{\partial R_i} + c_2 \frac{\partial V_2}{\partial R_i}.$$

Let us denote $c_1 = c_x/(c_x + c_y)$, where the unnormalized weights c_x and c_y come from the blending function $c_x = -2 + 1/\cos x$, $c_y = -2 + 1/\cos y$. Then

$$\frac{\partial c_1}{\partial R_1} = \frac{c_y}{(c_x + c_y)^2} \frac{\partial c_x}{\partial R_1} - \frac{c_x}{(c_x + c_y)^2} \frac{\partial c_y}{\partial R_1}.$$

For a triangle with sides (R_1, R_2, R_3) and opposite angles (γ, α, β) we have, by using the law of cosines,

$$c_\gamma = \frac{2R_2R_3}{R_2^2 + R_3^2 - R_1^2} - 2, \quad c_\alpha = \frac{2R_1R_3}{R_1^2 + R_3^2 - R_2^2} - 2, \quad c_\beta = \frac{2R_1R_2}{R_1^2 + R_2^2 - R_3^2} - 2$$

Then

$$\begin{aligned} \frac{\partial c_\gamma}{\partial R_1} &= \frac{4R_1R_2R_3}{(R_2^2 + R_3^2 - R_1^2)^2}, & \frac{\partial c_\gamma}{\partial R_2} &= \frac{2R_3(R_1^2 - R_2^2 - R_3^2)}{(R_2^2 + R_3^2 - R_1^2)^2}, \\ \frac{\partial c_\gamma}{\partial R_3} &= \frac{2R_2(R_1^2 - R_2^2 - R_3^2)}{(R_2^2 + R_3^2 - R_1^2)^2} \end{aligned}$$

and so on; or, in general,

$$c_{\text{angle}} = \frac{2 \text{adj}_1 \text{adj}_2}{\text{adj}_1^2 + \text{adj}_2^2 - \text{opp}^2} - 2,$$

$$\frac{\partial c_{\text{angle}}}{\partial R_{\text{opp}}} = \frac{4 \text{opp} \text{adj}_1 \text{adj}_2}{(\text{adj}_1^2 + \text{adj}_2^2 - \text{opp}^2)^2}, \quad \frac{\partial c_{\text{angle}}}{\partial R_{\text{adj}_1}} = \frac{2 \text{adj}_2 (\text{adj}_2^2 - \text{adj}_1^2 - \text{opp}^2)}{(\text{adj}_1^2 + \text{adj}_2^2 - \text{opp}^2)^2},$$

where $\text{opp} \equiv$ opposite side and $\text{adj} \equiv$ adjacent side.

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