

ABSTRACT

ABSTRACTION vs. INSERTION IN THE C + H_2 AND N^+ + H_2 REACTIONS, <u>AB INITIO</u> POTENTIAL ENERGY SURFACES; THE ELECTRONIC STRUCTURE OF THE ${}^{3}A_2$ AND ${}^{3}B_2$ STATES OF METHYLENE.

By

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The first part of this thesis is concerned with the reaction of $A({}^{3}P)$, where A = C or N^{+} , with $H_{2}({}^{1}\Sigma_{g}^{+})$ to form AH_{2} in its ground ${}^{3}B_{1}$ state (<u>i.e.</u>, insertion) and AH in its lowest Σ and Π states plus $H({}^{2}S)$ (<u>i.e.</u>, abstraction).

A minimal basis set was employed, and with the constraint that the 1s function on the heavy atom was always doubly occupied, a full CI wave function was used. Symmetry orbitals were constructed with the Gram-Schmidt technique, starting with the 1s function on A. A minimum energy reaction path (MERP) for each potential energy surface was determined by locating the minimum energy H-H separation as a function of the A-H₂ separation, where A-H₂ is the distance from A to (1) the center of mass of H₂ for C_{2V} geometries and (2) the nearest H in C_{∞V} geometries.

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Since $C({}^{3}P) + H_{2}({}^{1}\Sigma_{g}^{+})$ correlates with an excited ${}^{3}B_{1}$ state of CH_{2} and $C({}^{3}P) + H_{2}({}^{3}\Sigma_{u}^{+})$ correlates with the ground ${}^{3}B_{1}$ state, the lowest ${}^{3}B_{1}$ surface for the CH_{2} insertion reaction is characterized by a double trough, where the maximum or barrier in between is the result of an avoided crossing of two SCF surfaces whose lineages are $H_{2}({}^{1}\Sigma_{g}^{+})$ and $H_{2}({}^{3}\Sigma_{u}^{+})$. At a C-H₂ separation of ~2.8 bohrs, the ${}^{1}\Sigma_{g}^{+}$ trough merges with the barrier leaving a single trough which leads to $CH_{2}({}^{3}B_{1})$ at the global minimum. Except for the fact that the trough which leads to NH_{2}^{+} in its ground ${}^{3}B_{1}$ state traces its lineage to $N({}^{4}S) + H_{2}^{+}({}^{2}\Sigma_{u}^{+})$ rather than $N^{+}({}^{3}P) + H_{2}({}^{3}\Sigma_{u}^{+})$, the basic topology of the lowest ${}^{3}B_{1}$ surface for the NH_{2}^{+} insertion reaction is the same as the CH₂ surface.

At infinite A-H₂ separation, the H-H separation is 1.667 bohrs, E(C; ³P) = -37.4701 a.u., E(N⁺; ³P) = -53.5347 a.u., E(N; ⁴S) = -54.0629 a.u., and E(H₂; ¹ Σ_{g}^{+}) = -1.1131 a.u., while at the global minimum the A-H₂ separation is 1.050 bohrs (CH₂) and .395 bohrs (NH₂⁺), the H-H separation has increased to 4.142 bohrs (CH₂) and 4.468 bohrs (NH₂⁺), and E(CH₂; ³B₁) = -38.64563 a.u. and E(NH₂⁺; ³B₁) = -54.8200 a.u. The calculated Δ H is -39 and -108 kcal/mole for CH₂ and NH₂⁺ respectively. The barrier to reaction or activation energy is calculated to be 82 and 41 kcal/mole for CH₂ and NH₂⁺, respectively. The energy along the $CHH(^{3}\Sigma^{-})$ abstraction MERP increases monotonically from a $C-H_{2}$ separation of ~4.5 bohrs to ~2.2 bohrs (where the H-H minimum disappears and there is no barrier to dissociation into $CH(^{4}\Sigma^{-}) + H(^{2}S)$, while the H-H separation goes from 1.7 bohrs to infinity. The $CHH(^{3}\Pi)$ abstraction MERP behaves similarly and its barrier to dissociation into $CH(^{2}\Pi) + H(^{2}S)$ is zero at a $C-H_{2}$ separation of ~2.55 bohrs. We obtain E = -38.0214 a.u. at R_{e} = 2.335 bohrs for $CH(^{4}\Sigma^{-})$, E = -38.0346 a.u. at R_{e} = 2.552 bohrs for $CH(^{2}\Pi)$, and E = -.4970 a.u. for $H(^{2}S)$. The calculated ΔH is 41 and 32 kcal/mole for the Σ and Π abstraction reactions, respectively. The barrier to reaction is 42 and 35 kcal/mole for the Σ and Π reactions, respectively.

Since both of the NHH⁺ abstraction MERP's $({}^{3}\Sigma^{-}$ and ${}^{3}\Pi$) indicate rather large relative increases in energy would be required to stay on them until they become equal in energy to NH⁺ + H (the NH⁺(${}^{2}\Pi$) has R_e = 2.477 bohrs and E = -54.1383 a.u., and the NH⁺(${}^{4}\Sigma^{-}$) has R_e = 2.481 bohrs and E = -54.1569 a.u.), we did not extend the Σ or Π MERP to N-H₂ separations less than 1.9 and 2.0 bohrs, respectively. The energy of the Π MERP increases monotonically as the N-H₂ separation decreases. Since there is a deep minimum in the Σ MERP (-37.7 and -34 kcal/mole with respect to N⁺ + H₂ and NH⁺ + H, respectively) at an N-H₂ separation of 2.665 bohrs and an H-H separation of 2.13 bohrs, the global minimum on the Σ surface corresponds to the bound linear [NHH]⁺ complex in a ${}^{3}\Sigma^{-}$ state. Since the energy of both MERP's increase rapidly for N-H₂ separations less than 2.5 bohrs, the barrier to reaction at an N-H₂ separation of 2.5 bohrs is 0 and 8 kcal/mole for the Σ and Π abstraction reactions, respectively. The corresponding values of Δ H are -4 and 8 kcal/mole, respectively.

The barriers to reaction predict that (1) the abstraction reactions proceed with greater ease than the insertion reactions and (2) the NH_2^+ reactions proceed with greater ease than the analogous CH_2 reactions. A comparison with experimental results suggests that the rotation of the H_2 to form a system with C_S symmetry may be important in the dynamics of these reactions.

The second part of this thesis is concerned with existence of a bent ${}^{3}A_{2}$ state with an appropriate energy (~8.75 eV above the ground state) and angle (~125°), so as to be consistent with the interpretation of the electronic spectrum of CH₂ which predicts a ground ${}^{3}B_{1}$ state (~136°). This interpretation also predicts that the ${}^{3}A_{2}$ state is heterogeneously predissociated by a ${}^{3}B_{2}$ state.

A minimal STO-3G basis was augmented by a set of 3p and 3d functions, and $\zeta_{3p} = .47$ and $\zeta_{3d} = .34$ were determined by optimizing the energy of excited states of the carbon atom. The energy and angular dependence of the non-Rydberg or valence state and three Rydberg states for each symmetry and the ground ${}^{3}B_{1}$ state were determined by constructing solutions of the HFR restricted open shell equations.

The existence of three highly bent ${}^{3}A_{2}$ states with angles of 127°, 120°, and 113° corresponding to 0-0 transition energies of 8.86, 8.30, and 7.53 eV, respectively, was obtained. Several ${}^{3}B_{2}$ states, which may be responsible for predissociation, were obtained. ABSTRACTION VS. INSERTION IN THE C + H_2 AND N^+ + H_2 REACTIONS, <u>AB INITIO</u> POTENTIAL ENERGY SURFACES;

THE ELECTRONIC STRUCTURE OF THE ³A₂ AND ³B₂ STATES OF METHYLENE.

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INTRODUCTION

In the last 15 to 20 years there has been a rapid development in computer technology which has had a dramatic effect on science. The approximate solution from first principles of the Schrödinger equation for a polyatomic molecule with more than a few electrons is characterized by heavy computational requirements. Although the fundamental equations for the electronic structure of polyatomic systems have been known for over 40 years, the development of high-speed computers was crucial for the exploration and development of techniques for solving the required equations at an <u>ab initio</u> level. We have studied the electronic structure of several chemical reactions and several excited states of methylene at an ab initio level.

CHAPTER I

THE C + H_2 AND N^+ + H_2 REACTIONS

The first part of this thesis is concerned with the potential energy surfaces for the reactions of the carbon atom and the nitrogen cation with molecular hydrogen. The initial impetus for this study was an interest in the ease with which CH_2 in its ground ${}^{3}B_1$ state might be formed from $C({}^{3}P)$ and H_2 $({}^{1}\Sigma_{g}^{+})$. Two possible approaches were considered to be important. The first is the insertion reaction

$$C + \prod_{H}^{H} = C \left(\prod_{H}^{H} \right).$$
(1)

In this reaction, the C atom is assumed to insert itself into an H_2 molecule via an approach characterized by C_{2V} symmetry at all internuclear distances. The second approach is the abstraction reaction

C + H - H = C - H + H. (2)

In this reaction, the C atom is assumed to abstract a hydrogen atom from the H_2 molecule via an approach characterized by $C_{\infty V}$ symmetry at all distances. The abstraction is part of an overall reaction scheme whose second part is

 $CH + H = CH_2$ or $CH + H_2 = CH_2 + H$.

We considered only the initial abstraction represented by (2).

This problem is easily extended to include the reactive nitrenium ion, NH_2^+ . As in CH_2 , we considered the formation of NH_2^+ in its ground ${}^{3}B_1$ state from $N^+({}^{3}P)$ and $H_2({}^{1}\Sigma_{g}^+)$. The same insertion and abstraction reactions were considered for NH_2^+ . Although NH_2^+ is isoelectronic with CH_2 , the different nuclear charges in the two systems would lead one to anticipate the possibility of fundamentally different results.

Since equations (1) and (2) represent only two of many possible reactions, some of the other reactions that may be written may be equally important. However, we anticipate that a detailed study of the potential energy surfaces of the reaction of $C({}^{3}P)$ and $N^{+}({}^{3}P)$ with $H_{2}({}^{1}\Sigma_{g}^{+})$ will indicate whether abstraction $(C_{\infty V})$ or insertion (C_{2V}) is preferred. Since NH_{2}^{+} is isoelectronic with CH_{2} , we hope to determine the role the positive charge plays in differentiating between the two approaches and the two systems.

Potential Energy Surface Preliminaries

There are 3 internal or relative degrees of freedom in AH_2 systems. These are illustrated in Figure 1 and are represented by R, the distance from the A nucleus

to the center of mass H_2 , r, the H - H separation, and θ , the angle between \vec{r} and \vec{R} .



Figure 1.--The internal degrees of freedom of AH₂.

Although our calculations were restricted to $\theta = 90^{\circ}$ (C_{2V}) and $\theta = 0^{\circ}$ (C_{∞V}), we shall have occasion to discuss C_s geometries where $0^{\circ} < \theta < 90^{\circ}$.

We computed approximate eigenvalues and eigenfunctions of the Schrödinger equation for a large number of geometries. The eigenfunctions and their variations were used to give insight into the electronic changes as the nuclei assumed different configurations. From the eigenvalues, we extracted a minimum energy reaction path (MERP). That point on the MERP which corresponds to the maximum energy in the MERP is the saddle point. The saddle point may be viewed as separating the reactants and products. Since the MERP is usually defined [21] as the path of steepest descent from the saddle point of the potential energy surface, V, it may be generated by following the vector $-\vec{\nabla}V = -(\partial V/\partial R)\hat{i} - (\partial V/\partial r)\hat{j}$ from the saddle point (where $-\vec{\nabla}V = 0$). These definitions are illustrated in Figures 2 and 3.

In this work, we constructed the MERP by using a more pedestrian technique which allowed for the possibility of multiple local "MERP's." At a given value of R, the r distance was varied. The r distance which resulted in a minimum in the energy defined a point on the MERP. Since more than one minimum may be found, there may be more than one MERP. This process was repeated over the whole range of relevant R values. For those surfaces with more than one MERP, the overall MERP was defined by the set of r values, determined at various values of R, which correspond to the <u>lowest</u> energy minima. Our goal was to determine the overall MERP, not full potential energy surfaces for the reactions.

The barriers to reaction we calculated were defined as the energy at the highest maximum in the overall MERP minus the energy of the reactants. The barrier to reaction, $E_{\rm b}$, is illustrated in Figure 3 for the H₃ surface.

