

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

AVOIDED INTERSECTION OF POTENTIAL ENERGY SURFACES: THE (H+ + H<sub>2</sub>, H + H<sub>2</sub><sup>+</sup>) SYSTEM

### Permalink

<https://escholarship.org/uc/item/7kg4658f>

### Authors

Bauschlicher, Charles W.

O'Neil, Stephen V.

Preston, Richard K.

et al.

### Publication Date

1973-03-01

AVOIDED INTERSECTION OF POTENTIAL ENERGY SURFACES:  
THE ( $H^+ + H_2$ ,  $H + H_2^+$ ) SYSTEM

Charles W. Bauschlicher, Jr.,  
Stephen V. O'Neil, Richard K. Preston,  
Henry F. Schaefer III, and Charles F. Bender

March 1973

Prepared for the U.S. Atomic Energy  
Commission under Contract W-7405-ENG-48

**For Reference**

Not to be taken from this room



## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

## AVOIDED INTERSECTION OF POTENTIAL ENERGY SURFACES:

THE ( $H^+ + H_2$ ,  $H + H_2^+$ ) SYSTEM\*

Charles W. Bauschlicher, Jr., Stephen V. O'Neil<sup>†</sup>, Richard K. Preston,  
and Henry F. Schaefer III<sup>††</sup>

Department of Chemistry and  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

and

Charles F. Bender<sup>‡</sup>

Lawrence Livermore Laboratory  
University of California  
Livermore, California 94550

## ABSTRACT

Nonempirical electronic structure calculations have been carried out on the two lowest  $^1A_1$  states of  $H_3^+$ . When one proton is infinitely separated from the other two, these  $^1A_1$  potential surfaces cross each other. The nature of this avoided intersection is examined by means of potential curves, contour diagrams, and perspective plots. Surface hopping is discussed within a Landau-Zener-Stueckelberg (LZS) framework, and the LZS assumptions concerning the surfaces are shown to be reasonable near the avoided intersection. Ab initio LZS parameters are compared with those obtained from the semi-empirical diatomics-in-molecules surfaces of Preston and Tully. The agreement is good, better than might have been anticipated.

## INTRODUCTION

The avoided crossing of diatomic molecule potential energy curves is a phenomena familiar to most chemical physicists.<sup>1</sup> The most carefully studied<sup>2,3</sup> example of an avoided crossing is probably the E, F,  $^1\Sigma_g^+$  "double minimum" state of the hydrogen molecule. Many other theoretical examples are available.<sup>4</sup> The dynamic consequences of the avoided crossing have been the subject of a great deal of theoretical research, most notably the papers of Landau,<sup>5</sup> Zener,<sup>6</sup> and Stuckelberg.<sup>7</sup>

If only from our knowledge of diatomic potential curves, it is clear that the avoided intersection of potential energy surfaces must be a common occurrence in nature. However, it appears that there has not been a single careful ab initio study of an avoided intersection. Studies of the molecular dynamics accompanying an avoided intersection are almost equally scarce.<sup>8-10</sup> In fact, the only concrete example which has been studied is the  $H_3^+$  system, for which examination of the  $H_2$  and  $H_2^+$  ground state potential curves implies<sup>10</sup> the existence of an avoided intersection. Preston and Tully<sup>10</sup> have studied the dynamics of the reaction of  $H^+$  and  $D_2$  using semi-empirical diatomics-in-molecules<sup>11</sup> potential surfaces for the two lowest singlet states. In their work, Preston and Tully adopted a classical trajectory approach. However, in the spirit of Landau-Zener-Stuckelberg, they allowed for the possibility of "surface hopping" (nonadiabatic electronic transitions) at points of avoided intersection of the potential surfaces.

In light of the Preston-Tully research, it seemed sensible to concern the first ab initio study of an avoided intersection with the  $(H^+ + H_2, H + H_2^+)$  pair of potential surfaces. The  $H_3^+$  system has the additional obvious

advantage that the electronic structure calculations may be made sufficiently precise as to allow us to concentrate on the surfaces, rather than the possible deficiencies of the calculations. In addition to learning something about the nature of adiabatic potential surfaces near an avoided intersection, we should be able to evaluate the reliability of the semi-empirical diatomics-in-molecules method<sup>11</sup> for the  $H_3^+$  system.

#### DESCRIPTION AND RELIABILITY OF THE CALCULATIONS

An uncontracted set of gaussian basis functions, seen in Table I, was used in the present work. The set of five s functions are those found optimum for the hydrogen atom by van Duijneveldt.<sup>12</sup> For the H atom, this basis yields an energy of -0.499 810 hartrees, compared to the exact result, -0.5 hartrees. The p functions were taken from the work of Czismadia and co-workers,<sup>13</sup> and are nearly optimum for the hydrogen molecule. The total number of basis functions is 33, and for the  $C_{2v}$  geometries considered herein there will be 16  $a_1$  functions, 2  $a_2$  functions, 4  $b_1$  functions, and 11  $b_2$  functions.

For the  $H_2$  molecule at 1.4 bohrs internuclear separation, the present basis yields a full configuration interaction (CI) energy of -1.171 140 hartrees. This energy lies 2.1 kcal/mole above the corresponding exact  $H_2$  energy,<sup>14</sup> -1.174 475 hartrees. For  $H_2^+$  at  $R = 1.4$ , the calculated and exact energies are -0.569 245 and -0.569 984 hartrees, which differ by 0.5 kcal.

All the  $H_3^+$  calculations reported in the present work are full or complete (within the chosen basis) CI calculations. For  $C_{2v}$  geometries the full CI includes 215 configurations, making the computations rather straightforward. Concerning the accuracy of the  $H_3^+$  surfaces, we concur with Csizmadia et al.<sup>13</sup> in the opinion that the absolute error will be somewhat greater for  $H^+$

0 0 0 0 9 0 4 2 1

infinitely separated from  $H_2$  than for the  $H_3^+$  complex. More concretely, 3 kcal/mole appears to be a reasonable upper limit to the absolute error in the two calculated potential energy surfaces. Relative errors, of course, may be much smaller.

#### POTENTIAL ENERGY SURFACES

Only isosceles triangle configurations ( $C_{2v}$  geometries) were considered in the present work. Although the full three-dimensional surface could be obtained, it was not necessary to fulfill the goals of the present study. The coordinate system is seen in Fig. 1, where  $r$  is the separation of the two equivalent H atoms, and  $R$  is the distance between the third H atom and the midpoint of the two equivalent atoms.

As pointed out by Preston and Tully,<sup>10</sup> an easy way to envisage the avoided intersection is to set  $R = \infty$  and then plot the energy of the two states as a function of  $r$ . Two potential energy curves will be obtained in this manner, as can be seen in Fig. 2. The first is that for the ground state of  $H_2$ , and the second that for  $H_2^+$ . However, the  $H_2^+$  curve is uniformly lowered by 0.5 hartree due to the presence of an H atom at infinite separation. The crossing of the two potential curves only occurs if  $R = \infty$ . For finite values of  $R$ , the curves will avoid each other. The family of curves arising from all possible  $R$  values generates a two-dimensional potential energy surface.

The first series of calculations was carried out for  $R = 2, 4, 6, 8,$  and 100 and  $r = 1.0$  through 4.0 in 0.2 bohr intervals. In addition  $r = 2.5$  was included. These 85 points give us a broad picture of the two surfaces. In the interest of journal space, these 170 energies are not reproduced here, but may be obtained from the authors.

