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Henry F. Schaefer III, and Charles F. Bender

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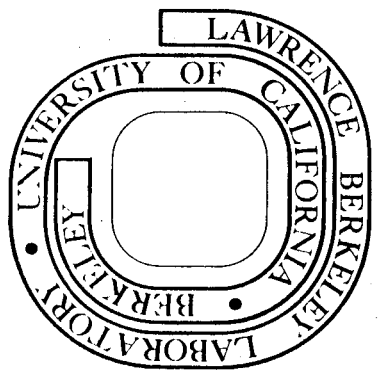
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Concerted Non-Least-Motion Pathway for the
Singlet Methylene Insertion Reaction $\text{CH}_2(^1\text{A}_1) + \text{H}_2 \rightarrow \text{CH}_4$

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and

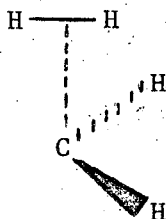
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Abstract

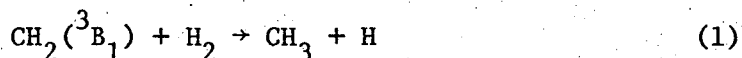
The least motion insertion reaction of singlet methylene into molecular hydrogen is forbidden in the sense of Woodward and Hoffman, and has been predicted to involve a barrier height of ~ 27 kcal/mole. Here ab initio electronic structure theory has been applied to the non-least-motion features of the same potential energy surface. A double zeta basis set of contracted gaussian functions was used in conjunction with moderately large (2120 configurations) configuration interaction (CI) techniques. For an initial C_s point group approach of the qualitative type



theory predicts no barrier or activation energy at all. This result is illustrated with the aid of contour maps showing several cuts through the potential energy hypersurface. It is also noted that the single determinant self-consistent-field (SCF) method does not properly describe several of the main features of this concerted non-least-motion pathway.

Introduction

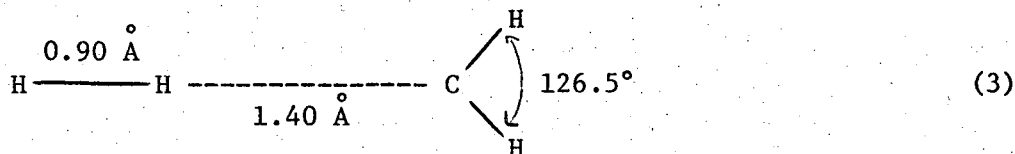
The simplest system allowing the possibility of both carbene triplet abstraction



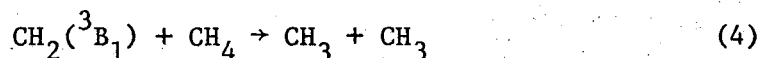
and singlet insertion



reactions is the $\text{CH}_2 + \text{H}_2$ system.^{1,2} In the anticipation³ that $\text{CH}_2 + \text{H}_2$ would serve as a prototype for the reactions of methylene with saturated hydrocarbons, we have made detailed theoretical studies^{4,5} of reactions (1) and (2). The triplet insertion reaction is predicted⁴ to have the transition state structure

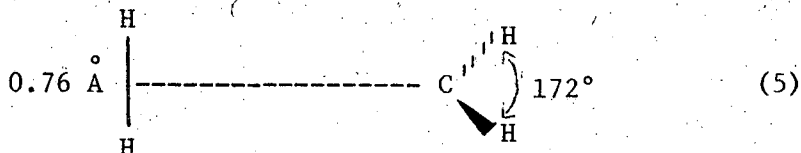


and a sizeable barrier height, 10-15 kcal/mole. The validity of $\text{CH}_2 + \text{H}_2$ as a prototype has been qualitatively verified⁶ for the reaction

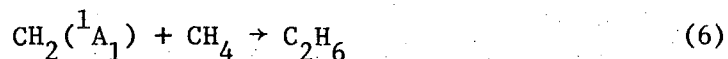


which is predicted to have a transition state analogous to (3) and a barrier height of ~ 20 kcal. For the singlet insertion reaction (2) only the least motion pathway has been considered to date⁵ and this approach is Woodward-Hoffmann forbidden.⁷ As a result a large barrier (~ 27 kcal) was predicted, corresponding to the constrained transition state

-3-



Since it seems well-established^{1,2} experimentally that at least one of the electronic states of methylene reacts with molecular hydrogen with little or no activation energy, further theoretical work is called for. Actually, the direction seems rather apparent from previous semi-empirical studies.^{8,9} For the



insertion reaction the groups of Hoffmann and Dewar concur (for the most part) that non-least-motion approaches provide reaction pathways with little or no activation energy. A more recent and more directly relevant semi-empirical study is Kollmar's modified CNDO treatment¹⁰ of reaction (2). Allowing consideration of four degrees of freedom, Kollmar predicted a transition state involving small valence angles and a three-center bond, with the activation energy for insertion predicted to be ~ 5 kcal/mole.

Kollmar's potential surface has taken on special significance since its use by Wang and Karplus¹¹ in one of the first classical trajectory studies¹² of the dynamics of an organic reaction. However there is at least one reason to question the quantitative accuracy of the Kollmar surface--namely that it predicts a least motion barrier height of 13 kcal, compared to the more reliable ab initio result⁵ of 27 kcal. In light of the role of reaction (2) as the prototype singlet carbene

insertion reaction, it was decided to complete our studies³⁻⁶ of the $\text{CH}_2 + \text{H}_2$ system by considering the non-least-motion portion of the $\text{CH}_2(^1\text{A}_1) + \text{H}_2$ hypersurface.

Scope of a Theoretical Study

Following the spirit of Kollmar's research,¹⁰ we adopted the coordinate system depicted in Figure 1. Our geometrical parameters R , r , β , and θ are closely related to the four degrees of freedom investigated by Kollmar. Our fifth parameter α was constrained by Kollmar to be such that R and r are perpendicular to each other, i.e., $\alpha = 90^\circ - \beta$. Four of the (α, β) values studied most carefully are shown explicitly in Figures 2-5. The $\alpha = 0^\circ$, $\beta = 75^\circ$ combination was also investigated in some detail. Configuration interaction (CI) studies were performed on a total of about 600 points on the five-dimensional potential surface. As will be noted, additional self-consistent-field (SCF) studies were carried out to determine the validity of this much simpler theoretical approach.