The C + H_2 Insertion Reaction

The lowest ${}^{3}B_{1}$ surface of CH_{2} is characterized by an avoided crossing with the second lowest ${}^{3}B_{1}$ surface. The two (SCF) surfaces which would have resulted if there were no avoided crossing are denoted by their lineage at



Figure 2.--Schematic H₃ equipotential curves.



Figure 3.--Schematic energy profile along the H₃ MERP.

R = ∞ . One surface originates from C(³P) + H₂(¹ Σ_{g}^{+}), while the other surface originates from C(³P) + H₂(³ Σ_{u}^{+}), or equivalently from C(³P) + 2H(²S).

A particularly lucid view of the avoided crossing and the two resulting surfaces is given by cross sectional views of the surfaces at various values of R. Figures 4 through 8 show cuts at $R = \infty$, 4.0, 3.4, 2.95, and 2.8 bohrs, respectively. When comparing Figures 4 through 8, note that different energy scales are used.

As shown in Figure 4, for $R = \infty$ we obtained the usual potential energy curves of $H_2({}^1\Sigma_g^+)$ and $H_2({}^3\Sigma_u^+)$ with a uniform energy lowering by an amount equal to the energy of $C({}^3P)$. The ${}^1\Sigma_g^+$ curve is characterized by a minimum at r = 1.667 bohrs and a monotonically increasing energy as r increases from 1.667 bohrs. The ${}^3\Sigma_u^+$ curve is repulsive and its energy decreases monotonically with increasing r. For all values of r, the ${}^1\Sigma_g^+$ curve is always equal to or below the ${}^3\Sigma_u^+$ curve. Both curves merge at $r = \infty$ resulting in a doubly degenerate pair of surfaces.

As the H₂ molecule is brought closer to the C atom, the above description remains essentially unchanged until R ~ 4.8 bohrs. At R ~ 4.8 bohrs, a maximum in the ${}^{1}\Sigma_{g}^{+}$ and a minimum in the ${}^{3}\Sigma_{u}^{+}$ curves are found at relatively large r values of ~ 5.5 to ~ 6.5 bohrs. This is the initial stage of the metamorphosis of each state into a resultant ${}^{3}B_{1}$ state. Although when the H₂ system is noninteracting with C(${}^{3}P$), the ${}^{1}\Sigma_{q}^{+}$ and ${}^{3}\Sigma_{u}^{+}$ states are of



Figure 4.--Cross sectional cuts of the two lowest ${}^{3}B_{1}$ surfaces of CH₂ at R = ∞ .



Figure 5.--Cross sectional cuts of the two lowest ${}^{3}B_{1}$ surfaces of CH₂ at R = 4.0 bohrs.





Figure 7.--Cross sectional cuts of the two lowest ${}^{3}B_{1}$ surfaces of CH₂ at R = 2.95 bohrs.



strictly different spatial and spin symmetry, in the presence of $C({}^{3}P)$, both states contribute to ${}^{3}B_{1}$ states of CH_{2} . The correlations are

$$C({}^{3}P; 2p_{X}^{1} 2p_{Z}^{1}) + H_{2}({}^{1}\Sigma_{q}^{+}; \sigma_{q}^{2}) = CH_{2}({}^{3}B_{1})$$

and $C({}^{3}P; 2p_{X}^{1} 2p_{Y}^{1}) + H_{2}({}^{3}\Sigma_{u}^{+}; \sigma_{g}^{1} \sigma_{u}^{1}) = CH_{2}({}^{3}B_{1})$.

At R ~ 4.8 bohrs, the two curves are almost degenerate at large values of r. The result is a mixing of the two curves (or surfaces) and an avoided crossing.

In Figures 5 through 8, the solid lines are cross sectional cuts of the two lowest ${}^{3}B_{1}$ surfaces. The two surfaces whose avoided crossing resulted in these surfaces are represented by dashed lines in the region of the avoided crossing. We define the $({}^{1}\Sigma_{g}^{+})$ minimum at smaller r values as the "first minimum" or "first trough." The $({}^{3}\Sigma_{u}^{+})$ minimum at larger r values is defined to be the "second minimum" or "second trough."

In Figure 5, where R = 4.0 bohrs, the lowest ${}^{3}B_{1}$ surface is characterized by the first minimum at r = 1.642bohrs, a slight maximum at the avoided crossing at r = 4.10bohrs, and the second minimum at r = 5.6 bohrs.

From R ~ 4.8 to R ~ 2.8 bohrs, the lowest ${}^{3}B_{1}$ surface is characterized by a double trough and a maximum or barrier in between. These extrema become more evident as R decreases from 4.8 bohrs, as may be seen in Figures 6

and 7. In this region, the character of these extrema change significantly. The energy at the bottom of the first trough and the energy at the maximum increase as R decreases. Since the energy of the barrier is not increasing as fast as the energy of the first trough, the first trough is disappearing. The energy of the second trough is decreasing very rapidly as R decreases. While the location of the first trough remains essentially unchanged at $r \sim 1.65$ bohrs, the location of the barrier and second trough are moving rapidly toward smaller r values.

At R ~ 2.8 bohrs, the maximum and thus the avoided crossing have moved to such small values of r so as to coalese with the first minimum, as shown in Figure 8. The lowest ${}^{3}B_{1}$ surface is now characterized by a single minimum. This single minimum is the second minimum whose lineage may be traced to $C({}^{3}P)$ and $H_{2}({}^{3}\Sigma_{u}^{+})$. It is this minimum that then leads directly to CH_{2} in its ground ${}^{3}B_{1}$ state as R decreases further.

It is worthwhile to point out that this assignment must be tempered with the knowledge that it is improper to speak of $C({}^{3}P)$ and $H_{2}({}^{3}\Sigma_{u}^{+})$ in this region of the surface. We are describing the ${}^{3}B_{1}$ state of CH_{2} with a linear combination of 51 configurations, and the characterization of the surface as having ${}^{3}\Sigma_{u}^{+}$ lineage is a result of detailed analysis of this function.

The nature of the avoided crossing is easily seen by considering the correlation diagram shown in Figure 9 for the two ${}^{3}B_{1}$ states. Note that the other possible ${}^{3}B_{1}$ state which arises from $C({}^{1}D)$ and $H_{2}({}^{3}\Sigma_{u}^{+})$ is not energetically relevant. Since $C({}^{3}P) + H_{2}({}^{1}\Sigma_{g}^{+})$ correlates with an excited ${}^{3}B_{1}$ state with an orbital occupation $la_{1}^{2} 2a_{1}^{2} lb_{2}^{0} 3a_{1}^{2} lb_{1}^{1} 4a_{1}^{1}$ and $C({}^{3}P) + H_{2}({}^{3}\Sigma_{u}^{+})$ correlates with the ground ${}^{3}B_{1}$ state with the orbitals occupied as $la_{1}^{2} 2a_{1}^{2} lb_{2}^{2} 3a_{1}^{1} lb_{1}^{1}$, the result is the indicated avoided crossing.

In Figure 10, the first MERP which corresponds to the first trough, the second MERP, and the values of r at the maximum energy in the barrier are plotted for the lowest ${}^{3}B_{1}$ surface. The rate of decrease of the second MERP, as R decreases, slows down for R values less than ~ 2.8 bohrs, where the first MERP and barrier have merged. There is a minimum in the second MERP at R ~ 2.1 bohrs. The merging of the second MERP with the barrier is at R ~ 4.8 bohrs.

The energy profile along the two MERP's and the maximum energy of the barrier are plotted in Figure 11. The global minimum corresponding to CH_2 in its ground ${}^{3}B_1$ state with an energy of - 38.64563 a.u. is at R = 1.050 bohrs and r = 4.142 bohrs. With respect to decreasing R, we see the first MERP merging with the barrier at R ~ 2.8 bohrs. With respect to increasing R, we see the second MERP merging with the barrier at R ~ 4.8 bohrs.



Figure 9.--C + H_2 correlation diagram (C_{2V}).



Figure 10.--The "MERP's" and barrier for the lowest ³B₁ surface of CH₂.





Figure 11.--The MERP energy profiles and barrier for the lowest ${}^{3}B_{1}$ surface of CH₂.

A rough hand-drawn set of equipotential curves for the lowest ${}^{3}B_{1}$ surface are presented in Figure 12. All available points were used to indicate the approximate topology of the surface. Although the curves are not quantitatively correct, we feel that they do provide a good qualitative overview of the surface. The dashed, dash-dot, and dotted lines represent the second MERP, the first MERP, and barrier, respectively. The first MERP cuts across and into the side of the barrier which may be likened to a mountain. Eventually, the first MERP disappears leaving a steep descent down the side of the mountain into the valley below (<u>i.e.</u>, the second MERP) and thus eventually to the global minimum at \bigotimes .

Our barrier to reaction, E_b , change in enthalpy for the reaction, ΔH , and overall MERP will be based on the formation of CH_2 from $C({}^{3}P) + H_2({}^{1}\Sigma_{g}^{+})$. As may be seen in Figure 11, the energy of each MERP is equal to - 38.484 a.u. at R = 3.125 bohrs. From R = ∞ to R = 3.125 bohrs the overall MERP is the first MERP. At R = 3.125 bohrs, the overall MERP proceeds from the first MERP at r = 1.65 bohrs to the second MERP at r = 4.45 bohrs while rising over the barrier, ε_{b} . For R < 3.125 bohrs, the overall MERP is the second MERP. For the overall MERP, the barrier to reaction is

$$E_{b} = \epsilon_{b} - E(C; {}^{3}P) - E(H_{2}; {}^{1}\Sigma_{g}^{+})$$

= .130 a.u. = 3.54 eV = 81.6 kcal/mole .



Figure 12.--Schematic equipotential curves for the lowest ${}^{3}B_{1}$ surface of CH₂.

Since there is a <u>very</u> slight minimum in the barrier at R = 4.2 bohrs, the lowest possible value of E_h is

$$E_{h} = .1176 \text{ a.u.} = 3.20 \text{ eV} = 73.8 \text{ kcal/mole}$$

This energy corresponds to the approximate energy required to break the H_2 bond.

Perhaps a more realistic prediction of the barrier to reaction would result if the H_2 were to remain bound in the first MERP until it became unbound at $R \sim 2.8$ bohrs. This results in $E_b = .155$ a.u. = 4.22 eV = 97.3 kcal/mole.

Our reaction surface yields an exthothermic reaction with

$$\Delta H(0^{\circ}K) = E(CH_2; {}^{3}B_1) - E(C; {}^{3}P) - E(H_2; {}^{1}\Sigma_g^+)$$

= - .0624 a.u. = - 1.70 eV = - 39.15
kcal/mole

This result is 50.6% of the experimental result [22], $\Delta H(0^{\circ}K) = -77.33 \text{ kcal/mole.}$

The $N^+ + H_2$ Insertion Reaction

The basic topology of the lowest ${}^{3}B_{1}$ surface of NH₂⁺ is the same as the lowest ${}^{3}B_{1}$ surface of CH₂. There is a first minimum, trough or MERP at smaller r values, a second minimum, trough, or MERP at larger r values, and

a maximum or barrier at intermediate r values. Figure 12 also describes the qualitative features of the NH_2^+ surface.

The first minimum traces its lineage to $N^+({}^{3}P)$ and $H_2(L_{q}^{1})$. The second minimum does not trace its lineage to $N^+({}^{3}P) + H_2({}^{3}\Sigma_{u}^+)$ (as suggested by the C + H₂ results) but to $N(^{4}S) + H_{2}^{+}(^{2}\Sigma_{u}^{+})$, or equivalently $N(^{4}S) +$ $H(^{2}S) + H^{+}$. The $N^{+}(^{3}P) + H_{2}(^{3}\Sigma_{u}^{+})$ surface as well as the $N(^{2}D) + H_{2}^{+}(^{2}\Sigma_{q}^{+})$ do interact significantly with these lower surfaces. The complexity of the situation is illustrated in Figure 13, where the relevant manifold of ${}^{3}B_{1}$ states are shown by a cross sectional cut with R fixed at 1 \times 10¹² bohrs. The potential energy curves of the $H_2({}^1\Sigma_{a}^+)$, $H_2({}^3\Sigma_{u}^+)$, $H_2^+({}^2\Sigma_{a}^+)$ and $H_2^+({}^2\Sigma_{u}^+)$ states may be easily seen. They are, of course, lowered uniformly by the energy of the appropriate state of N or N⁺. Since $R = 1 \times 10^{12}$ bohrs, the various states of H_2 and H_2^+ are non-interacting and there are no avoided crossings. As the two systems approach each other and the metamorphosis into an $NH_2^+ B_1$ description begins, each curve or surface crossing indicated in Figure 13 becomes avoided. We note that at very large values of R there will be a barrier or maximum due to the avoided crossing of the two lowest surfaces at r ~ 5.0 bohrs. The corresponding barrier in CH_2 merged with the second trough at R \sim 4.8 bohrs and was nonexistent at very large values of R.