0 0 0 0 6 0 0 0 0

For  $R = 100, 8, 6, 4,$  and  $2$  bohrs, the potential curves  $E(r)$  are shown in Figs. 2, 3, 4, 5, and 6. At  $R = 100$ , it is clear that the curves very nearly cross each other. Specifically the avoided crossing occurs at  $r = 2.456$  bohrs and the separation  $\Delta E_0$  is  $0.00002$  hartrees. This predicted avoided crossing point may be compared with the true crossing point for  $R = \infty$ , which we find to be  $\sim 2.50$  bohrs from the interpolated "exact" potential curves<sup>14,15</sup> for  $H_2$  and  $H_2^+$ . For  $R = 8$ , the avoided crossing is quite sharp also, but at  $R = 6$  the separation  $\Delta E_0$  becomes substantial,  $0.0264$  hartrees =  $16.6$  kcal. At  $R = 4$ , it is no longer clear that the two curves avoid each other. Finally, for  $R = 2$ , the upper curve no longer has a minimum, and thus bears no simple relation to the  $H_2$  and/or  $H_2^+$  potential energy curves.

We have plotted the same potential curves of  $H_3^+$  for the diatomics-in-molecules (DIM) surfaces of Preston and Tully. For  $R = 8$  and  $R = 6$  their curves are very similar to Figs. 3 and 4, the only noticeable difference at  $R = 8$  being that the lower curve is slightly ( $\sim 3$  kcal) deeper than ours. This is expected since the DIM surface should be quite accurate for large  $R$ , and we know that the ab initio calculations yield an  $H_2$  energy  $2.1$  kcal above the exact result. At  $R = 4$ , more noticeable deviations between the semi-empirical and ab initio results begin to appear. The DIM lower curve now lies  $\sim 5$  kcal below the ab initio curve near the bottom of the potential well. The upper  $^1A_1$  state results show the DIM curve  $\sim 3$  kcal below the ab initio curve at  $R = 1.8$ , but  $1$  kcal higher at  $R = 3.4$ .

Only for  $R = 2$  is there a qualitative difference between the DIM and ab initio potential curves. This is not really surprising since for these geometries the identities of the diatomic molecules become blurred, and one



must contend with an  $H_3^+$  molecule. Although the DIM potential curve for the second  $^1A_1$  state remains attractive, the ab initio curve, seen in Fig. 6, takes on an interesting repulsive shape. The two ground state curves remain similar in shape, but the DIM curve is  $\sim 20$  kcal deeper. Since the ab initio surfaces are estimated to have an absolute error of no more than 3 kcal, the DIM curve seems to be seriously in error.

As we shall see in the following section, there is virtually zero probability of surface hopping at  $R = 2$ . Thus, the DIM surfaces are qualitatively correct in the region of the avoided intersection. However, classical trajectories will sample the  $R = 2$  region, and detailed studies would be necessary to determine whether the deficiencies of the DIM surfaces affect the dynamics of the  $H^+ + H_2$  and  $H + H_2^+$  reactions.

Figures 7 and 8 give contour maps of the two lowest  $^1A_1$  potential energy surfaces of  $H_3^+$ . The ground state surface pertains to the adiabatic approach of  $H^+$  to  $H_2$ , while the excited surface refers to  $H + H_2^+$ . The surprising feature of the two contour maps is that the presence of the avoided intersection is not apparent. Thus, it is clear that the surface cuts of Figs. 2-6 give a more useful picture of the avoided intersection. The lowest  $^1A_1$  surface is very attractive, as  $H_3^+$  is bound by  $\sim 106$  kcal/mole<sup>13</sup> relative to  $H^+ + H_2$ . Our calculations do not include the equilibrium  $H_3^+$  geometry ( $R \sim 1.44$  bohrs,  $r \sim 1.66$  bohrs<sup>13</sup>), since it occurs in a region far from the avoided intersection. The first excited  $^1A_1$  surface is very different, its repulsive nature reflecting the relatively unfavorable interaction between H and  $H_2^+$ .

A more qualitative view of the two surfaces is given by the perspective plots of Figs. 9 and 10. The primary virtue of these graphical displays is

that they do indicate the presence of the avoided intersection. Although the area shown only goes to  $R = 10$ , it is clear that the avoided intersection will become more sharply avoided for larger  $R$ ; of course the surfaces will cross at  $R = \infty$ .

#### PARAMETERS DESCRIBING THE AVOIDED INTERSECTION

In the one-dimensional Landau-Zener-Stueckelberg (LZS) formulation,<sup>5-7</sup> the probability of potential curve hopping is given by

$$P = \exp \left[ - \frac{2\pi H_{12}^2}{\hbar v |\Delta H'_0|} \right] \quad (1)$$

where  $v$  is the relative velocity of the two particles.

The LZS approximation is formulated in terms of diabatic<sup>16</sup> potential curves, which do not interact and therefore must cross each other. The interaction term  $H_{12}$  is just

$$H_{12} = \langle \psi_1 | H | \psi_2 \rangle_{r=r_0} \quad (2)$$

and  $|\Delta H'_0|$  is the difference in slopes of the two diabatic curves

$$\Delta H'_0 = \frac{\partial}{\partial r} [\langle \psi_2 | H | \psi_2 \rangle - \langle \psi_1 | H | \psi_1 \rangle]_{r=r_0} \quad (3)$$

Since adiabatic potential surfaces result from our ab initio calculations, we transform the LZS expression to an adiabatic framework using the two-state approximation

$$H_{12} \cong \frac{1}{2} \Delta E_0 \quad (4)$$

The adiabatic energy difference, a function of  $r$ , is

$$\Delta E(r) = \sqrt{(\Delta H)^2 + 4 H_{12}^2} \quad (5)$$

Assuming  $H_{12}(r)$  is constant, this difference may be expanded in a truncated Taylor series about  $r_0$ , the point of avoided crossing

$$\Delta E(r) \cong \sqrt{\Delta H'_0 (r - r_0)^2 + \Delta E_0^2} \quad (6)$$

Assuming the above relation is exact, one obtains

$$|\Delta H'_0| = \frac{\sqrt{\Delta E(r)^2 - \Delta E_0^2}}{|r - r_0|} \quad (7)$$

Since  $\Delta H'_0$  is a constant in the LZS approximation, the deviation of (7) from constancy will provide a measure of the consistency of the LZS approximation.

An alternative expression for  $|\Delta H'_0|$  may be obtained by twice differentiating Eq. (6) with respect to  $r$

$$|\Delta H'_0| = \sqrt{\Delta E''_0 \Delta E_0} \quad (8)$$

The hopping probability  $P$  in terms of adiabatic curves is obtained by substituting Eqs. (4) and (8) into (1)

$$P = \exp \left[ - \sqrt{\frac{E_c}{E}} \right] \quad (9)$$

In Eq. (9),  $E$  is the collision energy and  $E_c$  is a "critical" energy

$$E_c = \frac{\pi^2}{8} \frac{\mu}{\hbar^2} \frac{\Delta E_o^3}{\Delta E_o''} \quad (10)$$

$E_c$  is the energy  $E$  at which the probability  $P$  of hopping is  $e^{-1} = 0.37$ .