In the notation of Figure 1, our previous study⁵ of the least motion pathway corresponds to fixing α and β at the $(90^\circ, 0^\circ)$ combination. For that C_{2v} geometry separated $CH_2(^1A_1) + H_2$ is described in the Hartree-Fock or SCF approximation by the single electron configuration

$$1a_1^2 \ 2a_1^2 \ 1b_2^2 \ 3a_1^2 \ 4a_1^2 \quad (7)$$

while CH_4 (after resolution¹³ of the T_d orbitals into those of point group C_{2v}) is written as

$$1a_1^2 \ 2a_1^2 \ 1b_2^2 \ 3a_1^2 \ 1b_1^2 \quad (8)$$

The fact that electron configurations (7) and (8) differ by one

doubly-occupied orbital is another way of saying that the $(90^\circ, 0^\circ)$ or least motion approach is Woodward-Hoffmann forbidden.⁷

However for the C_s (only a single plane of symmetry, the plane of the page containing Figure 1) geometries considered here, the a_1 and b_1 orbitals become a' and the b_2 orbital becomes a'' . Thus both (7) and (8) under resolution into C_s symmetry become

$$1a'^2 \quad 2a'^2 \quad 1a''^2 \quad 3a'^2 \quad 4a'^2 \quad (9)$$

with the implication that single-configuration Hartree-Fock theory is at least in principle capable of describing the non-least motion reaction. Of course one must remember that the $4a'$ orbital must be allowed (via the SCF procedure) to gradually transform from the $3a_1$ lone pair orbital of singlet methylene to the $1b_1$ component of the triply-degenerate methane $1t_2$ orbital as the reaction proceeds. From a qualitative viewpoint, the ability of the $4a'$ orbital to smoothly perform this change of character will determine the magnitude of the insertion reaction activation energy.

The present CI treatment begins with a two-configuration SCF description¹⁴ involving (9) plus

$$1a'^2 \quad 2a'^2 \quad 3a'^2 \quad 4a'^2 \quad 5a'^2 \quad (10)$$

Then all $^1A'$ configurations arising from orbital occupancies differing by one or two electrons from either (9) or (10) were added to yield a total of 2120 configurations. The latter number is obtained with the standard Huzinaga-Dunning gaussian double zeta basis¹⁵ used in our previous studies.^{4,5,14} As before our goal was to recover 95% or more

-7-

of the valence shell correlation energy obtainable with this type of basis. A nearly optimum set of molecular orbitals was guaranteed by use of the iterative natural orbital method.¹⁶ As discussed previously⁵ this theoretical procedure gives a good description of the singlet CH₂ and H₂ structures and the reaction exothermicity.

Results and Discussion

All four initial approaches sketched in Figures 2-5 are significantly less repulsive than the least motion pathway (LMP) reported previously.⁵ This is shown clearly in Figure 6, which gives potential energy curves for the case $r(\text{H-H}) = 1.4$ bohrs and $\theta(\text{HCH}) = 105^\circ$. There the LMP, corresponding to $(\alpha, \beta) = (90^\circ, 0^\circ)$, is compared to the four new approaches and in addition to the $(0^\circ, 75^\circ)$ curve.

Most similar to the LMP is the $(0^\circ, 45^\circ)$ approach (see Figure 2), which is nearly as repulsive. In the range of R values plotted the other four curves all begin to "turn over", i.e., to feel the attraction inevitable as the deep CH_4 potential well appears. Given the constraints of these curves (α , β , r , and θ fixed) barriers of a certain type are apparent in Figure 6. For the $(45^\circ, 45^\circ)$ approach this "barrier" is ~ 17 kcal. We were slightly surprised to find that the analogous barrier for the $(90^\circ, 45^\circ)$ case is significantly less (~ 12 kcal), since the two approaches are in roughly comparable relationships to the highly repulsive LMP. For the $(0^\circ, 75^\circ)$ case there is only a small constrained barrier, ~ 4 kcal, and for the $(0^\circ, 90^\circ)$ approach the barrier disappears entirely. In addition to the data illustrated in Figure 6, analogous computations were carried out for 95° and 115° . These results are essentially similar to those of Figure 6, although the larger θ value (115°) yields slightly lower energies as R is decreased to 3 bohrs. Thus it would appear that although the surface is attractive for the initial $(0^\circ, 90^\circ)$ approach, only (α, β) values quite close to $(0^\circ, 90^\circ)$ allow this pure attraction. This observation should have important dynamic consequences^{11,12} and it would certainly be of interest to see a classical trajectory study of

$\text{CH}_2(^1\text{A}_1) + \text{H}_2$ using the surface features predicted here. In this regard it is encouraging to note that Kollmar's semi-empirical surface also favors β values close to 90° for the initial approach. However it appears that the present surface favors a somewhat narrower range (about $\beta = 90^\circ$) of β values than does the modified CNDO surface. Nevertheless the essential agreement speaks highly of the Kollmar surface. The narrow range of initially attractive β values should be understood in the light of our surface restriction to five degrees of freedom. In particular it seems likely that bringing the H_2 molecule out of the plane of Figure 4 would not raise the energy significantly. Other degrees of freedom (there are a total of $3n - 6 = 9$) may very well allow the initially attractive multidimensional "opening" to be considerably wider than might be imagined solely on the basis of Figure 6.

Another critical feature of the surface is its shape after the initially attractive ($0^\circ, 90^\circ$) approach. In particular, does one encounter a barrier a bit further along the way? Clearly to reach methane from the ($0^\circ, 90^\circ$) approach we must decrease R (from ∞ to 0.63 \AA), increase r (from 0.74 \AA to 1.78 \AA), and decrease β from 90° to 0° . Figure 7 (obtained via two-dimensional spline fits for regularly spaced grids of points) gives the R and θ dependence of the hypersurface for r fixed at 1.4, 1.7, and 1.9 bohrs. This figure shows clearly that the most favorable value of r increases steadily as R decreases. In addition there is an initial tendency for θ to increase as the reactants approach each other in the ($0^\circ, 90^\circ$) manner. The latter tendency is also apparent in Kollmar's work.

Figure 7 makes it quite plain that the $\text{CH}_2(^1\text{A}_1) + \text{H}_2$ surface has no barrier height for the reaction to produce methane. The $r = 1.9$ cut shows that the surface has become attractive by 31 kcal at $R = 2.0$ bohrs. The existence of a barrier at smaller R values is completely unreasonable. Actually at $R = 2.0$ the surface is considerably more attractive, since the $(0^\circ, 90^\circ)$ approach is no longer the most favorable one. The lack of any barrier appears to be one of the most important qualitative differences between the ab initio surface and that of Kollmar.