Figures 14 through 16 show cross sectional cuts of the two lowest ${}^{3}B_{1}$ surfaces with R fixed at 3.5, 3.0, and 2.5 bohrs, respectively.

As we moved the two hydrogen nuclei toward the N nucleus, a minimum in the lowest ${}^{3}B_{1}$ surface starts at R ~ 5.0 bohrs and r ~ 8.0 bohrs. This is the second minimum which is the NH_2^+ analog of the second minimum in CH2. In CH2, the second minimum was associated with its lineage from $H_2({}^{3}\Sigma_{u}^{+})$. In NH_2^{+} , the second minimum is associated with its lineage from $H_2^+({}^2\Sigma_u^+)$. There is no corresponding maximum in the ${}^{1}\Sigma_{\alpha}^{+}$ curve, as was the case in CH₂. The lowest ${}^{3}B_{1}$ surface of NH₂⁺ is now characterized by the first minimum at r = 1.7 bohrs, the second minimum and the maximum or barrier in between as a result of the avoided surface crossing. The location of the barrier for R > 3.5 bohrs was not determined. Since it was at $r \sim 5.0$ bohrs at $R = 1 \times 10^{12}$ bohrs, it seems reasonable to assume it lies between r = 1.7 and 5.0 bohrs.

The basic features of the lowest ${}^{3}B_{1}$ surface of NH_{2}^{+} from R ~ 5.0 to R ~ 2.6 bohrs are the same as those for the CH_{2} surface from R ~ 4.8 to R ~ 2.8 bohrs. The energy of the first trough is rising and the energy of the second trough is decreasing as R decreases. Neither of these changes are as dramatic as in the CH_{2} surface. As R decreases, the r values which define the first and



Figure 14.--Cross sectional cuts of the two lowest ${}^{3}B_{1}$ surfaces of NH $_{2}^{+}$ at R = 3.5 bohrs.



Figure 15.--Cross sectional cuts of the two lowest ${}^{3}B_{1}$ surfaces of NH $_{2}^{+}$ at R = 3.0 bohrs.



Figure 16.--Cross sectional cuts of the four lowest ${}^{3}B_{1}$ surfaces of NH⁺₂ at R = 2.5 bohrs.

second MERP's remain essentially unchanged and decrease rapidly, respectively. The r values which characterize the maximum in the barrier decrease rapidly from R \sim 3.5 to R \sim 2.6 bohrs.

Eventually, as on the CH_2 surface, the barrier and the first minimum merge as R approaches ~ 2.6 bohrs. The result is a single minimum or trough for R less than ~ 2.6 bohrs in the lowest ${}^{3}B_{1}$ surface. This is the second minimum, whose lineage may be traced to $N({}^{4}S) + H_{2}^{+}({}^{2}\Sigma_{u}^{+})$, and it leads directly to NH_{2}^{+} in its ground ${}^{3}B_{1}$ state at the global minimum.

Cross sectional cuts of the third and fourth lowest ${}^{3}B_{1}$ surfaces are also plotted in Figure 16. The first minimum at R = 2.5 bohrs resides totally in the second lowest ${}^{3}B_{1}$ surface, which also has a maximum. The shape of the second lowest surface whose energy is rising appears to be affected by strong interactions with the third and fourth lowest ${}^{3}B_{1}$ surfaces.

The first MERP, second MERP, and the values of r at the maximum energy in the barrier are plotted for the lowest ${}^{3}B_{1}$ surface in Figure 17. The barrier was not determined for R > 3.5 bohrs. We suggest that it seems reasonable to assume that the barrier will monotonically increase from r = 3.38 bohrs at R = 3.5 bohrs to r ~ 5.0 bohrs at R = ∞ . Except for the fact that the barrier in the NH₂⁺ surface is present for all R > 2.6 bohrs, this



Figure 17.--The "MERP's" and barrier for the lowest ${}^{3}B_{1}$ surface of NH_{2}^{+} .

plot is remarkably similar to the corresponding plot obtained for CH₂ in Figure 10.

The energy profile along the two MERP's and the maximum energy of the barrier for lowest ${}^{3}B_{1}$ surface of NH₂⁺ are plotted in Figure 18. The global minimum corresponding to NH₂⁺ in its ground ${}^{3}B_{1}$ state with an energy of - 54.81995 a.u. is at R = .395 bohrs and r = 4.468 bohrs. The global minimum is substantially lower with respect to the reactants than the CH₂ global minimum. Except for the depth of the global minimum, the energy changes in Figure 18, though paralleling those for CH₂, are not as large or dramatic. The merging of the first trough and the barrier at R ~ 2.6 bohrs may be inferred from Figure 18. The global minimum is indeed very shallow. The barrier to linearity is so small so as to not be detectable on the scale of Figure 18.

There is a minimum in the energy of the barrier (see Figure 18) at R = 3.1 bohrs which also coincides with the value of R at which the two energy profiles for the two MERP's are equal. Thus, E_b for the overall MERP is equal to the lowest possible value of E_b for the reaction. The overall MERP (1) is the first MERP from R = ∞ to R = 3.1 bohrs, (2) proceeds from r = 1.8 bohrs at the first MERP to r = 4.5 bohrs at the second MERP, and (3) is the second MERP for R < 3.1 bohrs. The energy of the



Figure 18.--The MERP energy profiles and barrier for the lowest ${}^{3}B_{1}$ surface of NH_{2}^{+} .

barrier at R = 3.1 bohrs is $\varepsilon_{b} = -54.582$ a.u. Thus, the barrier to reaction is

$$\mathbf{E}_{\mathbf{b}} = \mathbf{\varepsilon}_{\mathbf{b}} - \mathbf{E}(\mathbf{N}^{+}; {}^{3}\mathbf{P}) - \mathbf{E}(\mathbf{H}_{2}; {}^{1}\boldsymbol{\Sigma}_{\mathbf{g}}^{+})$$

= .066 a.u. = 1.80 eV = 41.4 kcal/mole .

The NH_2^+ barrier is about one-half of the corresponding CH_2 barrier, a significant difference. Although the true barrier in the NH_2^+ reaction might easily be less than 50% of the calculated barrier, our results suggest that it is non-trivial. Although this is contrary to the hypothesis that reactions involving ions tend to proceed with little or no barrier, we caution that our result is based on an examination of only the C_{2V} approach.

If we consider the H_2 as remaining bound in the first trough until it becomes unbound when merging with the barrier, we estimate from Figure 18 that E_b is approximately .1 a.u. = 2.7 eV = 63 kcal/mole.

Our reaction surface predicts an exthothermic reaction with

$$\Delta H(0^{\circ}K) = E(NH_{2}^{+}; {}^{3}B_{1}) - E(N^{+}; {}^{3}P) - E(H_{2}; {}^{1}\Sigma_{g}^{+})$$

= -.172 a.u. = - 4.68 eV = - 108.0 kcal/mole ,

which is 75% of the experimental result [23], $\Delta H(298^{\circ}K) =$ - 144.0 kcal/mole, and represents a significantly higher

percentage of the experimental result than the calculated ΔH for CH₂ (50.6%).

The Abstraction Reactions

Figure 19.--Coordinates for the Abstraction Reactions

We fixed R and moved the far right proton by varying r until a minimum in the energy was found. At $r = \infty$, the energy of the system was that of the AH molecule at a separation of R plus the energy of $H(^{2}S)$. Neither CH⁻ + H⁺ nor NH + H⁺ were obtained as the lowest asymptotic limit for the abstraction reactions considered. The barrier for the far right hydrogen to leave was just the dissociation energy of A - H - H into AH + H. At R = ∞ , the barrier is D_e for $H_{2}(^{1}\Sigma_{\alpha}^{+})$.

As H_2 approaches A, there will always be a barrier to dissociation as long as the A - H - H energy is below the energy of AH + H at the same A - H separation. An important question is whether the energy of this barrier increases monotonically from the minimum as r increases or whether the energy barrier has a maximum. If A - H - H is bound with respect to AH + H and its energy has risen above energy of AH + H, then there must be a maximum in the barrier to dissociation.

The $C + H_2$ Reaction

We have studied the C + H₂ abstraction reactions for the lowest lying Σ and Π surfaces, ${}^{3}\Sigma^{-}$ and ${}^{3}\Pi$.

At $R = \infty$, the r value at the minimum energy is 1.67 bohrs which is characteristic of $H_2({}^{1}\Sigma_{g}^{+})$. Since both the Σ and Π surfaces correlate with $C({}^{3}P)$ and $H_2({}^{1}\Sigma_{g}^{+})$, the two surfaces are degenerate at $R = \infty$. Their barrier to dissociation is $D_e(H_2; {}^{1}\Sigma_{g}^{+}) = .1192$ a.u. There is no maximum in the barrier to dissociation, except at $r = \infty$.

This description remains essentially unchanged as R decreases until R ~ 4.5 bohrs. The minimum energy with respect to r for both the Σ and Π troughs begins to increase as R descreases from ~ 4.5 bohrs. The energy at the minimum, which is the energy profile along the MERP, is plotted for both surfaces as a function of R in Figure 20. Also plotted as a function of R are (1) the $CH({}^{4}\Sigma^{-})$ + $H({}^{2}S)$ and $CH({}^{2}\Pi)$ + $H({}^{2}S)$ curves for $r = \infty$; and (2) part of the barrier which corresponds to the maximum energies in the dissociation of $CHH({}^{3}\Pi)$ into $CH({}^{2}\Pi)$ + $H({}^{2}S)$. From R ~ 4.5 bohrs, the minimum energies increase very rapidly



Figure 20.--MERP energy profiles for the lowest Σ and Π surfaces of CHH and the Π barrier.

on the Σ surface until R ~ 2.2 bohrs and on the I surface until R ~ 2.55 bohrs. At R ~ 2.2 bohrs, the Σ surface is characterized by no barrier to dissociation into $CH({}^{4}\Sigma^{-})$ + $H({}^{2}S)$. On the I surface, the barrier to dissociation into $CH({}^{2}II)$ + $H({}^{2}S)$ disappears at R ~ 2.55 bohrs. Figures 21 and 22 follow these disappearances by displaying the r dependence of the energy for the Σ surface at R = 2.5, 2.4, 2.3, and 2.2 bohrs and for the I surface at R = 2.8, 2.6, 2.58, and 2.5 bohrs.

From Figure 21, we see that on the Σ surface, the H - H potential well broadens and the energy at minimum rises as R decreases. The Σ MERP moves to larger values of r as R decreases. There is no maximum in the barrier to dissociation for R < 3.0 bohrs for the Σ surface. The <u>very</u> slight barrier at R = 2.2 bohrs in Figure 21 is energetically insignificant, especially at our level of description. At R ~ 2.2 bohrs, the H - H minimum disappears and the system can drop into $CH({}^{4}\Sigma^{-}) + H({}^{2}S)$.

From Figure 22, we see that the II surface behaves similarly, except that it is characterized by a maximum in the barrier to dissociation for the range of R values considered. The location of this maximum moves to smaller values of r as R decreases and at R ~ 2.55 bohrs, coaleses with the H - H minimum. For R less than ~ 2.55 bohrs, the energy of $CHH(^{3}II)$ decreases monotonically to the energy of $CH(^{2}II) + H(^{2}S)$ as r increases.



Figure 21.--Cross sectional cuts of the lowest Σ surface of CHH at R = 2.5, 2.4, 2.3 and 2.2 bohrs.



Figure 22.--Cross sectional cuts of the lowest I surface of CHH at R = 2.8, 2.6, 2.58 and 2.5 bohrs.

The Σ MERP, I MERP and the values of r at the maxima in the I barrier are plotted as a function of R in Figure 23. Both MERP's show a rapid increase toward larger values of r as they approach the R values where they have no barrier to dissociation. When the MERP's reach these R values, they rise vertically to $r = \infty$ since there is no barrier to dissociation.