For a specified value of  $R$  (the distance between the third proton and the center of mass of the two equivalent protons), the present ( $H^+ + H_2, H + H_2^+$ ) problem becomes one-dimensional. The accuracy of the LZS parameters for this series of one-dimensional problems should give a clear picture of the suitability of any pair of potential surfaces for the description of the surface hopping phenomena. To calculate these parameters, it was necessary to carry out an additional series of computations for geometries close to the avoided intersection. For each value of  $R$  considered, the value (to within an integer multiple of 0.01 bohr) of  $r$  for which  $\Delta E$  is a minimum was determined. Finally, calculations were performed for this  $r$  value  $\pm 0.01$ , and  $\pm 0.02$  bohr. One feature of the surfaces that should be stated immediately is that the avoided intersection "disappears" between  $R = 4.0$  and  $R = 5.0$  bohrs. That is, for  $R = 4.0$ ,  $\Delta E(r)$  does not pass through a minimum, but rather decreases monotonically from  $r = 1.0$  to  $r = 4.0$ .

Table II compares the values of the diabatic quantity  $|\Delta H'_o|$  obtained using Eqs. (7) and (8). In the limit of  $r = r_o$  it is clear that the value obtained using Eq. (7) must equal that found from Eq. (8). However, the values calculated for neighboring  $r$  are also in reasonable agreement with  $\sqrt{\Delta E_o'' \Delta E_o}$ . For  $R = 5, 6, 7,$  and  $8$ , the largest deviations are 5.3%, 1.8%, 4.0%, and 2.6%. Thus, it appears that near the avoided crossing, the LZS assumptions of a) linearity of  $\Delta H$  in  $(r - r_o)$  and b) constancy of  $H_{12}$  are reasonably valid.

The LZS parameters of interest are summarized in Table III and compared with the diatomics-in-molecules results of Preston and Tully.<sup>10</sup> The distance of closest approach is remarkably constant as a function of  $R$  in the ab initio calculations. The  $r_0$  values range from 2.469 to 2.478, a span of only 0.009 bohrs. The DIM results for  $r_0$  increase monotonically from 2.349 ( $R = 5.0$ ) to 2.498 ( $R = 8.0$ ), a span of 0.149 bohrs. At  $R = 5.0$ , we expect the ab initio results to be much more reliable. However, at  $R = 8.0$ , it seems clear that at least one of the DIM parameters,  $r_0$ , is more accurate than the ab initio result. This is because the DIM value of  $r_0$  at  $R = 8$  is very close to the exact<sup>14,15</sup> crossing point,  $\sim 2.50$ , for  $R = \infty$ . Since the avoided crossing is quite sharp at  $R = 8.0$ ,  $r_0$  should be essentially determined by the diatomic curves.

As is also clear from Figs. 2-6, the separations  $\Delta E_0$  of Table III increase with decreasing  $R$ . In each case the DIM separation is greater than the ab initio, although the results are qualitatively quite similar. At  $R = 5, 6$ , and  $7$ , the ab initio results are quite likely to be the more reliable, but at  $R = 8$  the situation is less clear. Although the diatomic potential curves guarantee the avoided crossing point  $r_0$  to be accurate for large  $R$ , the separation  $\Delta E_0$  is not related to experimentally known quantities in such a transparent way. The good agreement between the DIM and ab initio values of  $\Delta E_0$  suggests that the DIM surfaces are more accurate than could have reasonably been expected.

The difference  $\Delta E''_0$  in the curvatures of the two curves at the point  $r_0$  of avoided intersection is expected to be rather sensitive to the potential energy surfaces. Except at  $R = 5$ , where DIM may begin to have serious weaknesses,

the ab initio values of  $\Delta E''_0$  are greater than the DIM values. The  $\Delta E''_0$  values are reflected through Eq. (10) in the critical energies  $E_c$  and therefore in the hopping probabilities  $P$ . The critical energies from the ab initio and DIM surfaces are seen to differ significantly, by nearly a factor of four at  $R = 8.0$  and by more than a factor of two at  $R = 7.0$ . However, these differences are noticeably damped out in the calculated hopping probabilities, which are in good qualitative agreement. From both the ab initio and DIM surfaces, the hopping probability is found to fall off very sharply below  $R = 6.0$  bohrs. This result is crucial to the viability of the DIM description of the avoided intersection, since as pointed out earlier, the DIM surfaces begin to have serious errors for  $R < 5.0$ .

#### CONCLUDING REMARKS

Potential surfaces for the two lowest  $^1A_1$  states of  $H_3^+$  have been obtained ab initio to an absolute accuracy of  $\sim 3$  kcal. The surfaces are appropriate to the  $H^+ + H_2$  and  $H + H_2^+$  chemical reactions. Near the avoided intersection, the ab initio surfaces are quite similar to the semi-empirical diatomics-in-molecules surfaces. For closer approaches of  $H^+$  to  $H_2$  or  $H$  to  $H_2^+$ , the semi-empirical surfaces become less accurate.

#### ACKNOWLEDGEMENTS

The work was supported in part by the National Science Foundation, grant GP-31974. We thank Professor William H. Miller and Mr. Peter K. Pearson for helpful discussions.

FOOTNOTES AND REFERENCES

\* Work performed under the auspices of the U. S. Atomic Energy Commission.

† Neshan Zovick Fellow.

†† Alfred P. Sloan Fellow.

‡ M. H. Fellow.

1. G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Princeton, 1950). See especially pages 295-298.
2. E. R. Davidson, J. Chem. Phys. 33, 1577 (1960); 35, 1189 (1961).
3. W. Kolos and L. Wolniewicz, J. Chem. Phys. 50, 3228 (1969).
4. The  $^2\Pi$  states of CN are a particularly interesting case. See H. F. Schaefer and T. G. Heil, J. Chem. Phys. 54, 2573 (1971).
5. L. D. Landau, Physik. Z. Sowjetunion U.R.S.S. 2, 46 (1932).
6. C. Zener, Proc. Roy. Soc. (London) A137, 696 (1932).
7. E. C. G. Stueckelberg, Helv. Phys. Acta 5, 369 (1932).
8. E. E. Nikitin, in Chemische Elementarprozesse, edited by H. Hartmann (Springer, Berlin, 1968).
9. W. H. Miller and T. H. George, J. Chem. Phys. 56, 5637 (1972).
10. R. K. Preston and J. C. Tully, J. Chem. Phys. 54, 4297 (1971); 55, 562 (1971).
11. F. O. Ellison, J. Am. Chem. Soc. 85, 3540, 3544 (1963).
12. F. B. van Duijneveldt, Report RJ 945, IBM Research Laboratory, San Jose, California.
13. I. G. Csizmadia, R. E. Kari, J. C. Polanyi, A. C. Roach, and M. A. Robb, J. Chem. Phys. 52, 6205 (1970).
14. W. Kolos and L. Wolniewicz, J. Chem. Phys. 49, 404 (1968).
15. D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. A246, 215 (1953).
16. F. T. Smith, Phys. Rev. 179, 111 (1969).

Table I. Basis set of gaussian functions centered on each proton.

Type	Gaussian exponent $\alpha$
1s	33.865 014
1s	5.094 788
1s	1.158 786
1s	0.325 840
1s	0.102 741
$2p_x, 2p_y, 2p_z$	2.0
$2p_x, 2p_y, 2p_z$	0.5



Table II. Evaluation of the Landau-Zener-Stuckelberg quantity  $|\Delta H'_0|$  by two methods. Results are in hartrees (1 hartree = 627.5 kcal/mole).