For the $(0^\circ, 90^\circ)$ approach it is also possible to construct a minimum energy path by performing a three-dimensional spline fit¹⁷ to the surface and following the gradient in the direction of steepest descent.^{3,5} Table I gives the result of carrying out this procedure, and it is seen that the three parameters change rather smoothly, in a manner consistent with a concerted pathway. Again we emphasize that the path of Table I is a constrained minimum energy path. For the smaller R values, the optimum values of α and β are not 0° and 90° . For example, at $R = 2.50$, the $(15^\circ, 75^\circ)$ point with $r = 1.8$ bohr and $\theta = 115^\circ$ has a total energy of -40.1297 hartrees, or 21.7 kcal below the $\text{CH}_2 + \text{H}_2$ result of -40.0951 . This result is 6.1 kcal lower than the optimum $(0^\circ, 90^\circ)$ energy reported in Table I. An even lower energy (-22.3 kcal) is obtained for the same r and θ values and the $(45^\circ, 45^\circ)$ approach. Before leaving Table I, it is well to note that the grid used is considerably more sparse than those used in constructing our previous pathways.^{3,5} However, the general trends (if not the precise values of any single entry) should be correct to $\pm 0.5^\circ$, ± 0.5 kcal, and ± 0.05 bohrs. In light of the sparsity

-11-

of our grid we have not bothered to construct a coordinate independent path.^{3,5}

From the tabulated list of ~ 600 points (available upon request from CWB), one can estimate the point at which the $(15^\circ, 75^\circ)$ approach becomes more favorable than the initial $(0^\circ, 90^\circ)$ approach. From the previous paragraph we know that this occurs for $R > 2.5$ bohrs. At $R = 2.75$, $r = 1.6$ bohrs, and $\theta = 115^\circ$ the $(15^\circ, 75^\circ)$ and $(0^\circ, 90^\circ)$ points are attractive by 10.5 and 9.1 kcal. At $R = 3.00$, $r = 1.5$, and $\theta = 115^\circ$ the analogous two results are -3.7 and -4.6 kcal. Thus it appears that the crossover from $(0^\circ, 90^\circ)$ to $(15^\circ, 75^\circ)$ as the optimum orientation of approach occurs at about $R = 2.9$ bohrs. A comparable analysis suggests that the $(45^\circ, 45^\circ)$ approach becomes more favorable than $(15^\circ, 75^\circ)$ at $R \sim 2.55$ bohrs. Presumably an intermediate approach, say $(30^\circ, 60^\circ)$, would be optimum in the range $R = 2.7 - 2.8$. Although these conclusions are very qualitative, they should be helpful in visualizing the shape of the $\text{CH}_2(^1\text{A}_1) + \text{H}_2$ hypersurface.

A final topic worthy of discussion is the degree to which the single-configuration SCF approximation reproduces the more reliable CI results. We have noted previously⁵ that for the least motion $(90^\circ, 0^\circ)$ approach, CI lowers the SCF barrier by ~ 30 kcal. For a direct comparison of several non-least motion approaches, in Figure 8 are illustrated computations completely analogous to Figure 6, except at the SCF level of theory. Our general conclusion is that the SCF calculations are not only quantitatively but as well qualitatively different from the CI results. This is most apparent for the $(0^\circ, 90^\circ)$ approach, which shows no sizeable

well at all for $r = 1.4$ bohrs. In contrast the CI predictions of Figure 6 suggest a considerable well. It can also be noted that SCF calculations for $R < 2.5$ bohrs show a continuing repulsive potential curve. The $(0^\circ, 75^\circ)$ curve of Figure 10 is in much better agreement with the CI results but again too repulsive, a barrier of 6 kcal being evident. Another major discrepancy occurs for the $(90^\circ, 45^\circ)$ curve, which "turns over" (i.e., begins to become attractive) at $R \sim 3.5$ in the CI treatment, but only at ~ 2.5 from the SCF curve of Figure 8. The three most repulsive curves, the $(45^\circ, 45^\circ)$, $(0^\circ, 45^\circ)$, and $(90^\circ, 0^\circ)$ have the same general shape in both SCF and CI descriptions.

Concluding Remarks

The non-least-motion hypersurface for the $\text{CH}_2(^1\text{A}_1) + \text{H}_2 \rightarrow \text{CH}_2$ insertion reaction has been studied in detail. There is a range of pathways leading from reactants to products with no barrier at all. In general there is good qualitative agreement between the present ab initio results and the modified CNDO surface of Kollmar.¹⁰ The two most serious discrepancies appear to be the prediction of a 5 kcal barrier by Kollmar and his smaller (13 vs. 27 kcal here) barrier for the least motion approach. Thus the differences between the least motion and non-least-motion pathways appears much greater than indicated by the modified CNDO surface.