The overall Σ MERP is the MERP plotted in Figure 23. The barrier in the Σ abstraction reaction is

$$E_{b} = E(CHH \text{ at } R = 2.2 \text{ bohrs}; {}^{3}\Sigma^{-})$$

- E(C; {}^{3}P) - E(H₂; {}^{1}\Sigma_{g}^{+})
= .0673 \text{ a.u.} = 1.83 eV = 42.4 kcal/mole .

For the overall reaction,

$$\Delta H(0^{\circ}K) = E(CH \text{ at } R_{e}; {}^{4}\Sigma^{-}) + E(H; {}^{2}S)$$

- E(C; {}^{3}P) - E(H_{2}; {}^{1}\Sigma_{g}^{+})
= .0649 \text{ a.u.} = 1.77 \text{ eV} = 40.7 \text{ kcal/mole}.

Since the energy of $CH(^{2}\Pi) + H(^{2}S)$ equals the $CHH(^{3}\Pi)$ energy at R ~ 2.65 bohrs, the overall Π MERP will follow the Π MERP in Figure 23 from R = ∞ to R = 2.65 bohrs. At R = 2.65 bohrs, the overall MERP will go from r = 1.98 bohrs to r = ∞ . Since the energies of the maxima in the barrier are essentially equal from R ~ 2.55 to



Figure 23.--The "MERP's" for the lowest Σ and Π surfaces of CHH and the Π barrier.

R ~ 2.7 bohrs, we calculated only one barrier to reaction:

$$E_{b} = \varepsilon_{b}$$
 (CHH at R = 2.65 bohrs; ³II) - E(C; ³P) - E(H₂; ¹ Σ_{g}^{+})
= .0563 a.u. = 1.53 eV = 35.4 kcal/mole

For the overall reaction,

$$\Delta H(0^{\circ}K) = E(CH \text{ at } R_{e}; {}^{2}\Pi) + E(H; {}^{2}S)$$
$$- E(C; {}^{3}P) - E(H_{2}; {}^{1}\Sigma_{g}^{+})$$

= .05165 a.u. = 1.405 eV = 32.4 kcal/mole .

This result is 39.5% larger than the experimental value [22], $\Delta H(0^{\circ}K) = 23.2 \text{ kcal/mole.}$

The $N^+ + H_2$ Reaction

As in the C + H₂ abstraction reactions, all the nuclei were on the Z axis with the N - H and H - H separations represented by R and r, respectively. When N⁺(³P) is infinitely far from H₂, we have R = ∞ and r = 1.67 bohrs (the H₂(¹Σ⁺_g) R_e value) at the minimum energy. When NH⁺(⁴Σ⁻ or ²Π) + H(²S) is formed, we have R = 2.5 bohrs for both states and r = ∞ . In Figure 24, we display the minimum energy as a function of R and r for the Σ and Π surfaces. There is a relatively deep global minimum (1.63 eV with respect N⁺(³P) and H₂(¹Σ⁺_g)) occurs in the Σ surface corresponding to the linear complex [NHH]⁺ in a



Figure 24.--MERP energy profiles for the lowest Σ and Π surfaces of NHH⁺.

 ${}^{3}\Sigma^{-}$ state. This may be compared with the monotonically increasing energy of the ${}^{3}\Sigma^{-}$ state of CHH shown in Figure 20. The binding energy of 1.63 eV for the $[N - H - H]^{+}$ ${}^{3}\Sigma^{-}$ state is about one-third of the corresponding computed value for $NH_{2}^{+}({}^{3}B_{1})$, 4.68 eV. In the complex, the N - H distance is 2.665 bohrs while the H - H separation has increased to 2.13 bohrs; the energy is - 54.7079 a.u.

Also plotted as a function of R, in Figure 24, are the $\text{NH}^+({}^{4}\Sigma^-) + \text{H}({}^{2}\text{S})$ and the $\text{NH}^+({}^{2}\Pi) + \text{H}({}^{2}\text{S})$ curves at $r = \infty$. At R = 2.0 bohrs, well past the $\text{NH}^+({}^{2}\Pi)$ minimum at R = 2.477 bohrs, the energy of the I MERP still lies below the energy of $\text{NH}^+({}^{2}\Pi) + \text{H}({}^{2}\text{S})$. At R = 1.9bohrs, well past the $\text{NH}^+({}^{4}\Sigma^-)$ minimum at R = 2.481 bohrs, the energy of the Σ MERP still lies below the energy of $\text{NH}^+({}^{4}\Sigma^-) + \text{H}({}^{2}\text{S})$. Both states are characterized by a potential which is less favorable to dissociation than their CH₂ counterparts. Since both surfaces indicate that rather large relative increases in energy will be required to stay on the NHH⁺ MERP's until they become equal in energy to the NH⁺ +H curves, we did not extend the Σ or I MERP to R values less than 1.9 and 2.0 bohrs, respectively.

Since the NH⁺ ${}^{4}\Sigma^{-}$ and ${}^{2}\Pi$ minima are both close to R = 2.5 bohrs, we focused our attention on the section of both surfaces at R = 2.5 bohrs. This decision was also influenced by the facts that the [N - H - H]⁺ complex has its minimum energy near R = 2.5 bohrs, and the energy along the II MERP increased quite rapidly for R < 2.5 bohrs.

Cross sectional cuts, as a function of r with R = 2.0, 2.25 and 2.5 bohrs, are plotted in Figures 25 and 26 for the Σ and Π surfaces, respectively. At R = 2.5 bohrs, the energy increases monotonically as $r \neq \infty$ on both surfaces to $NH^+ + H$. We have assumed that the curves for the other values of R behave similarly.

In Figure 25, the energies at the Σ minima rise rapidly, while there is only a small shift to larger r values at the minima, as R decreases. If we assume that the interpolated portions of Figure 25 are correct, then the barrier to dissociation decreases rather slowly from .0612 a.u. at R = 3.0 bohrs to .0528 a.u. at R = 2.5 bohrs to .0390 a.u. at R = 2.0 bohrs. At R = 1.9 bohrs, the barrier is ~ .03 a.u., and the rate of decrease of the barrier seems to be slowing. When the barrier does go to zero, it will be at a high energy compared to the scale of Figure 25.

In Figure 26, the energy and the H - H separation at the Π minima rise rapidly as R decreases. If we assume that the interpolated portions of Figure 26 are correct, then the barrier is decreasing rapidly from .0253 a.u. at R = 3.0 bohrs to .0073 a.u. at R = 2.5 bohrs to .0022 a.u. at R = 2.0 bohrs and vanishes at R ~ 1.8 bohrs and a relatively high energy.



Figure 25.--Cross sectional cuts of the lowest Σ surface of NHH⁺ at R = 2.0, 2.25 and 2.5 bohrs.



Figure 26.--Cross sectional cuts of the lowest I surface of NHH⁺ at R = 2.0, 2.25 and 2.5 bohrs.

In Figure 27 the Σ and Π MERP's are plotted as a function of R. The rate of increase in the Σ MERP is fairly constant from R ~ 5.0 to R ~ 1.9 bohrs. The Σ MERP shows no tendency to increase rapidly as the CH₂ MERP's did. The Π MERP increases rapidly and linearly for 2.0 < R < 3.0 bohrs. For the R values considered, neither MERP shows a very rapid increase to $r = \infty$ as the CH₂ MERP's did just prior to their barriers to dissociation going to zero.

The barrier to reaction is zero for the Σ surface. For the Σ abstraction reaction, we calculate

$$\Delta H(0^{\circ}K) = E(NH^{+} \text{ at } R = 2.5; {}^{4}\Sigma^{-}) + E(H; {}^{2}S)$$

- $E(N^{+}; {}^{3}P) - E(H_{2}; {}^{1}\Sigma_{g}^{+})$
= - .0061 a.u. = - .165 eV = - 3.8 kcal/mole .

This result is only 27.3% of the experimental value [23], $\Delta H(298^{\circ}K) = -13.9 \text{ kcal/mole.}$

In our reaction scheme, $NHH^+(^{3}\Sigma^-)$ is a reaction intermediate, and $NH^+(^{4}\Sigma^-) + H(^{2}S)$ are the products. Since the global minimum on the Σ surface corresponds to the bound $[N - H - H]^+$ complex, the $[N - H - H]^+$ complex might be described as the product where $E_{\rm b} = 0$ and $\Delta H(0^{\circ}K) =$ - .0589 a.u. = 1.605 eV = - 36.8 kcal/mole. The barrier to dissociation of $NHH^+(^{3}\Sigma^-)$ into $NH^+(^{4}\Sigma^-) + H(^{2}S)$ at R = 2.5 bohrs is 33 kcal/mole. Since the prediction of



Figure 27.--The "MERP's" for the lowest Σ and Π surfaces of NHH⁺.

the products and their relative probabilities of being realized requires a detailed consideration of the dynamics of the system, we can say little more.

Since there is no maximum (except at $r = \infty$) in the barrier to reaction on the I surface,

$$E_{b} = \Delta H(0^{\circ}K) = E(NH^{+} \text{ at } R = 2.5; {}^{2}\Pi) + E(H; {}^{2}S)$$
$$- E(N^{+}; {}^{3}P) - E(H_{2}; {}^{1}\Sigma_{g}^{+})$$

and $E_{b} = \Delta H(0^{\circ}K) = .0125 \text{ a.u.} = .34 \text{ eV} = 7.85 \text{ kcal/mole}$.

Discussion

The experimental values for the ΔH of reaction for the lowest surfaces which correspond to $NH_2^+({}^{3}B_1)$, $CH_2({}^{3}B_1)$, $CH({}^{2}\Pi) + H({}^{2}S)$ and $NH^+({}^{4}\Sigma^-) + H({}^{2}S)$, are - 144.0, - 77.33, 23.2 and - 13.9 kcal/moles, respectively, while our corresponding computed values are - 108.0, - 39.15, 32.4 and - 3.8 kcal/mole. There seems to be correlation between the magnitude of the experimental values and our ability to predict them. As the magnitude of ΔH_{expt} increases, the quantity $|(\Delta H_{expt}$ - $\Delta H_{here})/\Delta H_{expt}|$ also increases. The smaller the energy difference between the reactants and products, the less sensitive our predictive capabilities become at our level of description.

The effect of increased nuclear charge in the insertion reactions, as discussed earlier, could be seen by a large decrease in the barrier to reaction for NH_2^+ relative to CH2. However, a sizable barrier was still inferred for the true NH_2^+ surface. The barrier to reaction for the C + H₂ Σ and Π abstraction reactions were 42.25 and 35.4 kcal/mole, while the NH_2^+ analogs were 0 and 7.85 kcal/mole, respectively. Even though the differences in these barriers are about the same or less than the difference in the insertion reactions, the effect of increased nuclear charge appears to be more significant in the abstraction reactions. Since the H must dissociate from an NH⁺, the charge in the NHH⁺ system seemed to have a profound effect on the NHH⁺ abstraction reactions. The Σ and Π NHH⁺ barriers do not reflect this, since we computed them at the lowest possible barrier to reaction. The nature of the NHH⁺ Σ and I "MERP's" do reflect this effect. Nevertheless, we suggest there will be barriers in the true $C + H_2$ abstraction surfaces and little or no barriers in the true N^+ + H₂ abstraction surfaces.

In order to compare abstraction vs. insertion, we will use the results for the Σ abstraction reactions, since they correlate directly with CH_2 in its ground ${}^{3}B_1$ state. Both abstraction reactions have barriers to reaction which are about 40 kcal/mole less than the corresponding barriers in the insertion reactions. A straightforward comparison using the barriers to reaction predicts the abstraction mechanisms to be preferred in both systems.

There is not very much experimental information on these reactions. There are two previous experimental studies which tend to suggest by comparison with our results that the description of these reactions is more complex than the constrained systems we considered.

Braun, Bass, Davis and Simmons [24] considered the reaction of $C({}^{3}P)$ with H_{2} to form CH_{2} in an inert argon medium. The $C({}^{3}P)$ was generated by the flash photolysis of $C_{2}O_{3}$. At high total pressures, where the argon pressure was 7×10^{4} Nm⁻² and the H_{2} pressure was of the order of 1×10^{3} Nm⁻², they described the reaction as being highly efficient and characterized by having a high collision efficiency estimated to be within 1 and .1 They concluded that the reaction had a very low activation energy. Since our results suggest that the barrier to reaction on lowest true ${}^{3}B_{1}$ surface describing $C + H_{2} + CH_{2}$ is substantial, there may well be a path to CH_{2} in its ground ${}^{3}B_{1}$ state from $C({}^{3}P)$ and $H_{2}({}^{1}\Sigma_{g}^{+})$ that avoids the predicted barrier.