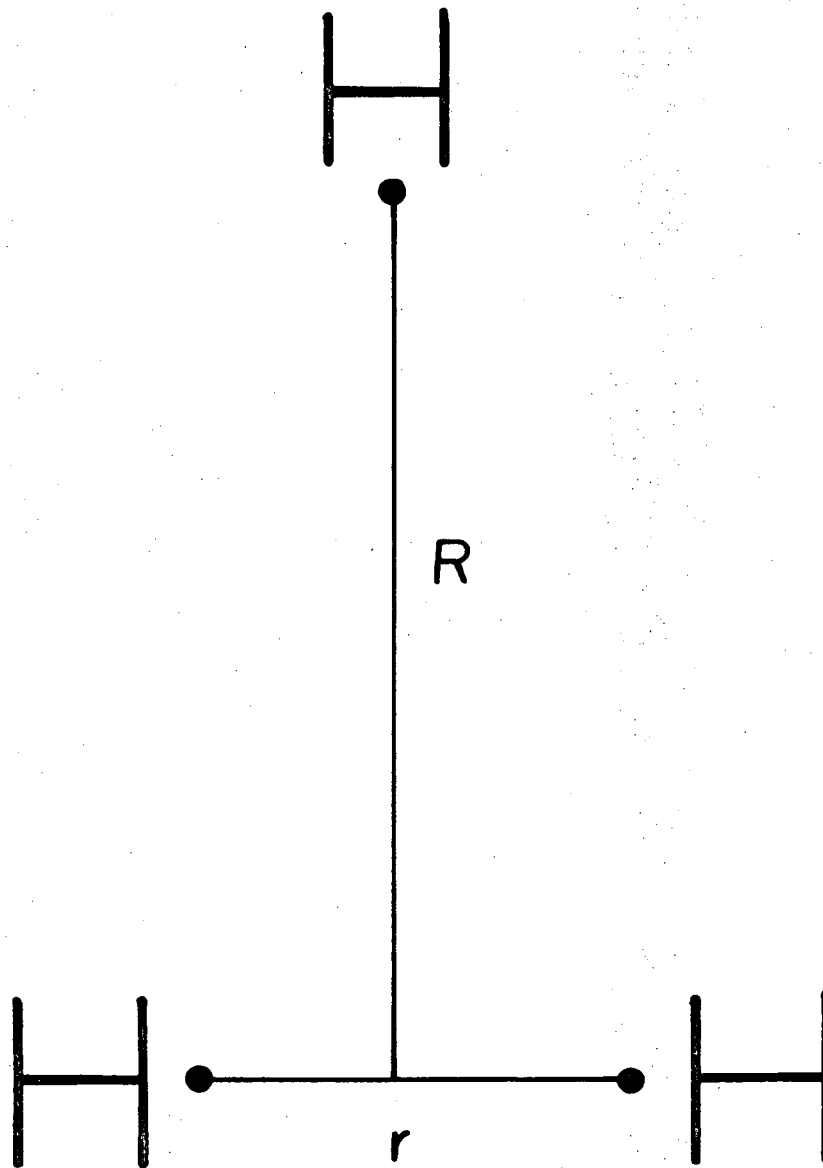
	R = 5.0	R = 6.0	R = 7.0	R = 8.0
Eq. (7)				
r = 2.45	0.05228	0.05 461	0.05 488	0.05 558
r = 2.46	0.05303	0.05 425	0.05 436	0.05 532
r = 2.47	0.05026	0.05 354	0.05 299	0.05 538
r = 2.48	0.04916	0.05 417	0.05 269	0.05 421
r = 2.49	0.04948	0.05 344	0.05 406	0.05 408
r = 2.50	0.05036	0.05 304	0.05 374	0.05 371
Eq. (8)	0.05038	0.05403	0.05277	0.05512

Table III. Ab initio parameters related to the avoided intersection of the  $H^+ + H_2$  and  $H + H_2^+$  potential energy surfaces. 1 hartree = 627.5 kcal. Results obtained from the semi-empirical surfaces of Preston and Tully<sup>10</sup> are given in parentheses.

R(bohrs)	5.0	6.0	7.0	8.0
Distance $r_0$ (bohrs) of closest approach	2.469 (2.349)	2.478 (2.458)	2.477 (2.491)	2.472 (2.498)
Separation $\Delta E_0$ (kcal) at $r_0$	37.08 (39.41)	16.59 (18.13)	7.20 (8.34)	3.01 (3.84)
Curvature $\Delta E''$ (kcal/bohr <sup>2</sup> )	27.0 (37.7)	69.3 (57.0)	152.3 (113.7)	397.1 (236.1)
Slope $\partial E/\partial r$ (kcal/bohrs) at $r_0$	35.17 (34.66)	35.23 (34.67)	35.25 (34.55)	35.28 (34.52)
Critical energy $E_c$ (kcal)	3413.27 (2931.01)	118.83 (188.47)	4.42 (9.20)	0.124 (0.434)
Hopping probability P for $E = 1$ eV = 23.06 kcal	$5.2 \times 10^{-6}$ ( $1.3 \times 10^{-5}$ )	0.1033 (0.0573)	0.6455 (.5317)	0.9292 (.8718)