Acknowledgments

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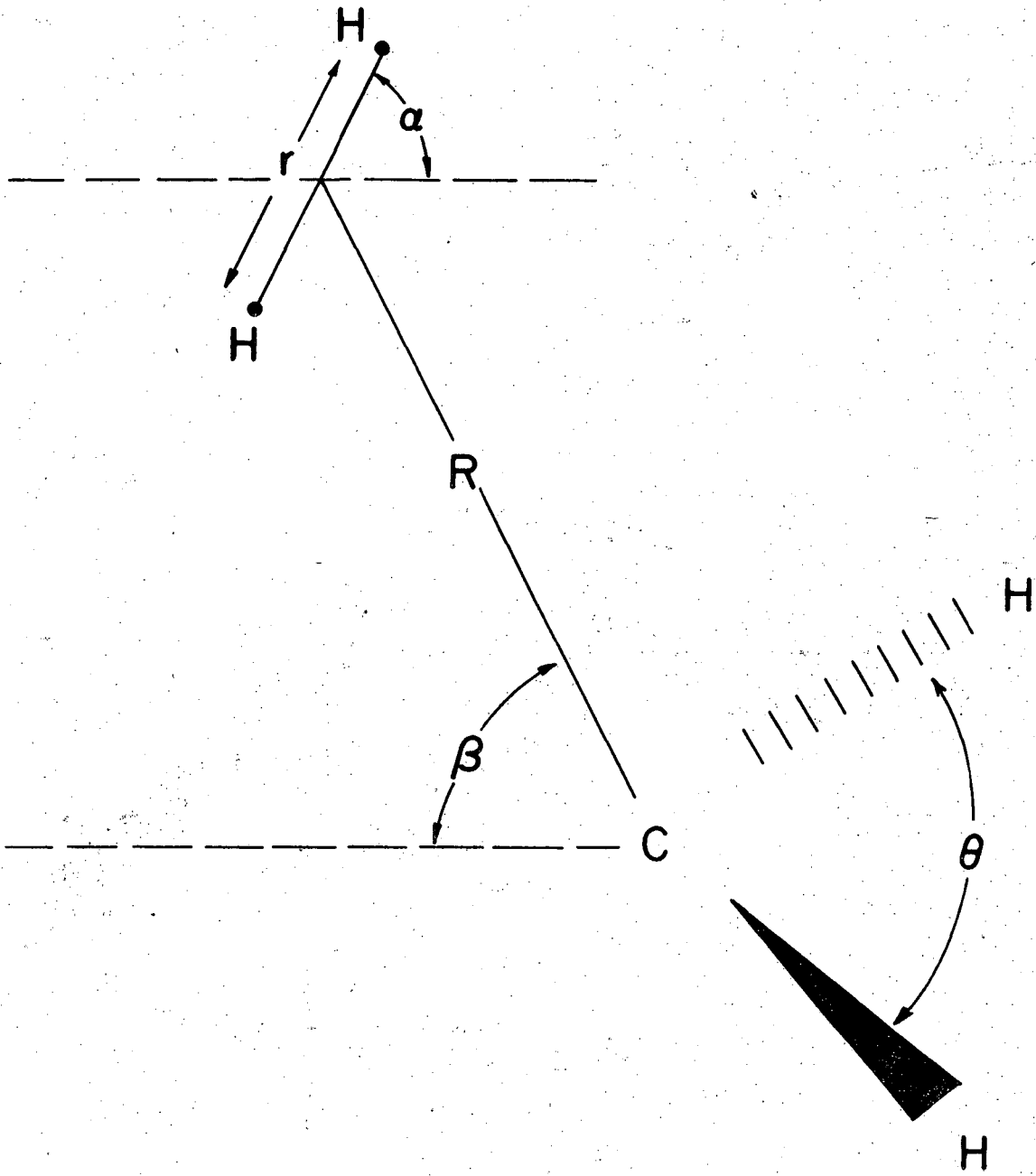
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Table I. Minimum energy path for the (0° , 90°) approach of $\text{CH}_2(^1\text{A})$ and H_2 . Energies are given relative to infinitely separated $\text{CH}_2(^1\text{A}_1) + \text{H}_2$.

R(bohrs)	r(bohrs)	θ (degrees)	Energy (kcal)
3.6	1.44	107.4	- 1.3
3.5	1.45	107.6	- 1.5
3.4	1.46	107.9	- 1.8
3.3	1.47	108.1	- 2.2
3.2	1.48	108.4	- 2.9
3.1	1.50	109.3	- 3.6
3.0	1.52	110.7	- 4.9
2.9	1.54	111.5	- 6.4
2.8	1.57	112.1	- 7.9
2.7	1.60	112.5	-10.3
2.6	1.65	113.2	-12.8
2.5	1.69	114.1	-15.6
2.4	1.75	115.6	-19.3
2.3	1.81	117.0	-23.1
2.2	1.90	118.1	-27.0

Figure Captions

- Figure 1. General coordinate system adopted for study of the $\text{CH}_2 + \text{H}_2$ singlet insertion reaction.
- Figure 2. $\text{CH}_2(^1\text{A}_1) + \text{H}_2$ coordinate system for $\alpha = 0^\circ$ and $\beta = 45^\circ$.
- Figure 3. $\text{CH}_2(^1\text{A}_1) + \text{H}_2$ coordinate system for $\alpha = 45^\circ$, $\beta = 45^\circ$.
- Figure 4. $\text{CH}_2(^1\text{A}_1) + \text{H}_2$ coordinate system for $\alpha = 0^\circ$, $\beta = 90^\circ$.
- Figure 5. $\text{CH}_2(^1\text{A}_1) + \text{H}_2$ coordinate system for $\alpha = 90^\circ$, $\beta = 45^\circ$.
- Figure 6. One-dimensional representations of several approaches (α, β) of singlet methylene to H_2 . The coordinate system adopted is depicted in Figure 1. These results were obtained using large scale configuration interaction techniques.
- Figure 7. Dependence on R and θ of the $\text{CH}_2(^1\text{A}_1) + \text{H}_2$ hypersurface. Here α , β , and r are constrained to be 0° , 90° , and either 1.4 or 1.7 or 1.9 bohrs.
- Figure 8. Single-configuration SCF results analogous to Figure 6, which is based on large scale CI.