Fair and Mahan [25] have studied the $N^+({}^{3}P) + H_2({}^{1}\Sigma_{g}^+) \rightarrow NH^+ + H$ reaction using crossed beams. At relative energies near and below 1 eV, they interpret

their results as predicting a long-lived collision complex. At relative energies above 2 eV, they find no evidence of a long-lived complex and describe the reaction as proceeding by a direct interaction mechanism. They associated the long-lived complex with the system visiting the deep ground state ${}^{3}B_{1}$ potential well of NH $_{2}^{+}$. The correlation diagram they presented predicted only a slight minimum of ~ .5 eV with respect to N⁺(${}^{3}P$) + H $_{2}({}^{1}\Sigma_{g}^{+})$ for NHH⁺(${}^{3}\Sigma^{-}$) in C_{∞ V} geometry. Since our surface predicts the existence of a bound (1.63 eV) [N - H - H]⁺ complex, this ${}^{3}\Sigma^{-}$ state may also result in a long-lived complex.

The NHH⁺(${}^{3}\Sigma^{-}$) may also provide a low energy path to NH₂⁺(${}^{3}B_{1}$). In the NH₂⁺ insertion reaction (C_{2V}), the barrier is encountered until R decreases to ~ 3 bohrs. From R at ~ 3 bohrs to the global minimum, the energy is monotonically decreasing. In C_{wV} geometries, the energy decreases monotonically as R decreases to ~ 2.7 bohrs and then increases as R decreases from ~ 2.7 bohrs. The NH₂⁺ system may find a considerable potential energy constraint to be in a C_{wV} geometry until R has decreased to this range and thereby avoid the large barrier in a C_{2V} geometry. At R from ~ 2.7 bohrs or less, the potential energy may dictate a rotation of the H₂ to yield NH₂⁺(${}^{3}B_{1}$) whose energy then decreases rapidly.

The rotation of H_2 to yield a system with a C_s symmetry could be important in explaining the discrepancy between our prediction and the results of Braun et al. The essence of this theory was discussed by Fair and Mahan. In order to find a direct interaction mechanism for the higher relative energies leading to NH^+ + H, they noted that if the system is initially in C_{2V} geometry, a rotation of the H_2 gives the system C_s symmetry. The ${}^{3}B_1$ and ${}^{3}A_{2}$ states arising from N⁺(${}^{3}P$) and H₂(${}^{1}\Sigma_{\sigma}^{+}$) become ${}^{3}A$ " states which are degenerate and should exhibit an avoided crossing. This is shown in the schematic C_{2V} correlation diagram in Figure 28. The avoided crossing of the ${}^{3}B_{1}$ surfaces we characterized is indicated. The avoided crossing of the ³A" surfaces is inferred by the dotted lines. Fair and Mahan proposed a diadiabatic surface jump so as to avoid the long-lived $NH_2^+({}^{3}B_1)$ complex at higher relative energies.

The results of Braun <u>et al.</u> may well result if (1) the $C({}^{3}P)$ and $H_{2}({}^{1}\Sigma_{g}^{+})$ initially form $CH_{2}({}^{3}A_{2})$ before the ${}^{3}A$ " avoided crossing, (2) rotate into C_{S} geometry, and (3) adiabatically via the avoided crossing end up on the portion of the lowest ${}^{3}A$ " surface which leads to $CH_{2}({}^{3}B_{1})$ when rotation of the H₂ occurs again. This path should provide a much lower barrier than staying in a C_{2V} geometry when forming $CH_{2}({}^{3}B_{1})$.



Figure 28.--N⁺ + H₂ correlation diagram (C_{2V}).

Since the ${}^{3}A_{2}$ state also correlates directly with the lowest ${}^{3}\Pi$ of AHH and therefore with the lowest ${}^{2}\Pi$ state of AH, the rotation of H₂ into C_S geometries provides a number of possible paths to AH + H and AH₂(${}^{3}B_{1}$).

The determination of the CH_2 and NH_2^+ potential energy surfaces for C_S geometries would be very important in exploring the hypotheses presented. The apparent complex nature of chemical reactions for even these relatively simple systems presents a formidable problem. Our increasing ability to understand chemical reactions has brought a very important dimension of chemistry into better focus.

CHAPTER II

THE ³A₂ AND ³B₂ STATES OF CH₂

In 1961, Herzberg [1] published an interpretation of the UV spectrum of CH_2 based on a linear or nearly linear ground state. In this interpretation, the diffuse band at 1415 Å was assigned to the ${}^{3}\Sigma_{u}^{-} + {}^{3}\Sigma_{\sigma}^{-}$ transition.

In 1971, Herzberg and Johns [2] proposed a new interpretation of the 1415 Å band which was consistent with more recent experimental and theoretical predictions of a ground ${}^{3}B_{1} ({}^{3}\Sigma_{g}^{-}$ in $D_{\infty h})$ state. As Herzberg noted in his earlier paper, the K' = 0 + K" = 0 subbands could be the result of a bent-bent type transition. However, the absence of the higher subbands K' = 1 + K" = 1, K' = 2 + K" = 2, etc. favored a linear-linear type transition. On the other hand, the absence of these higher subbands could be the result of heterogeneous predissociation of an excited ${}^{3}A_{2}({}^{3}\Sigma_{u}^{-}$ in $D_{\infty h})$ state by a ${}^{3}B_{2}$ state. The 1415 Å band may then be ascribed to a ${}^{3}A_{2} + {}^{3}B_{1}$ transition.

The predissociation mechanism would involve a radiationless transition from the discrete vibrational levels of the ${}^{3}A_{2}$ state to the continuous levels of the ${}^{3}B_{2}$ state. This implies that the continuous levels be

energetically appropriate so as to overlap with the discrete levels and lead to dissociation.

Since an electronic state of different symmetry (B_2) is responsible for the predissociation, it will be heterogeneous. The total symmetry of the wave function will be the direct product of the symmetry of the electronic and rotational states. For non-linear CH₂ rotating about the Y' axis (see Figure 29), the rotational wave function is of B_1 symmetry. The total symmetry of the rotating excited ${}^{3}A_2$ state for $K \neq 0$ is A_2^{el} & $B_1^{rot} = B_2$, while that of the non-rotating state (<u>i.e.</u>, K = 0) is A_2^{el} & $A_1^{rot} = A_2$.

In view of the ad-hoc nature of this interpretation and its significance in determining the geometry of the lowest ${}^{3}B_{1}$ state of CH_{2} , we attempted to confirm it theoretically by constructing representations of the excited states of CH_{2} of ${}^{3}A_{2}$ and ${}^{3}B_{2}$ symmetry.

The States Considered

The SCF function describing the ground ${}^{3}B_{1}$ state of CH₂ is characterized by the orbital occupancy $1a_{1}^{2} 2a_{1}^{2}$ $1b_{2}^{2} 3a_{1}^{1} 1b_{1}^{1}$ (3). The $2a_{1}$ and $1b_{2}$ orbitals are responsible for virtually all of the bonding in CH₂. On the basis of a preliminary CI calculation, we found that a basis set with orbitals up to principal quantum number N = 2 on the carbon atom resulted in CI wave functions whose





Figure 29.--Molecular orientations for linear and non-linear CH₂.

energies predicted only one significant ${}^{3}A_{2}$ state. The predominant configuration in the wave function describing this ${}^{3}A_{2}$ state was $la_{1}^{2} 2a_{1}^{2} lb_{2}^{1} 3a_{1}^{2} lb_{1}^{1}$ (4). Harrison and Allen [26], by using valence-bond (CI) wave functions, found that the energy of this lowest ${}^{3}A_{2}$ state decreased monotonically with $\theta_{\rm HCH}$ from $\theta_{\rm HCH} = 180^{\circ}$. This non-Rydberg state is predicted to be unbound with respect to $C({}^{3}P)$ and $H_{2}({}^{1}\Sigma_{g}^{+})$; it could not be the state responsible for the observed 1415 Å band.

Harrison and Allen also predicted a minimum in the energy (vs. $\theta_{\rm HCH}$) for the lowest ${}^{3}B_{2}$ state, making it unlikely that it is the state required for heterogeneous predissociation. Since the main thrust of our work was concerned with the existence of the appropriate ${}^{3}A_{2}$ state, we did not attempt to find a mechanism for predissociation.

Since there are no energetically appropriate non-Rydberg ${}^{3}A_{2}$ and ${}^{3}B_{2}$ states, we decided to consider the N = 3 Rydberg states of ${}^{3}A_{2}$ and ${}^{3}B_{2}$ CH₂. For comparison, we also considered the non-Rydberg ${}^{3}A_{2}$ state (4) and the non-Rydberg ${}^{3}B_{2}$ state

$$la_1^2 2a_1^2 lb_2^1 3a_1^1 lb_1^2$$
. (5)

In order to leave the CH_2 bonds intact, we considered states arising from excitations of an electron from the $3a_1$ and $1b_1$ orbitals in (3). Figure 29 gives
the molecular orientations for linear and non-linear CH_2 . Table 1 lists the atomic functions and their symmetries. The 6 gaussian d functions d_X^2 , d_{XY} , d_{XZ} , d_Y^2 , d_{YZ} , and d_Z^2 have been transformed into a 3s function $d_X^2 + d_Y^2 + d_Z^2$ and five 3d functions: $2d_Y^2 - d_X^2 - d_Z^2$, $d_X^2 - d_Z^2$, $d_X^2 - d_Z^2$, d_X^2 , and d_{YZ} .

c _{2V}	symmetry	$\mathtt{D}_{\infty \mathbf{h}}$ symmetry	Orbital type
	a ₁	٥d	s, H ₁ + H ₂
	^b 2	σu	$p_{Y}, H_{1} - H_{2}$
	^b 1	πu	PX
	a _l	^π u	Pz
	a ₁	٥g	$2d_{y}^{2} - d_{x}^{2} - d_{z}^{2}$
	a ₂	πg	d _{XY}
	^b 2	πg	dyz
	b ₁	م ع	dxz
	a _l	δg	$d_{\chi}^2 - d_{\chi}^2$

Table 1.--Orbital symmetries for CH2.

Four ${}^{3}A_{2}$ and four ${}^{3}B_{2}$ states were studied, one non-Rydberg and 3 Rydberg states of each symmetry. These 8 states are listed in Table 2 with their electron configurations and the excitations which generated them from the ground ${}^{3}B_{1}$ electron configuration. Also included is

Table 2.--Electron configurations for the eight ${}^{3}A_{2}$ and ${}^{3}B_{2}$ states of CH₂ generated by single excitations from the ground ${}^{3}B_{1}$ state. The major atomic function component of the orbitals involved in the excitations.

State	Electron configuration	Excitation
1 ³ A ₂ >	$la_1^2 2a_1^2 lb_2^2 3a_1^1 la_2^1$	$lb_1 \rightarrow la_2$
2 ³ A ₂ >	$la_1^2 2a_1^2 lb_2^2 lb_1^1 2b_2^1$	$3a_1 \rightarrow 2b_2$
3 ³ A ₂ >	$la_1^2 2a_1^2 lb_2^2 lb_1^1 3b_2^1$	$3a_1 \rightarrow 3b_2$
4 ³ A ₂ >	$la_1^2 2a_1^2 lb_2^1 3a_1^2 lb_1^1$	$lb_2 \rightarrow 3a_1$
1 ³ B ₂ >	$la_1^2 2a_1^2 lb_2^2 3a_1^1 2b_2^1$	$lb_1 \rightarrow 2b_2$
2 ³ B ₂ >	$la_1^2 2a_1^2 lb_2^2 lb_1^1 la_2^1$	$3a_1 \rightarrow 1a_2$
3 ³ B ₂ >	$la_1^2 2a_1^2 lb_2^2 3a_1^1 3b_2^1$	$lb_1 \rightarrow 3b_2$
4 ³ B ₂ >	$la_1^2 2a_1^2 lb_2^1 3a_1^1 lb_1^2$	$lb_2 \rightarrow lb_1$
lb ₂	~ 2p _Y 2b ₂ ~	3py
^{3a} 1	~ 2p _Z 3b ₂ ~	^{3d} yz
lbl	~ 2p _X la ₂ ~	^{3d} xy

a list of the atomic functions which are the major components in the orbitals involved in the excitations. The $|4 \ {}^{3}A_{2}\rangle$ and $|4 \ {}^{3}B_{2}\rangle$ states are the non-Rydberg states. The corresponding linear states and their electron configurations are listed in Table 3.