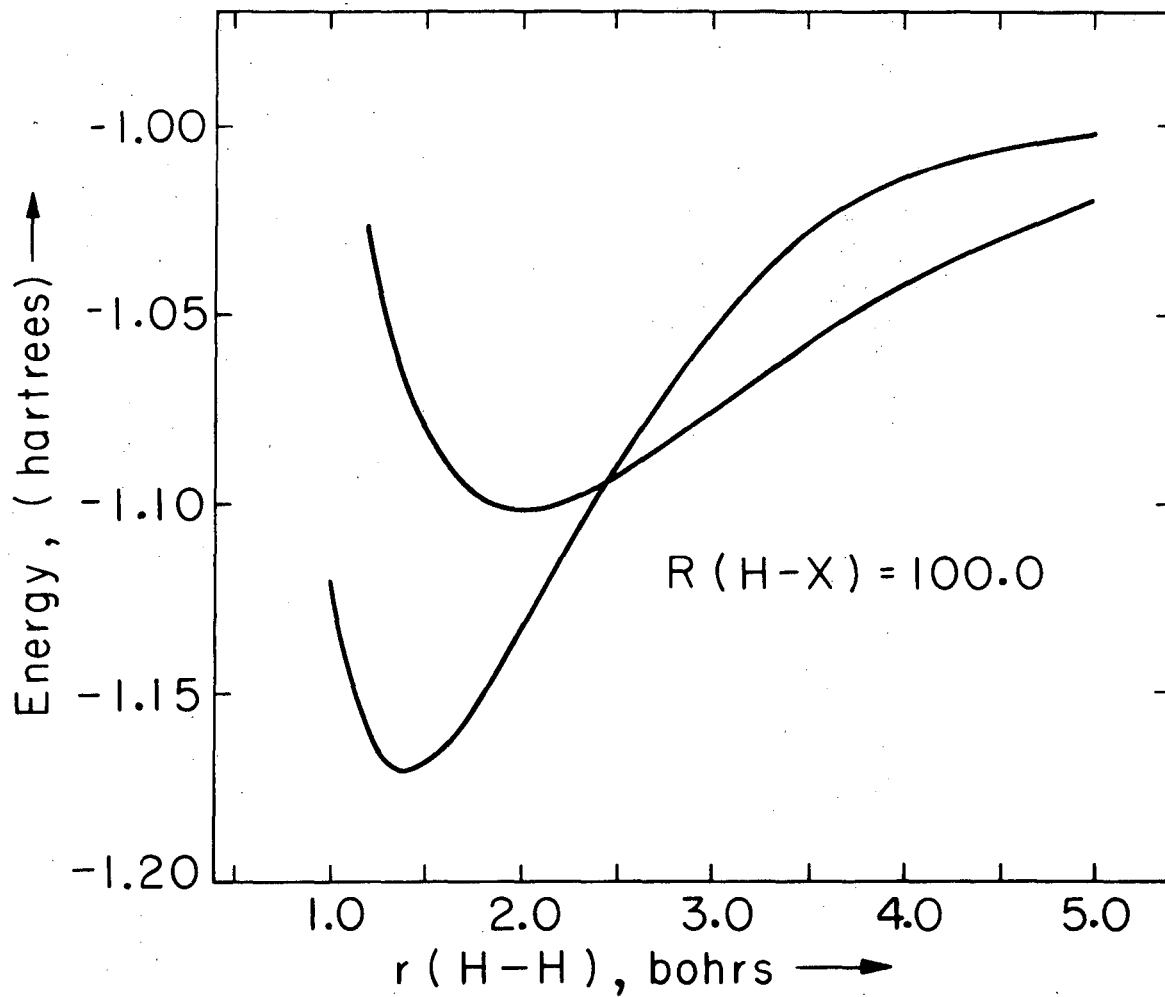
## FIGURE CAPTIONS

- Fig. 1. Coordinate system used to describe that part of the  $H_3^+$  potential surfaces considered in the present work.
- Fig. 2. Potential curves for the lowest two  $^1A_1$  states of  $H_3^+$  for  $R = 100$  bohrs.
- Fig. 3. Potential curves for the lowest two  $^1A_1$  states of  $H_3^+$  for  $R = 8$  bohrs.
- Fig. 4. Potential curves for the lowest two  $^1A_1$  states of  $H_3^+$  for  $R = 6$  bohrs.
- Fig. 5. Potential curves for the lowest two  $^1A_1$  states of  $H_3^+$  for  $R = 4$  bohrs.
- Fig. 6. Potential curves for the lowest two  $^1A_1$  states of  $H_3^+$  for  $R = 2$  bohrs.
- Fig. 7. Contour map of the lowest  $^1A_1$  potential energy surface of  $H_3^+$ .  $r$  is the distance between the two equivalent protons, and  $R$  the distance between the midpoint of the two equivalent protons and the third proton. This surface pertains to the adiabatic approach of  $H^+$  to  $H_2$ .
- Fig. 8. Contour map of the first excited  $^1A_1$  potential surface of  $H_3^+$ . This surface pertains to the adiabatic approach of  $H$  to  $H_2^+$ .
- Fig. 9. Perspective plot of the lowest  $^1A_1$  potential energy surface of  $H_3^+$ .
- Fig. 10. Perspective plot of the first excited  $^1A_1$  potential surface of  $H_3^+$ .