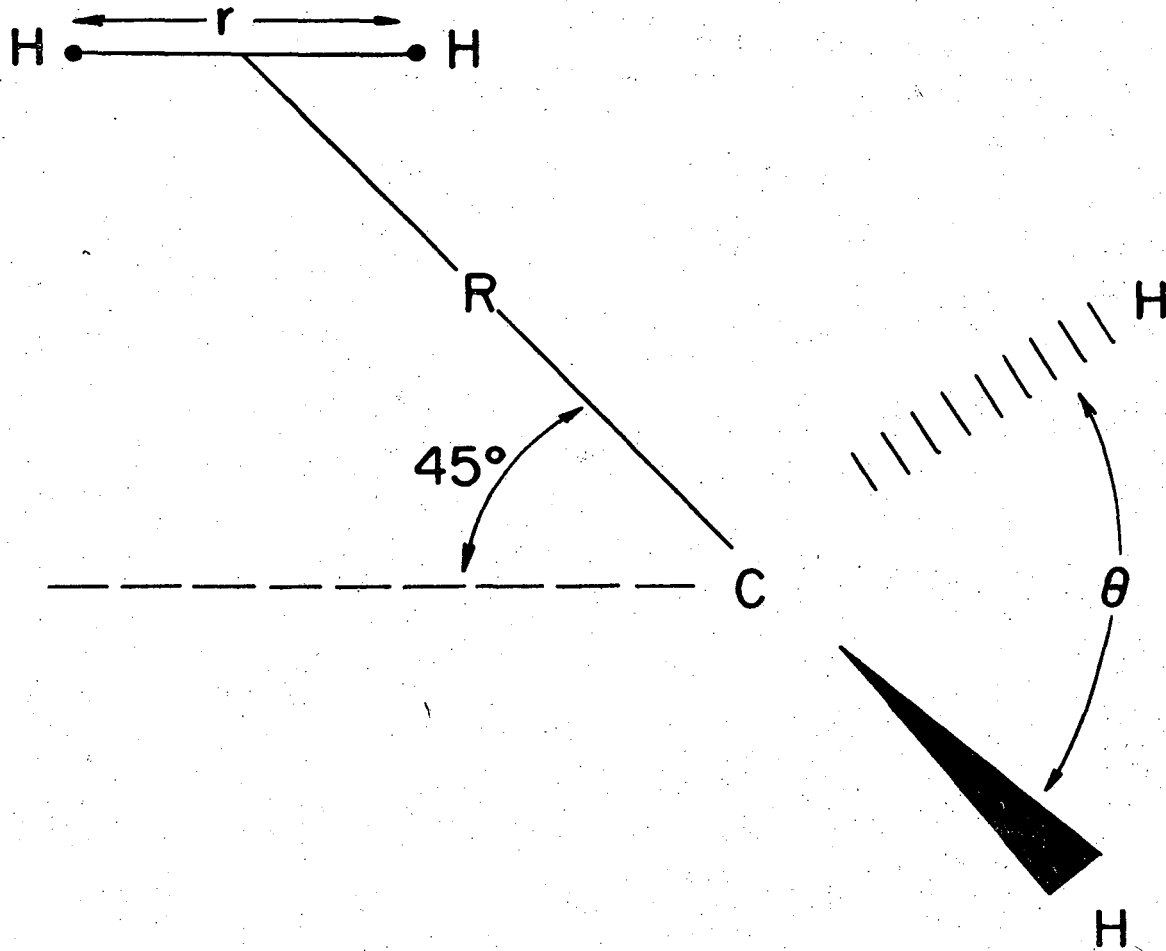


Geometry (α, β)

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Fig. 1

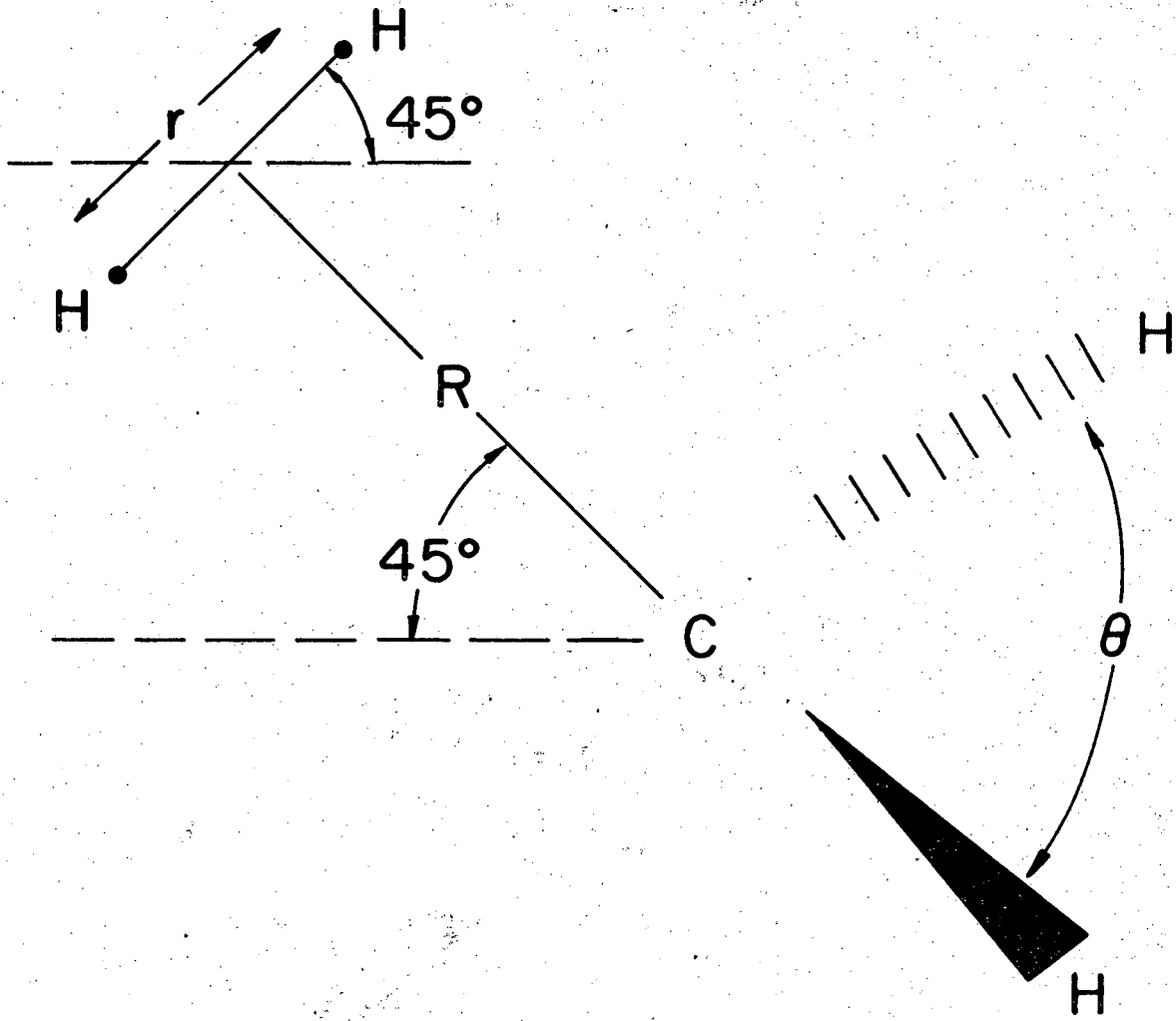
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Geometry (0°, 45°)