Non-linear state	Linear state	Configuration
1 ³ A ₂ >	³ ⁴ ³ ² ^u	$\sigma_g^2 \sigma_g^2 \sigma_u^2 \pi_u^1 3d\pi_g^1$
2 ³ A ₂ >	з _П д	$\sigma_{g}^{2} \sigma_{g}^{2} \sigma_{u}^{2} \pi_{u}^{1} 3p\sigma_{u}^{1}$
3 ³ A ₂ >	³ Δ _u , ³ Σ _u	$\sigma_g^2 \sigma_g^2 \sigma_u^2 \pi_u^1 3d\pi_g^1$
4 ³ A ₂ >	з _п д	$\sigma_{g}^{2} \sigma_{g}^{2} \sigma_{u}^{1} \pi_{u}^{3}$
1 ³ B ₂ >	з _п д	$\sigma_g^2 \sigma_g^2 \sigma_u^2 \pi_u^1 3p\sigma_u^1$
2 ³ B ₂ >	³ Δ _u , ³ Σ _u	$\sigma_g^2 \sigma_g^2 \sigma_u^2 \pi_u^1 3d\pi_g^1$
3 ³ B ₂ >	³ Δ _u , ³ Σ _u	$\sigma_g^2 \sigma_g^2 \sigma_u^2 \pi_u^1 3d\pi_g^1$
4 ³ B ₂ >	з ^{II} а	$\sigma_{g}^{2} \sigma_{g}^{2} \sigma_{u}^{1} \pi_{u}^{3}$

Table 3.--The linear states of CH₂ and their electron configurations.

Our wave functions for these states were linear combinations of two Slater determinants which resulted in spin eigenfunctions. Since our basis functions did not have spherical harmonics as angular functions, our wave functions for the linear geometry were not eigenfunctions of the \hat{L}_{y} operator (see Figure 29). The appropriate linear combinations which do have the correct rotational symmetry about the Y axis are

$${}^{3}\Delta_{u} = |2 {}^{3}B_{2} \rangle - |3 {}^{3}B_{2} \rangle$$

$${}^{3}\Delta_{u} = |1 {}^{3}A_{2} \rangle + |3 {}^{3}A_{2} \rangle$$

$${}^{3}\Sigma_{u}^{+} = |2 {}^{3}B_{2} \rangle + |3 {}^{3}B_{2} \rangle$$

$${}^{3}\Sigma_{u}^{-} = |1 {}^{3}A_{2} \rangle - |3 {}^{3}A_{2} \rangle .$$
(6)

The following pairs of states were degenerate at $\theta_{\rm HCH}$ 180°: $|1 \ {}^{3}A_{2}\rangle$ and $|3 \ {}^{3}A_{2}\rangle$, $|2 \ {}^{3}B_{2}\rangle$ and $|3 \ {}^{3}B_{2}\rangle$, $|2 \ {}^{3}A_{2}\rangle$ and $|1 \ {}^{3}B_{2}\rangle$, and $|4 \ {}^{3}A_{2}\rangle$ and $|4 \ {}^{3}B_{2}\rangle$. If we had used the linear combinations in equation (6), the Δ states would have been degenerate at $\theta_{\rm HCH}$ = 180°, while the Σ states would not have been.

Finally, as a reference from which we may calculate excitation energies, the ground ${}^{3}B_{1}$ state (3) was characterized.

The Basis Set

A minimal basis set of atomic functions was supplemented by a set of 3p and 3d atomic functions on the carbon atom. The ls, 2s and 2p atomic functions on the carbon atom and the ls function on the hydrogen atom were linear combinations of 3 gaussian functions. The coefficients were determined by Hehre, Stewart and Pople [27] by a least squares fit to Slater-type functions. The 3p and 3d atomic function expansions were characterized by Stewart [28] in the same fashion. The expansions were determined with the Slater exponent, ζ , set equal to 1. The exponents in the expansion must be scaled by the ζ appropriate for the atom involved. The values of ζ for the N = 1 and N = 2 atomic functions on carbon and the N = 1 atomic function on hydrogen were the standard molecular values for an average molecular environment given by Hehre, Stewart and Pople [27]. There are no reported values of ζ_{3p} and ζ_{3d} for the carbon atom. We determined ζ_{3p} and ζ_{3d} by minimizing the energy of excited states of the carbon atom.

There is no particular excited state of carbon which would have allowed us to calculate the one best value for ζ_{3p} and ζ_{3d} for all of the ${}^{3}A_{2}$ and ${}^{3}B_{2}$ states involved. Since all of our Rydberg states were triplets with an unpaired N = 2 electron and an unpaired N = 3 electron, we decided to consider the ${}^{3}P$, ${}^{3}D$ and ${}^{3}F$ states arising from the carbon atom electron configuration $1s^{2}$ $2s^{2} 2p^{1} 3d^{1}$ in the determination of ζ_{3d} . Similarly, the ${}^{3}P$ and ${}^{3}D$ states which arise from the configuration $1s^{2}$ $2s^{2} 2p^{1} 3p^{1}$ were used in the determination of ζ_{3p} .

The energies were determined by the CI method. Orthogonal atomic functions, which were generated by the Gram-Schmidt technique by means of a FORTRAN program [7], are listed in Table 4. Of the 36 determinants which arise from $1s^2 2s^2 2p^1 3p^1$, only two were required to

Table 4.--The orthogonal Gram-Schmidt C atom basis functions.

$$\begin{split} \phi_{1} &= x_{1s} \\ \phi_{2} &= x_{2s} - ax_{1s} \\ \phi_{3} &= x_{2p_{X}} \\ \phi_{4} &= x_{2p_{Y}} \\ \phi_{5} &= x_{2p_{Z}} \\ \phi_{6} &= x_{3p_{X}} - bx_{2p_{X}} \\ \phi_{7} &= x_{3p_{Y}} - bx_{2p_{Y}} \\ \phi_{8} &= x_{3p_{Z}} - bx_{2p_{Z}} \\ \phi_{9} &= x_{3s} - cx_{1s} - ex_{2s} \\ \phi_{10} &= 2x_{3d_{Z}2} - x_{3d_{X}2} - x_{3d_{Y}2} \\ \phi_{11} &= x_{3d_{X}2} - x_{3d_{Y}2} \\ \phi_{12} &= x_{3d_{XY}} \\ \phi_{13} &= x_{3d_{XZ}} \\ \phi_{14} &= x_{3d_{YZ}} \\ \end{split}$$
where $x_{3s} &= x_{3d_{X}2} + x_{3d_{Y}2} + x_{3d_{Z}2} \\ a &= \\ b &= \\ c &= \frac{ac_{1} - c_{2}}{1 - a^{2}} \end{split}$

Table 4.--Continued

$$e = \frac{ac_{2} - c_{1}}{1 - a^{2}}$$

$$c_{1} = \frac{3 < \chi_{1s} | \chi_{3d_{x}2} > 2}{c_{2}}$$

$$c_{2} = \frac{3 < \chi_{2s} | \chi_{3d_{x}2} > 2}{2}$$

represent the $M_L = 0$, $M_S = 0$ components of the ${}^{3}P$ and ${}^{3}D$ states. Of the 60 determinants which arise from $1s^{2} 2s^{2}$ $2p^{1} 3d^{1}$, only five were required to represent the $M_S = 0$, $M_L = 0$ components of the ${}^{3}P$, ${}^{3}D$ and ${}^{3}F$ states.

The minimum energy for the ³P state was at $\zeta_{3p} = .48$, and for the ³D state it was at $\zeta_{3p} = .46$. We chose $\zeta_{3p} = .47$.

The minimum energy for the ${}^{3}P$, ${}^{3}D$ and ${}^{3}F$ states were at $\zeta_{3d} = .33$, .35 and .34, respectively. We chose $\zeta_{3d} = .34$, which Coulson and Stamper [31] also found in their study of the Rydberg levels of linear CH₂.

The Method of Calculation

The wave functions and energies of the four ${}^{3}A_{2}$, four ${}^{3}B_{2}$ and ground ${}^{3}B_{1}$ states were constructed by solving the HFR - OS - SCF equations outlined in Appendix I. The required one- and two-electron integrals over atomic functions were generated by the IBMOL program [6]. The HFR - OS -SCF routine was part of the POLYATOM system [29]. Our intention was to qualitatively represent the features of these states and determine which are bound. To this end, we fixed the CH bond length in the ${}^{3}A_{2}$ and ${}^{3}B_{2}$ states at $R_{CH} = 2.2$ bohrs, the value used by O'Neil, <u>et al.</u> [30]. The HCH angle was varied from 90 to 180°. Although we did not determine the global energy minimum for the surfaces, by varying the angle we were able to predict whether a minimum in the energy existed. A preliminary investigation of the first, second, and fourth ${}^{3}A_{2}$ states by means of a CI wave function revealed that they were bound with respect to a variation of R_{CH} from ~ 2.1 to ~ 2.3 bohrs, at $\theta_{HCH} = 120^{\circ}$.

Since previous calculations on CH_2 (${}^{3}B_1$) predicted $\theta_{\rm HCH} \sim 130^{\circ}$ and $R_{\rm CH} \sim 2.1$ bohrs, we fixed $R_{\rm CH}$ at 2.1 bohrs and calculated the energy of the ${}^{3}B_1$ state at $\theta_{\rm HCH} = 120$, 130 and 140°.

The Results

The calculated energies of the ${}^{3}A_{2}$ and ${}^{3}B_{2}$ states at $\theta_{\rm HCH} = 90$, 120, 150 and 180° and the ${}^{3}B_{1}$ state at $\theta_{\rm HCH} = 120$, 130 and 140° are plotted in Figure 30. The ${}^{3}B_{1}$ minimum energy was found by interpolation to be at $\theta_{\rm HCH} = 124°$ with an energy of - 38.4430 a.u.

Since the curves in Figure 30 are for SCF states, curves for the same symmetry will cross. The true curves will be those which result when avoided crossings (dotted lines) are included.



Figure 30.--The ${}^{3}A_{2}$, ${}^{3}B_{2}$ and ${}^{3}B_{1}$ energy curves.

Herzberg's prediction [2] resulting in the bent triplet ground state requires that the excited triplet is bent (~ 125°) and ~ 8.75 eV above the ground state. Our curves, when avoided crossings are used, indicate three ${}^{3}A_{2}$ states with minimum energies at ~ 125°. These ${}^{3}A_{2}$ states have angles of 113, 120 and 127° with 0 - 0 transition energies of 7.53, 8.30 and 8.86 eV, respectively. The quality of our representation precludes any quantitative predictions or assignments; however, we do predict three likely candidates for the required bound ${}^{3}A_{2}$ state. The existence of these bent ${}^{3}A_{2}$ states lends support to Herzberg's hypothesis.

The nature of our results precludes any definite statement concerning an appropriate ${}^{3}B_{2}$ state to cause predissociation. There is a bound ${}^{3}B_{2}$ state at $\theta_{\rm HCH} = 180^{\circ}$ which has a maximum energy at $\theta_{\rm HCH} \sim 120^{\circ}$. Since this ${}^{3}B_{2}$ state is unbound for $\theta_{\rm HCH} \sim 120^{\circ}$ and has a favorable location energetically, it may be the required ${}^{3}B_{2}$ state.

Discussion

The existence of 3 bound ${}^{3}A_{2}$ states with appropriate energies and angles so as to be consistent with Herzberg's prediction has been demonstrated. The existence of an appropriate ${}^{3}B_{2}$ state was neither demonstrated nor precluded.

An extension of this work could (1) use a better quality basis set, (2) consider the full surfaces around the global minimum and include C_{g} geometries, and (3) include correlation effects by means of a CI calculation. The first and second points would be controlled by simple economic and time factors. The third aspect is, however, more complicated. If an SCF calculation were used to generate the molecular orbitals for the CI, the choice of which state would be appropriate for generating the SCF orbitals would be difficult since there are a number of avoided crossings and the ${}^{3}A_{2}$ states are very close to each other. Even for a minimal basis set calculation, the CI expansion would have to be truncated. The selection of a single set of configurations to represent the various ${}^{3}A_{2}$ states would be difficult. An iterative natural orbital scheme or a multi-configuration SCF approach should provide a costly but realistic solution.