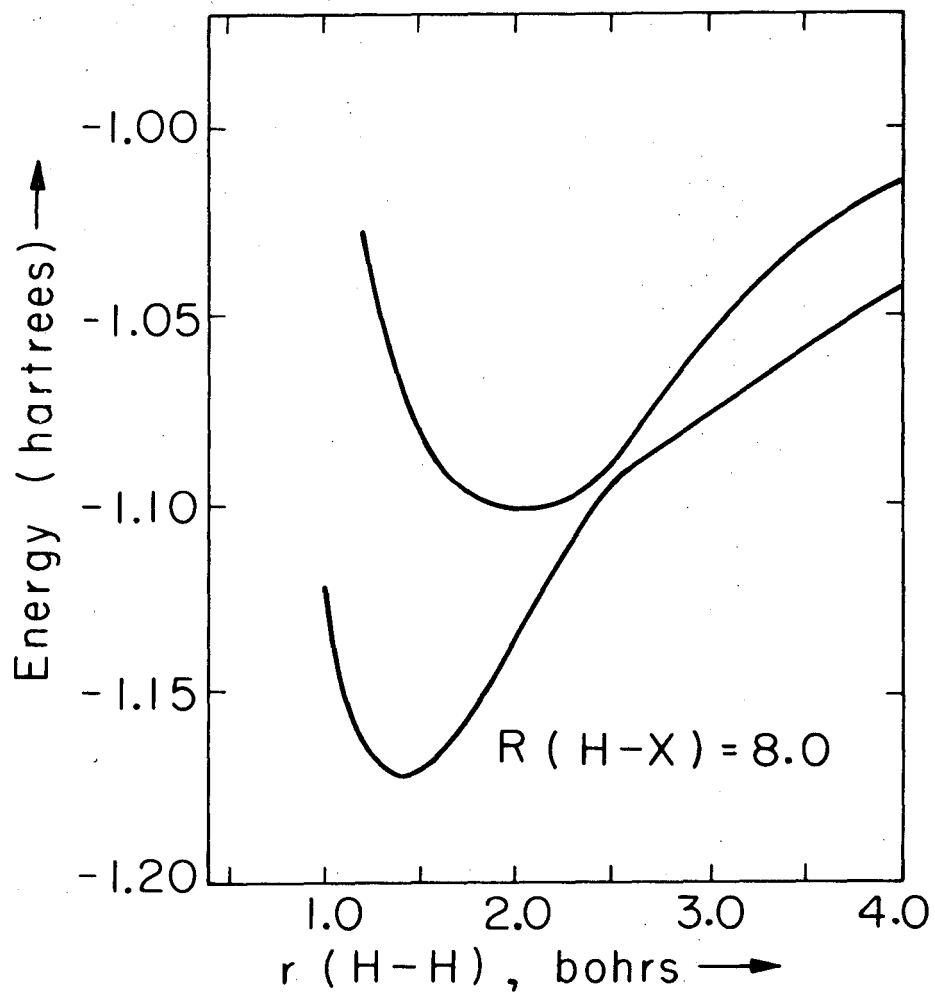
XBL733-2391

Fig. 1



XBL 733-2390

Fig. 2



XBL 733-2389

Fig. 3

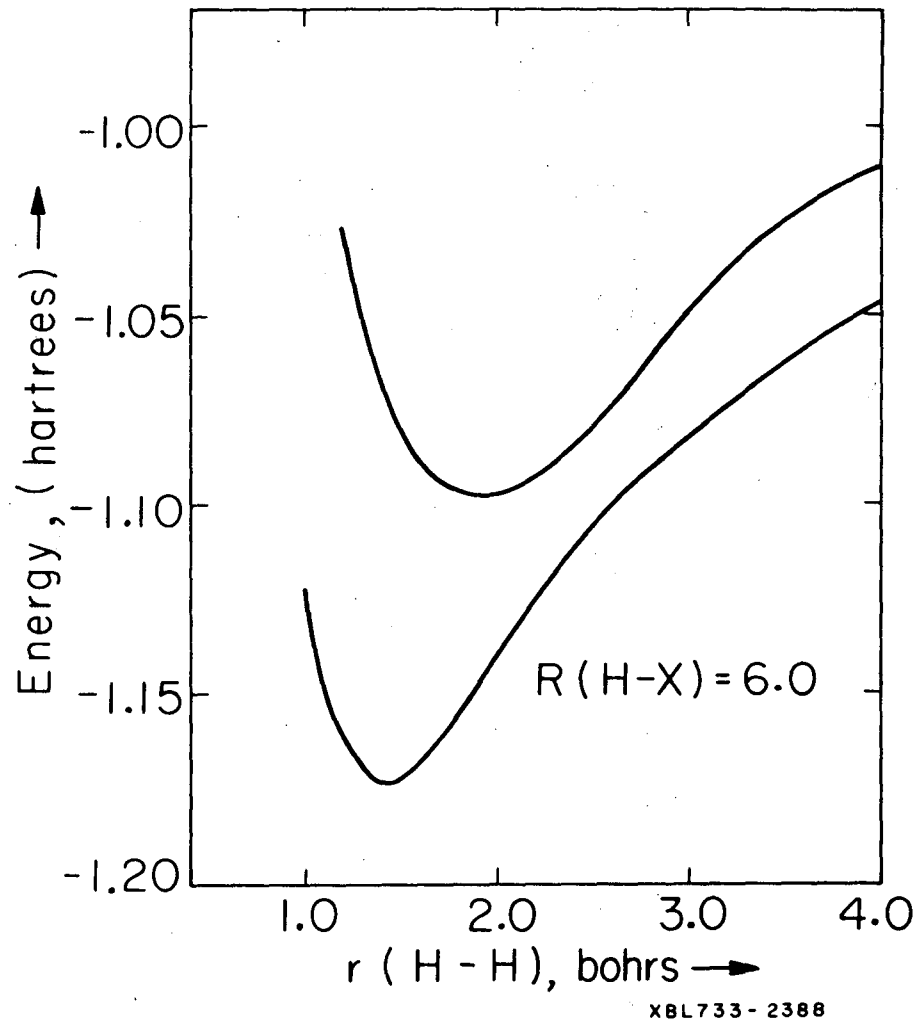


Fig. 4

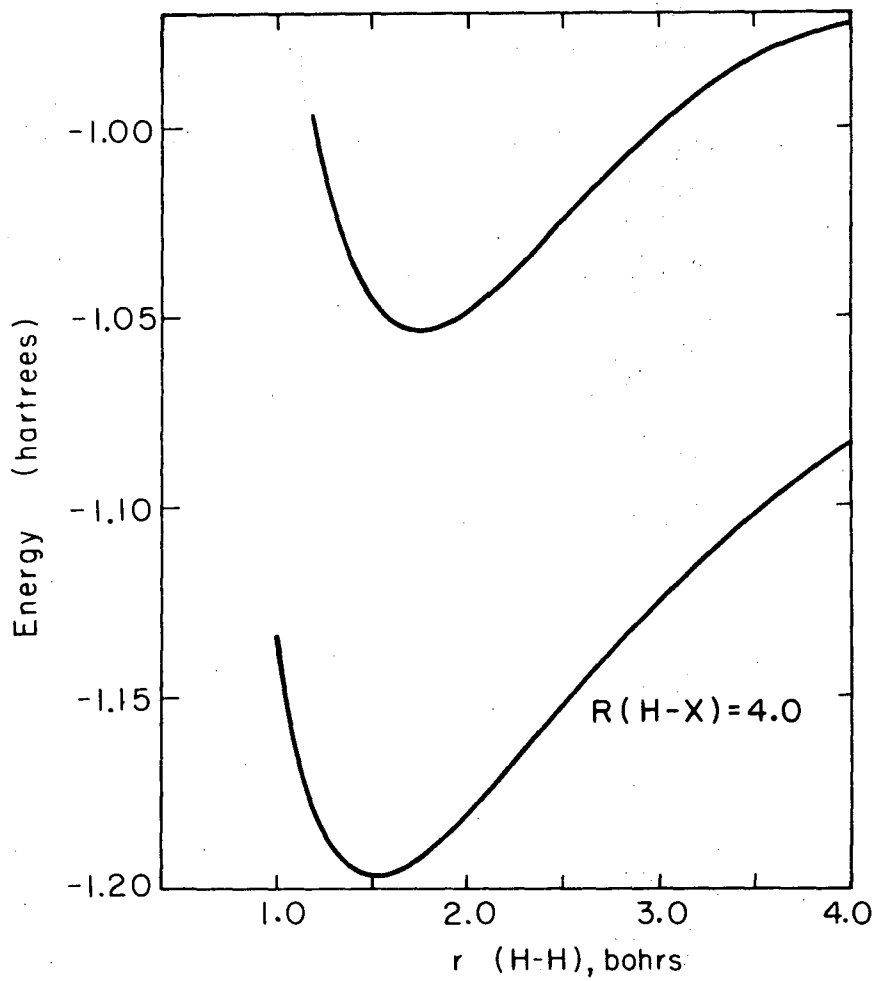
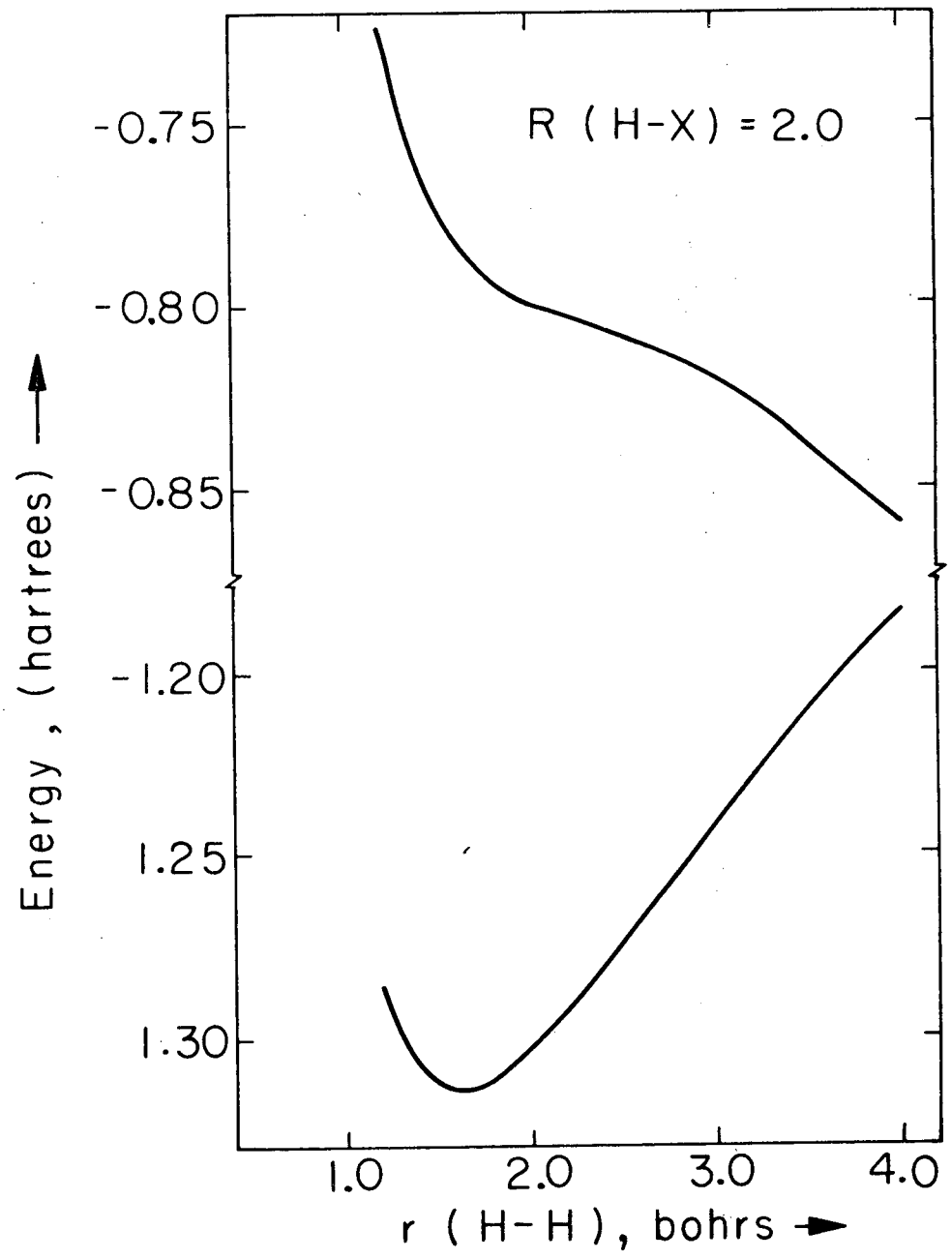