XBL749 - 4314

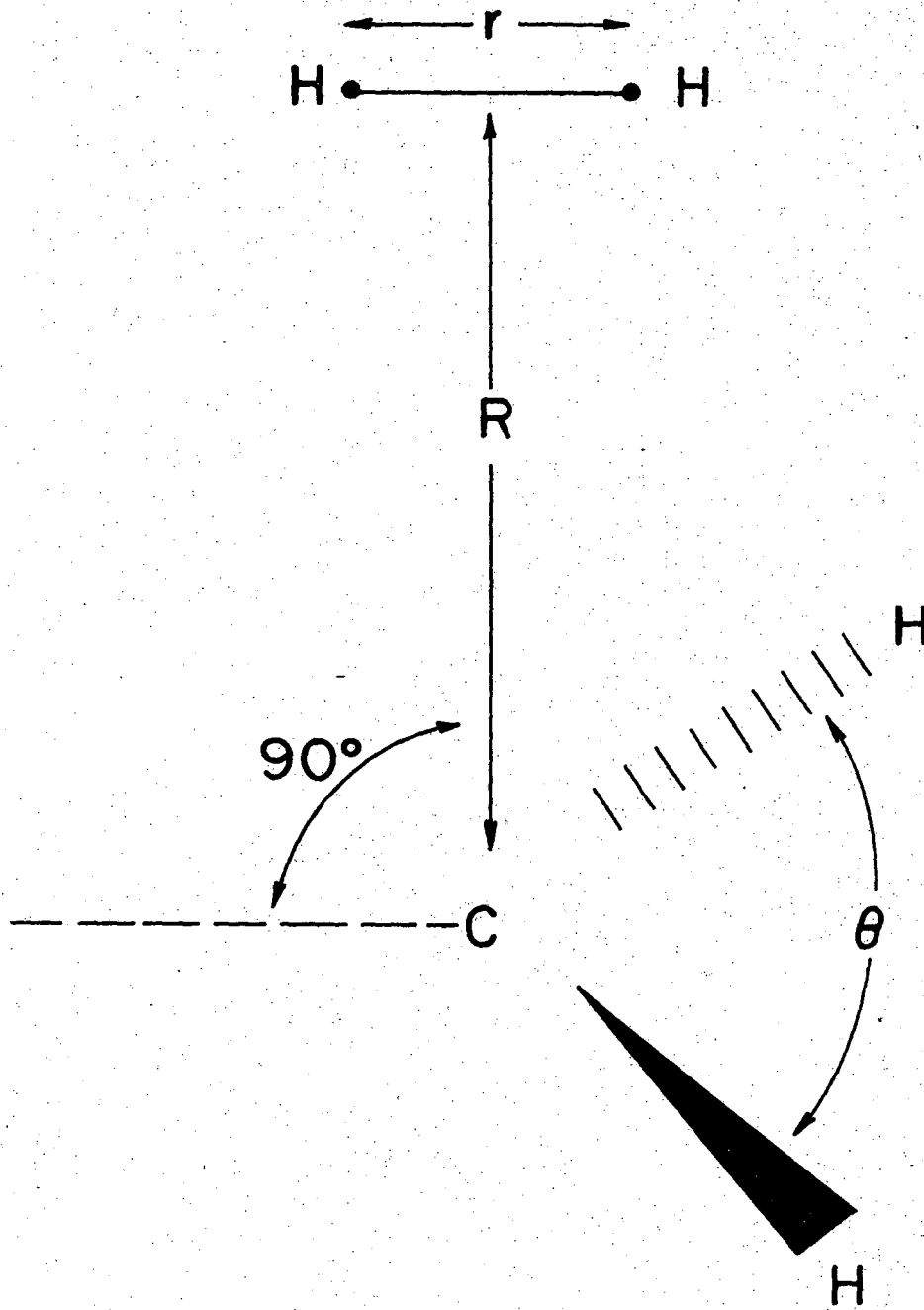
Fig. 2



Geometry ($45^\circ, 45^\circ$)