APPENDIX I

THE THEORY

The Schrödinger Equation

This thesis deals with the approximate solution of the Schrödinger equation for the CH_2 and NH_2^+ systems and is based on three general approximations: (1) the individual system is not subject to any external forces, (2) the Born-Oppenheimer approximation is used, and (3) a non-relativistic formalism is used where all particles are assumed to be point masses.

The first approximation implies that there are no applied external fields such as magnetic or electric fields. Further, it implies that there are no interactions between similar systems. This approximation is tantamount to saying that we are considering an isolated system. The potential energy of our system may be written with no time dependence. For a general M particle system, the non-relativistic time-dependent Schrödinger equation is

$$\lambda_{\mathbf{T}} \Psi = \mathbf{i} \mathbf{T} \, \frac{\partial}{\partial \mathbf{t}} \, \Psi \,, \tag{7}$$

where

 $\Psi = \Psi(\dot{r}_1, \dot{r}_2, ..., \dot{r}_M, t)$,

$$\hat{\nabla}_{T} = \hat{T} + \hat{V} ,$$

$$\hat{T} = \left(-\frac{\pi^{2}}{2}\right) \sum_{\substack{\Sigma \\ i=1}}^{M} \left(\frac{\nabla_{i}^{2}}{m_{i}}\right) = \text{kinetic energy operator } ,$$

$$\hat{V} = \hat{V} (\vec{r}_{1}, \vec{r}_{2}, \dots, \vec{r}_{M}, t) = \text{potential energy}$$
operator .

Unless otherwise stated, we will use atomic units. The following conversions are used:

(2) 1 bohr =
$$.529177 \times 10^{-8}$$
 cm, and

(3) mass of the electron = electronic charge = \overline{h} = 1.

Since \hat{V} is not a function of time, equation (7) results in the time-independent non-relativistic Schrödinger equation,

$$\hat{c}_{\mu}\psi = E_{\mu}\psi , \qquad (8)$$

where

$$\psi = \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_M) ,$$

and

$$\Psi = \psi e^{-iE} T^{t}$$

The energy of the system is postulated to be E_{T} .

The Born-Oppenheimer approximation allows us to solve for the electronic motion with the assumption that the nuclei are in fixed positions. Let the subscripts α,β,\ldots denote nuclei and i,j,... denote electrons. The Hamiltonian for a 2N electron system may be written as

 $\hat{v}_{T} = \hat{v}_{E} + \hat{v}_{N} + T_{N}$,

where
$$\hat{\nabla}_{E} = (-\frac{1}{2}) \sum_{i}^{2N} \nabla_{i}^{2} + \sum_{i < j}^{2N} (\frac{1}{r_{ij}}) - \sum_{i}^{2N} \sum_{\alpha} (\frac{z_{\alpha}}{r_{i\alpha}})$$
,
 $\hat{\nabla}_{N} = \sum_{\alpha < \beta}^{M-2N} (\frac{z_{\alpha}}{r_{\alpha\beta}})$,
 $\hat{T}_{N} = (-\frac{1}{2}) \sum_{\alpha}^{M-2N} (\frac{\nabla_{\alpha}^{2}}{r_{\alpha\beta}})$.

The Born-Oppenheimer approximation allows us to separate the electronic and nuclear coordinates, and we may write $\psi \simeq \psi_{\rm E} \psi_{\rm N} = \psi_{\rm E} (\vec{r}_{\rm i}; \vec{r}_{\rm a}) \psi_{\rm N} (\vec{r}_{\rm a})$ where $\psi_{\rm E}$ depends parametrically on the nuclear coordinates. Equation (8) breaks up into a purely electronic Schrödinger equation,

$$\widehat{\boldsymbol{\mathcal{A}}}_{\mathbf{E}} \boldsymbol{\psi}_{\mathbf{E}} = \mathbf{E}_{\mathbf{E}} \boldsymbol{\psi}_{\mathbf{E}} , \qquad (9)$$

where $E_E = purely$ electronic energy and a Schrödinger equation for the nuclear motion,

> $\hat{}_{N}\psi_{N} = E_{T}\psi_{N} ,$ (10)

where $\hat{\mathcal{H}}_{N} = \hat{T}_{N} + \hat{E}$,

 $\hat{E} = E_E + \hat{V}_N = \text{electronic energy.}$ and

The electrons move much faster than the more massive nuclei and adjust rapidly to any nuclear changes. Thus, the electronic energy is a smoothly varying function of the nuclear parameters and provides the potential which governs the nuclear motions in equation (10).

Our work will be concerned with the approximate solution of the purely electronic Schrödinger equation (9) which will henceforth be called the Schrödinger equation and be written as

$$\widehat{\forall}\psi = \mathbf{E}_{\mathbf{E}}\psi , \qquad (11)$$

where $\hat{\nabla} \equiv \hat{\Psi}_{E}$ and $\psi \equiv \psi_{E}$

By the word energy, we will mean the electronic energy, E. Equation (11) is solved by fixing the nuclear coordinates and solving for ψ and E_E for 2N electrons in the field of the fixed nuclei. Since \hat{V}_N is a constant, we simply add it onto E_E to find E.

Configuration Interaction

In general, the exact solution of the Schrödinger equation (11), for a system with one electron is

$$\psi(\vec{r}) = \sum_{i=1}^{\infty} a_i^{i} \phi_i^{i}(\vec{r})$$
(12)

where the set of functions Φ_{i}^{\prime} is complete. In order to account for electron spin, we redefine our expansion (12) in terms of a complete set of spin functions or spin-orbitals, Φ_{i}^{\prime} , which are products of spatial and spin functions. We write

$$\psi = \sum_{i=1}^{\infty} a_i \Phi_i$$
(13)

with $\Phi_1 = \Phi_1' \alpha$, $\Phi_2 = \Phi_1' \beta$, $\Phi_3 = \Phi_2' \alpha$, etc. Equation (13), which defines a configuration interation (CI) wave function, can be extended to a 2N electron system. The result is

$$\psi(\vec{r}_{1}, \vec{r}_{2}, \dots, \vec{r}_{2N}) = \sum_{i_{1}=1}^{\infty} \sum_{i_{2}=1}^{\infty} \dots \sum_{i_{2N}=1}^{\infty} c_{i_{1}} c_{i_{2N}} \dots c_{i_{2N}}^{P} i_{1} i_{2} \dots i_{2N},$$

where
$$P_{i_1 i_2 \dots i_{2N}} = \phi_{i_1}(\vec{r}_1) \phi_{i_2}(\vec{r}_2) \dots \phi_{i_{2N}}(\vec{r}_{2N})$$
.

For simplicity, we will write

$$\psi(1,2,3,\ldots,2N) = \sum_{I=0}^{\infty} c_I P_I$$
(14)

and $P_{i_1 i_2 \cdots i_{2N}} \equiv P_{I} = \phi_{i_1}(1) \phi_{i_2}(2) \cdots \phi_{i_{2N}}(2N)$.

Implicit in the sum in (14) is, of course, the omission of all terms or orbital products with any two electrons in the same spin-orbital, due to Fermi-Dirac statistics.

The Pauli principle requires that our wave function, which describes a system of fermions, be antisymmetric with respect to interchange of the coordinates of any two electrons. This may be insured by replacing each group of 2NI orbital products which have the same set of spin-orbitals occupied with a Slater determinant. The Slater determinant, D_I , may be generated by operating with the antisymmetrization operator, \hat{A} , on any one of the 2NI orbital products in a group:

$$D_{I} = \hat{\mathcal{L}} P_{I} = \begin{pmatrix} \phi_{1}(1) \ \overline{\phi}_{1}(1) & \cdots & \overline{\phi}_{N_{0}}(1) \\ \phi_{1}(2) \ \overline{\phi}_{1}(2) & \cdots & \overline{\phi}_{N_{0}}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{1}(2N) \ \overline{\phi}_{1}(2N) & \overline{\phi}_{N_{0}}(2N) \end{pmatrix} (2N1)^{-1/2}$$

If $\hat{(r)}$ is the permutation operator which interchanges the coordinates of electrons, then $\hat{\Lambda} = (2N1)^{-1/2}$ $\sum_{\alpha} \hat{(r)} \hat{\epsilon}_{\alpha}$ where $(2N1)^{-1/2}$ is for normalization and $\hat{\epsilon} = +1$ if $\hat{\cdot}$ is equivalent to an even number of transpositions and -1 if $\hat{\cdot}$ is equivalent to an odd number. Equation (14) then becomes

$$\psi(1,2,\ldots,2N) = \sum_{I=0}^{\infty} c_{I} D_{I}$$
 (15)

Practical considerations dictate that we truncate expansion (15), by truncating our set of spatial functions, Φ_i^i , to obtain

$$\psi \simeq \sum_{\mathbf{I}=\mathbf{0}} \mathbf{c}_{\mathbf{I}} \mathbf{D}_{\mathbf{I}} \cdot$$
(16)

The choice of the set of functions Φ_{i}^{\prime} and the selection of the subspace of Φ_{i}^{\prime} is of fundamental importance in obtaining the best possible representation of ψ . Since the expansion in (16) is frequently truncated even further for a particular subspace of Φ_{i}^{\prime} , the search for the subset which provides the most rapidly convergent expansion becomes even more important.

Two common forms for the functions or orbitals Φ_{i}^{*} for polyatomic systems have been atomic orbitals and molecular orbitals (MO) which are often represented by linear combinations of atomic orbitals (LCAO). The familiar valence bond method results if atomic orbitals are used. The use of molecular orbitals, which we have employed, results in the LCAO-MO method. If the full expansion in (16) is used, the two methods will, of course, yield the same results. The larger the number of atomic orbitals (basis set or basis functions) used, the larger the expansion will be.

The use of atomic or molecular orbitals is determined by the severity of the truncation of the expansion (16). As the number of terms retained in the expansion decreases, the more important the form of the orbitals used becomes from the point of view of generating the most rapidly convergent expansion. Historically, this has usually been accomplished by the use of selfconsistent field (SCF) molecular orbitals. If only one term, <u>i.e.</u>, a single determinant, is kept in equation (16), the best single determinant wave function may be generated by the Hartree-Fock-Roothaan (HFR) SCF method. We will make use of the properties of SCF molecular orbitals in our discussion in this section, although the HFR-SCF method will be outlined in the next section.

In Hartree-Fock (HF) theory the potential experienced by an electron due to the other electrons is constructed to be an average potential of the other electrons. This potential felt by an electron should be governed by Coulomb's law which provides for instantaneous electron-electron interactions. As a result, the electrons in HF theory are not allowed to adequately correlate their motions in response to the actual potential they feel. This effect causes the HF energy, E_{HF} , to be higher than the exact non-relativistic energy, E_{exact} , by an amount called the "correlation energy," E_{C} : $E_{C} = E_{exact} - E_{HF}$. Although E_{C} is only a small fraction of the total energy (less than 1% for the systems of concern here), it is of

the same order of magnitude as bond energies, for example. HF wave functions frequently provide good results for properties which are relatively insensitive to electron correlation-properties such as geometries, ionization potentials and some one-electron properties.

Attempts to use HF theory for the description of reactions have provided some of the most glaring examples of the failure of HF theory. In chemical reactions bonds are broken and new bonds are formed. In this process electrons may become paired and unpaired, and they must redistribute in response to a completely new environment. It is in just such a situation as this that we need a description which allows the electrons to correlate their motions, if we hope to provide a physically reasonable picture of a reaction.

For each atom in a molecule we must provide at least one atomic orbital or basis function for every orbital occupied in the electron configuration of that atom. The number of basis functions, M, is invariably larger than this minimum number required. The result is that in the solution of the Schrödinger equation we obtain N_0 occupied SCF orbitals and $M-N_0$ unoccupied or virtual SCF orbitals. Since the complete set of SCF orbitals is by definition an orthonormal set, the space of the virtual orbitals must be othogonal to the space of the occupied orbitals. The increased flexibility of allowing

electrons to be in virtual orbitals will let the electrons correlate their motions better. Virtual orbitals provide a convenient way of allowing the electrons the flexibility of getting further from each other.