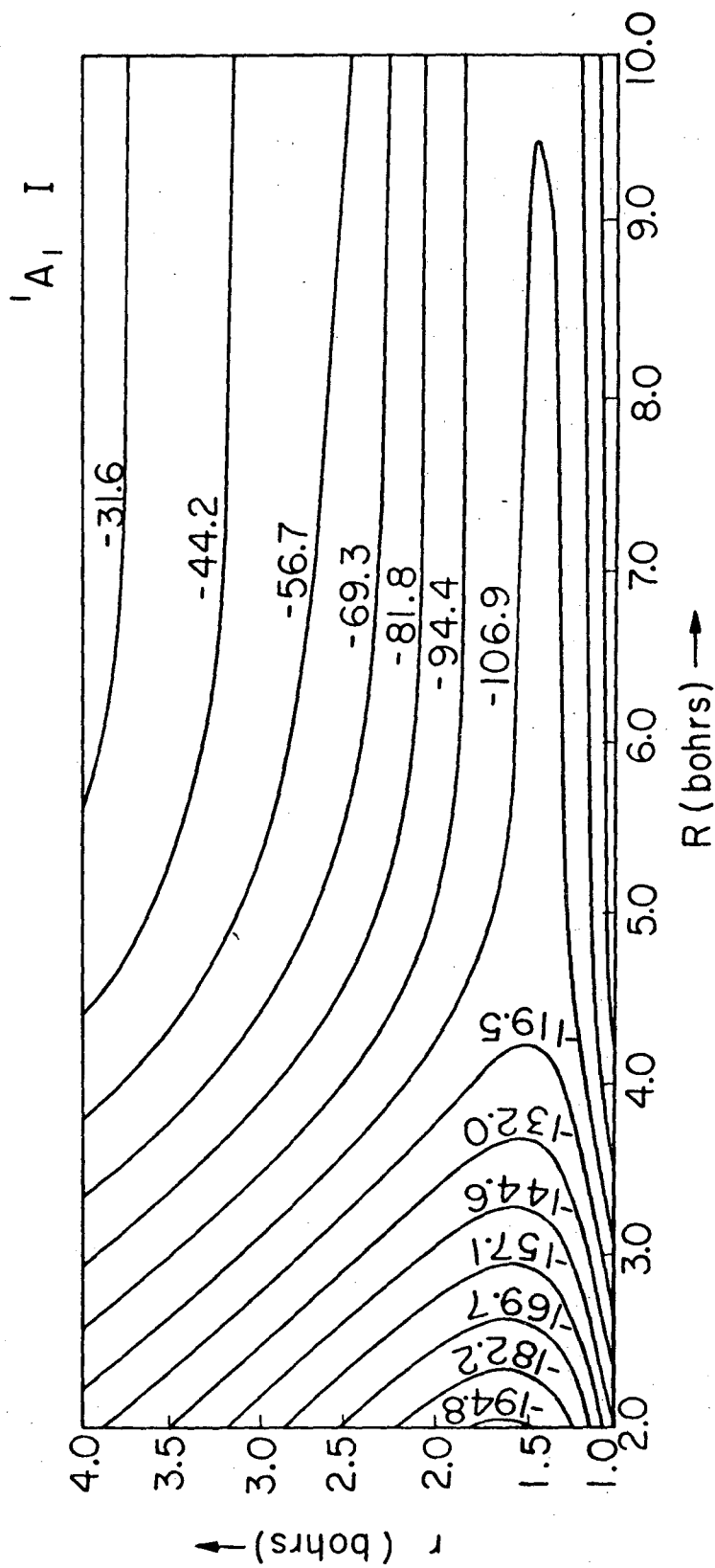
Fig. 5





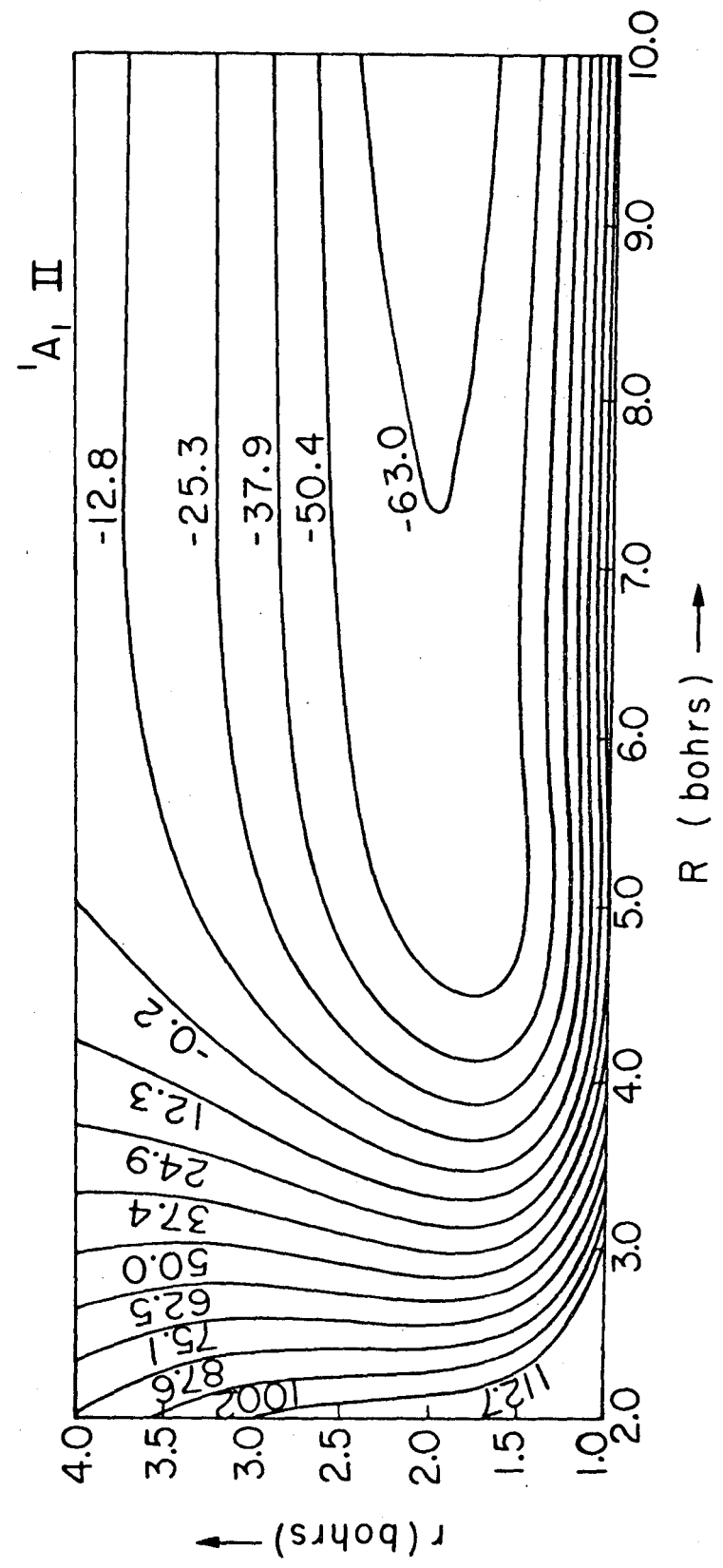
XBL 733-2386

Fig. 6



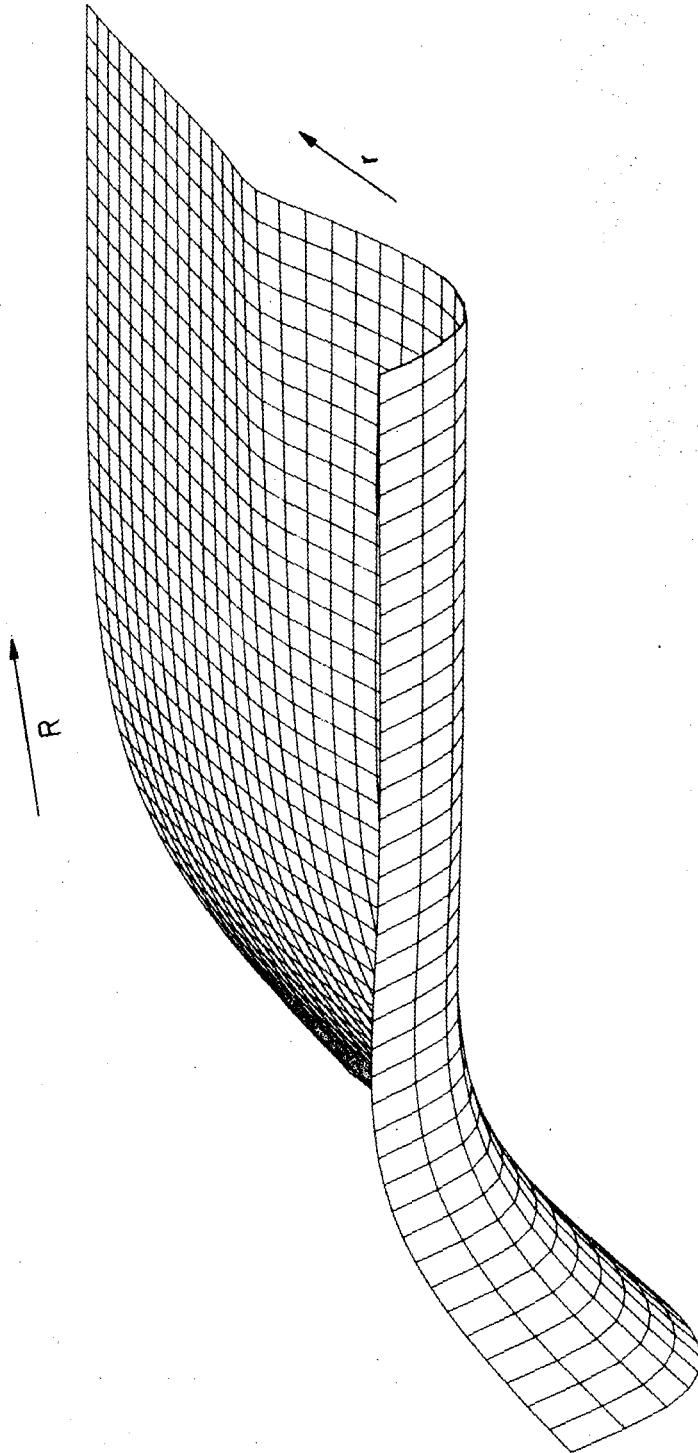
XBL733-2392

Fig. 7



XBL733-2393

Fig. 8



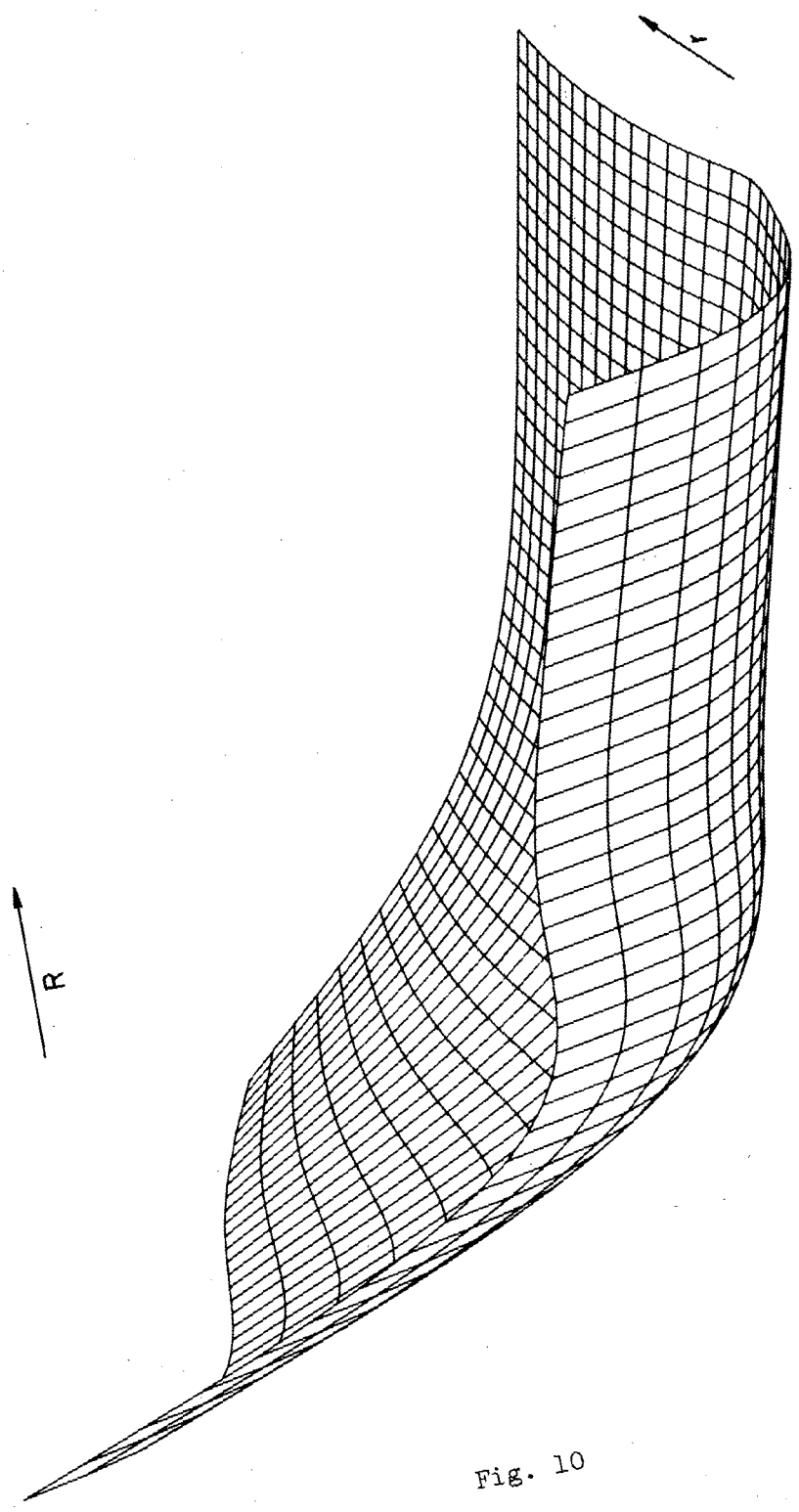
XBL 733-2468

FIG. 9

0 0 0 0 0 0 0 0 0 0 3 2

LBL-1664

-25-



XBL 733-2469

Fig. 10

LEGAL NOTICE

*This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.*

TECHNICAL INFORMATION DIVISION  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720