XBL 749 - 4315

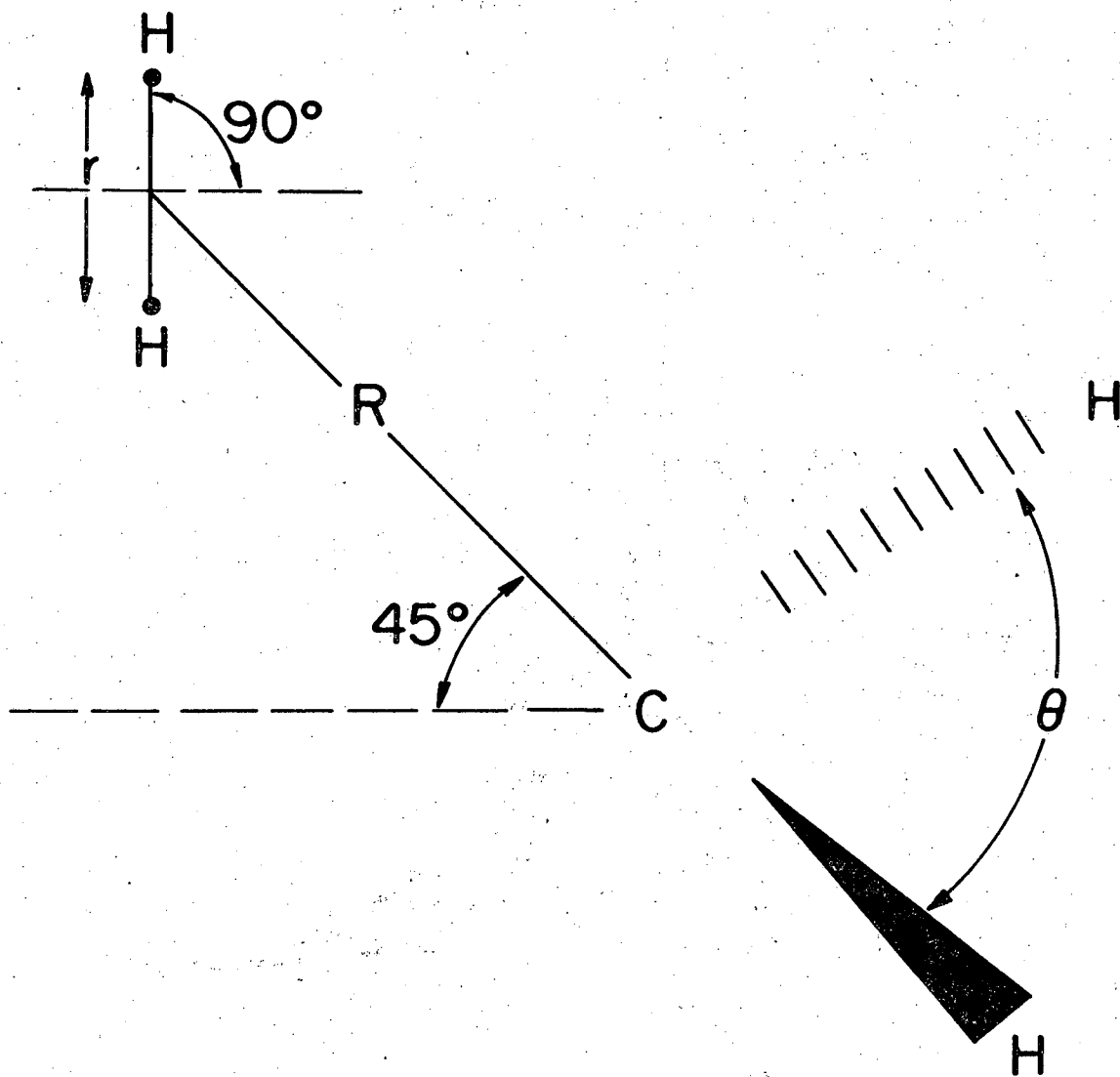
Fig. 3



Geometry ($0^\circ, 90^\circ$)

XBL749-4316

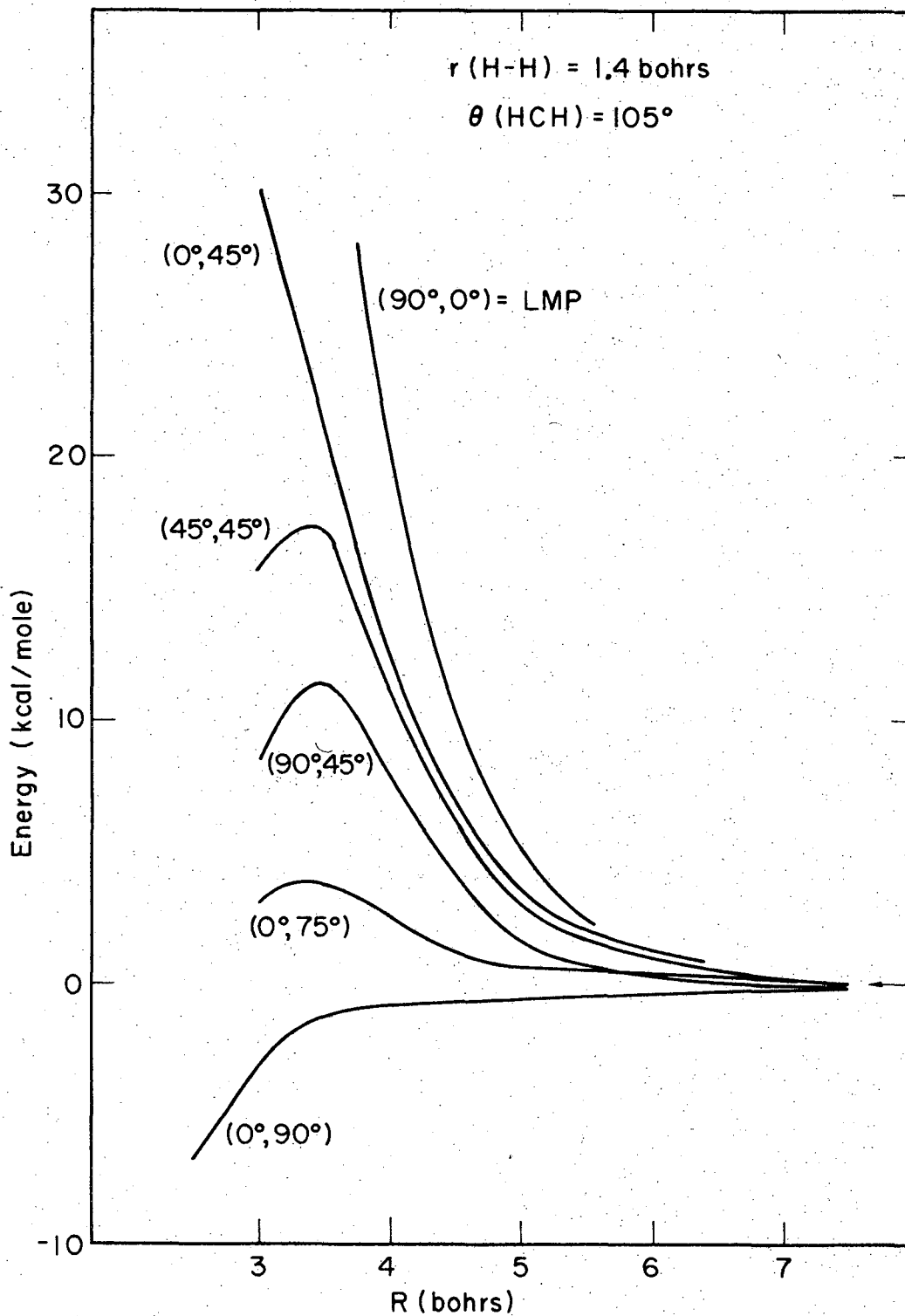
Fig. 4



Geometry (90°, 45°)

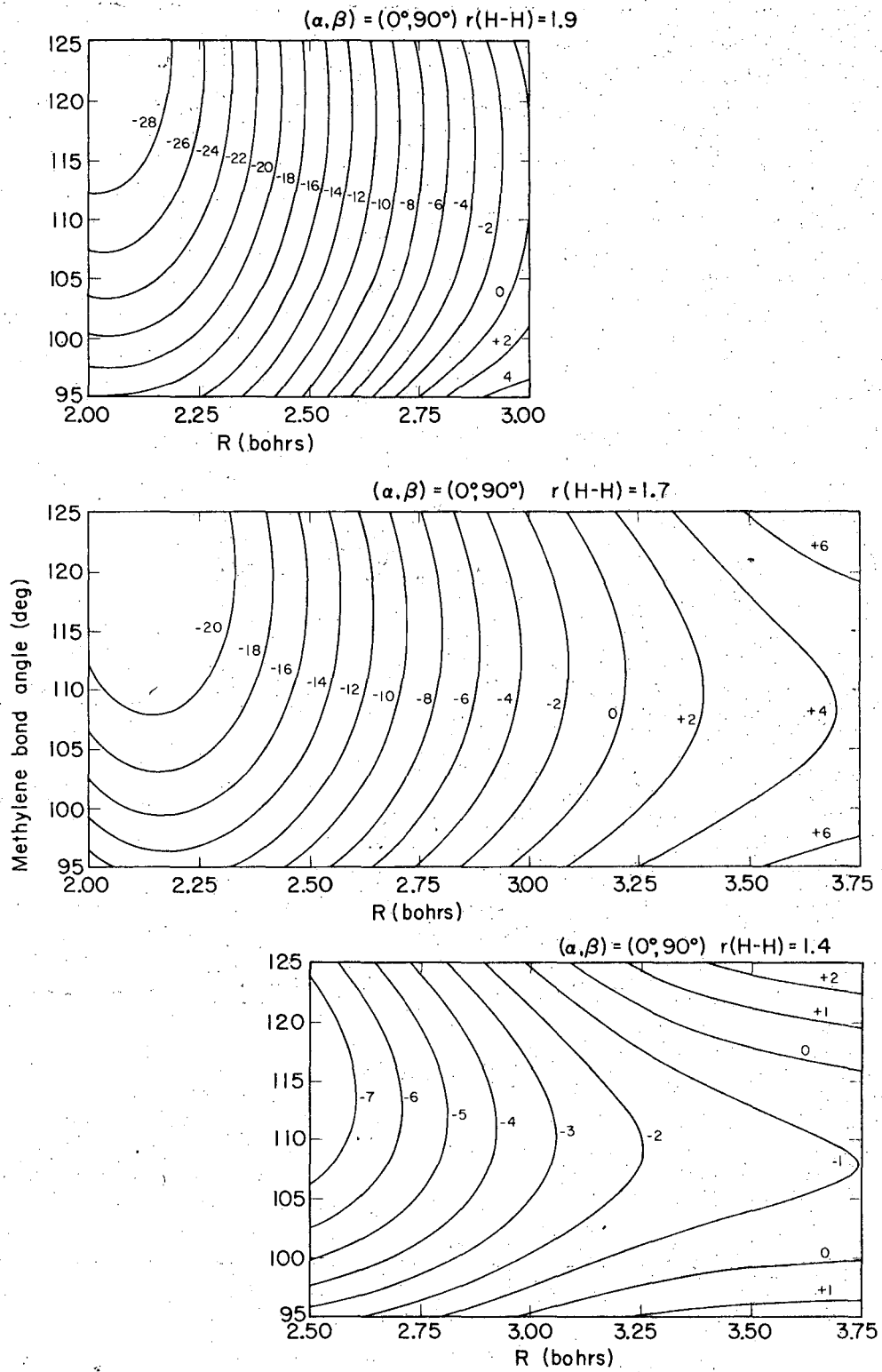
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Fig. 5



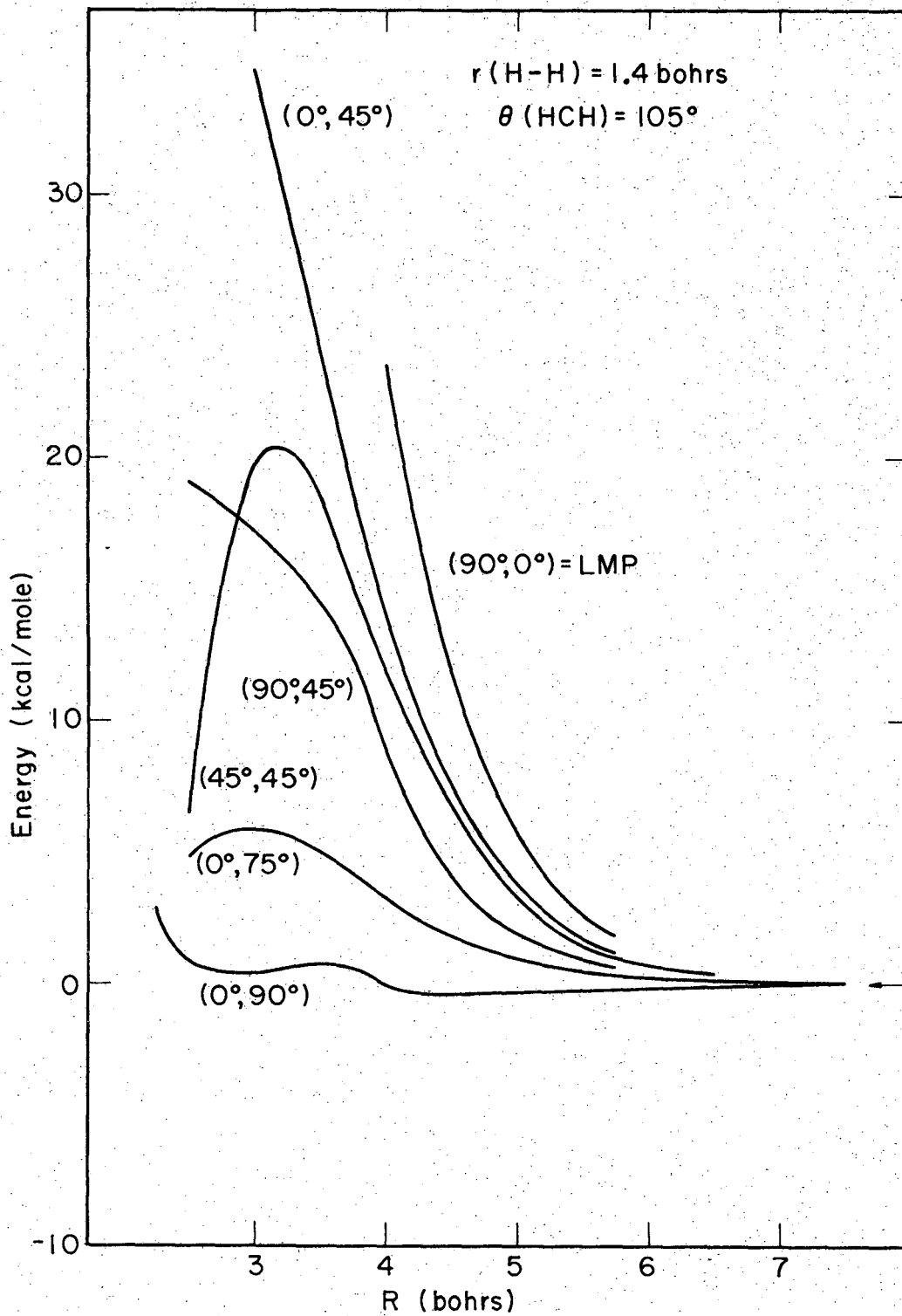
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Fig. 6



XBL766-9031

Fig. 7



XBL766-9029

Fig. 8

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