There is, however, a serious drawback in the use of SCF orbitals for our CI expansion. The original motivation for the use of SCF orbitals was to facilitate the convergence of equation (16) when the expansion is severely truncated. Since the virtual orbitals are part of an orthogonal set of SCF orbitals, they are frequently used because of this property rather than as a result of their convergence properties when used in a CI expansion. There is nothing in HF theory which ascribes to them this desired property. Rather than try to overcome this flaw by a multi-configurational SCF or natural orbital method, we chose a very modest size set of basis functions and retained the majority of the resultant terms which rise in equation (16), in describing the C + H₂ and N⁺ + H₂ reactions.

Slater determinants provide a convenient basis in which to expand our wave function, since they are orthonormal. Since a full CI is one characterized by including all possible determinants in (16), the number of terms in a full CI frequently becomes totally unmanageable. If, for example, we were considering a 6

electron system using 10 basis functions, we would have 6 electrons to be placed in 20 spin-orbitals. A full CI would have $\frac{201}{14161} = 38,760$ terms in it.

Besides arbitrarily truncating the CI expansion (16), we may use spin and spatial symmetry to reduce the size of the expansion. Our orbitals for non-linear geometries were constructed to be symmetry orbitals which transform according to one of the irreducible representations of the symmetry group of the molecule. The CI expansion for a B_1 state of a system with C_{2V} symmetry can be restricted to include only those determinants with B_1 symmetry.

Our CI expansion will be a linear combination of configurations rather than a simple sum of Slater determinants. A configuration is a linear combination of determinants which is a spin eigenfunction; i.e.,

$$\psi \simeq \sum_{\mathbf{T}} \mathbf{a}_{\mathbf{I}} \mathbf{C}_{\mathbf{I}} , \qquad (17)$$

where $C_{I} = \sum_{J} b_{IJ} D_{J}$.

The details of determining the b_{IJ} values such that each C_I is an eigenfunction of the \hat{S}^2 operator are given in Appendix II. The CI expansion for a ${}^{3}B_{1}$ state may be restricted to only those configurations with B_{1} symmetry

and \hat{s}^2 eigenvalue = 2. We may further reduce the size of a CI expansion by considering, for example, only the $M_S = 0$, $M_L = 0$ component of the 9-fold degerate atomic carbon 3P state.

The problem of determining the wave function (17) and energy is solved by applying the variational principle to $E = \langle \psi | \hat{\mathcal{H}} | \psi \rangle$. The energy is minimized by varying the expansion coefficients. The result is the usual matrix eigenvalue problem or secular equation

$$\mathbf{H} \, \boldsymbol{a} = \boldsymbol{a} \, \mathbf{E} \,, \tag{18}$$

where $H_{IJ} = \langle C_I | \hat{c} | C_J \rangle$.

A "double scripting" of the symbols or "parallax" notation will be used to denote matrices. The H matrix is constructed and then diagonalized to yield P eigenvalues, E_{I} , and P eigenvectors, a_{I} ; P is the number of configurations in (17).

Open Shell Self-Consistent Field Theory

There are a number of open shell self-consistent field (OS-SCF) theories currently being used. The OS-SCF theory outlined here is that given by Roothaan [3]. Rather than giving all the details of his theory, an overview will be presented. The 2N electron wave function is an antisymmetrized product of N_0 spin-orbitals or N_0 one-electron orbitals

$$\Psi = \hat{\mathbf{A}} \left[\phi_1(1) \overline{\phi}_1(2) \dots \phi_{N_0}^{-1}(2N-1) \phi_{N_0}^{-1}(2N) \right] .$$
 (19)

The spatial orbitals which are doubly occupied are referred to as the closed shell and are placed at the front of the orbital product. The spatial orbitals which are singly occupied (with α spins) are referred to as the open shell and are placed at the end of the orbital product.

A matrix notation is appropriate for simplicity and clarity. The subscripts i,j will denote open or closed shell orbitals, k,l will denote closed shell orbitals, and m,n will denote open shell orbitals.

The orbitals are constrained such that (1) $\langle \psi | \psi \rangle = 1$, (2) $\langle \phi_i | \phi_j \rangle = \delta_{ij}$, and (3) the ϕ_C or closed shell space is orthogonal to the ϕ_0 or open shell space. The combined set of N₀ orthonormal orbitals is collected into a row vector $\phi = (\phi_C, \phi_0)$.

Our Hamiltonian for the 2N electron system is

$$\hat{f}_{\alpha} = \sum_{\alpha=1}^{2N} \hat{H}_{\alpha} + \sum_{\alpha<\beta}^{2N} (1/r_{\alpha\beta}) ,$$

where \hat{H}_{α} is a one electron operator which includes the kinetic energy of the α th electron and the ineteraction of the α th electron with the nuclei

$$\hat{H}_{\alpha} = -\frac{1}{2}\nabla_{\alpha}^{2} - \sum_{\gamma}^{\text{all nuclei}} (Z_{\gamma}/r_{\alpha\gamma})$$

Roothaan's OS-SCF theory is valid when the energy may be written as

$$E = \langle \psi | \chi (| \psi \rangle = E_{C} + E_{0} + E_{C0} ,$$
 (20)

Where $E_{C} = 2 \sum_{k} H_{k} + \sum_{kl} (2J_{kl}-K_{kl})$,

$$E_0 = f[2\Sigma H_m + f \Sigma (2aJ_{mn} - bK_{mn})] ,$$

$$E_{C0} = 2f \sum_{km} (2J_{km} - K_{km}) .$$

Unless otherwise indicated, all summations are over the N_0 orbitals, and the following definitions have been used

$$H_{i} = \langle \phi_{i} | \hat{H} | \phi_{i} \rangle$$

$$J_{ij} = \langle \phi_{i}(1) \phi_{j}(2) | \frac{1}{r_{12}} | \phi_{i}(1) \phi_{j}(2) \rangle$$

$$K_{ij} = \langle \phi_{i}(1) \phi_{i}(2) | \frac{1}{r_{12}} | \phi_{j}(1) \phi_{j}(2) \rangle$$

 E_{C} , E_{0} , and E_{C0} are energies associated with the closed, open, and closed and open shell orbitals, respectively. The calculations performed on the ${}^{3}A_{2}$ and ${}^{3}B_{2}$ states of CH_{2} made use of this theory. Both states have wave functions whose energies are in the form dictated by equation (20) with a = 1, b = 2 and f = $\frac{1}{2}$. The variational principle is now applied to equation (2) subject to the contraints $S_{ij} \equiv \langle \phi_i | \phi_j \rangle = \delta_{ij}$. We want to minimize E with respect to the set of orbitals , and we use Lagrangian multipliers, λ_{ij} to impose the constraints. Therefore,

$$(\delta E) - \sum_{ij} \lambda_{ij} (\delta S_{ij}) = 0 ,$$
 (21)

where $\delta E = E(\phi_1 + \delta \phi_1, \phi_2 + \delta \phi_2, \dots) - E(\phi_1, \phi_2, \dots)$,

and
$$\delta S_{ij} = \langle \phi_i + \delta \phi_i | \phi_j + \delta \phi_j \rangle - \langle \phi_i | \phi_j \rangle$$

When equation (21) is written out, a lengthy integrodifferential equation results. Since this equation must vanish for arbitrary variations of the set of orbitals $\mathbf{\phi}$, the coefficients of all $\delta \phi_i$ must be zero. If we set the coefficients of $\delta \phi_i = 0$ and note that λ is a Hermitian matrix, we obtain two coupled integro-differential equations,

$$(H + 2J_{C} - K_{C} + 2J_{0} - K_{0}) \phi_{k} = \sum_{l} \phi_{l} \theta_{lk} + \sum_{n} \phi_{n} \theta_{nk} , \quad (22)$$

and

$$f(H + 2J_C - K_C + 2aJ_0 - bK_0) \phi_m = \sum_{n=1}^{\infty} \phi_1 \theta_{1m} + \sum_{n=1}^{\infty} \phi_n \theta_{nm} , \quad (23)$$

where $\theta_{lk} = -2\lambda_{kl}$.

In equations (22) and (23) the Coulomb operator associated with orbital ϕ_i , the closed shell Coulomb operator, the open shell Coulomb operator, and the total Coulomb operator are respectively,

$$J_{i}(1)\phi_{j}(1) = \langle \phi_{i}(2) | \frac{1}{r_{12}} | \phi_{i}(2) \rangle \phi_{j}(1)$$
$$J_{C} = \sum_{k} J_{k}$$
$$J_{0} = f \sum_{m} J_{m}$$
$$J_{T} = J_{C} + J_{0}$$

Similarly, the analogous exchange operators are

$$K_{i}(1)\phi_{j}(1) = \langle \phi_{i}(2) | \frac{1}{r_{12}} | \phi_{j}(2) \rangle \phi_{i}(1)$$

$$K_{C} = \sum_{k}^{\Sigma} K_{k}$$

$$K_{0} = f \sum_{m} K_{m}$$

$$K_{T} = K_{C} + K_{0}$$

The operators in equations (22) and (23) are invariant under the unitary transformations

$$\dot{\phi}_{C}^{\dagger} = \dot{\phi}_{C} \quad \mathbf{U}_{C} \text{ and } \dot{\phi}_{0}^{\dagger} = \dot{\phi}_{0} \quad \mathbf{U}_{0} \quad . \tag{24}$$

These transformations can be chosen to eliminate the offdiagonal multipliers θ_{lk} and θ_{nm} within the closed and open shells. They will not in general eliminate the offdiagonal multipliers θ_{nk} and θ_{lm} coupling the closed and open shells. In order to uncouple equations (22) and (23), Roothaan defines a new set of Hermitian operators. The Coulomb, closed shell Coulomb, open shell Coulomb, and total Coulomb coupling operators are

$$L_{i}\phi_{j} = \langle \phi_{i} | J_{0} | \phi_{j} \rangle \phi_{i} + \langle \phi_{i} | \phi_{j} \rangle J_{0}\phi_{i}$$

$$L_{C} = \sum_{k} L_{k}$$

$$L_{0} = f \sum_{m} L_{m}$$

$$L_{m} = L_{C} + L_{0}$$

Similarly, the analogous exchange operators are

$$M_{i}\phi_{j} = \langle \phi_{i} | K_{0} | \phi_{j} \rangle \phi_{i} + \langle \phi_{i} | \phi_{j} \rangle K_{0}\phi_{i}$$

$$M_{C} = \sum_{k} M_{k}$$

$$M_{0} = f \sum_{m} M_{m}$$

$$M_{T} = M_{C} + M_{0} .$$

With these coupling operators, equations (22) and (23) are easily uncoupled to yield two pseudo-eigenvalue equations. However, the closed shell Fock Hamiltonian is not very different from the open shell Fock Hamiltonian. The result is that the ϕ_C space will be quite similar to the ϕ_0 space, and by definition the two spaces should be orthogonal. With the aid of the coupling operators and by using some straight-forward manipulations the problem may be avoided by rewriting the closed and open shell equations with a common Fock Hamiltonian,

$$\hat{\mathbf{F}} \boldsymbol{\phi}_{C} = \boldsymbol{\phi}_{C} \boldsymbol{\mu}_{C} ,$$
$$\hat{\mathbf{F}} \boldsymbol{\phi}_{0} = \boldsymbol{\phi}_{0} \boldsymbol{\mu}_{0} ,$$

where

 $\hat{\mathbf{F}} = \mathbf{H} + 2\mathbf{J}_{T} - \mathbf{K}_{T} + 2\alpha(\mathbf{L}_{T} - \mathbf{J}_{0}) - \beta(\mathbf{M}_{T} - \mathbf{K}_{0})$,

The μ matrices may now be diagonalized by the transformations of equation (24)

 $\hat{\mathbf{F}}\phi_{\mathbf{i}} = \varepsilon_{\mathbf{i}}\phi_{\mathbf{i}} , \qquad (25)$

where $\varepsilon = U^{\dagger} \mu U$.

In terms of the ε_i , the energy becomes

$$E = \sum_{k} (H_{k} + \varepsilon_{k}) + f \sum_{m} (H_{m} + \varepsilon_{m})$$
$$- f \sum_{km} (2\alpha J_{km} - \beta K_{km}) - f^{3} \sum_{mn} (2\alpha J_{mn} - \beta K_{mn}) .$$

The solution of the Hartree-Fock-Roothaan open shell equation, equation (25), for molecules is based on the linear combination of atomic orbitals (LCAO) method. This procedure was first introduced by Roothaan for the closed shell Hartree-Fock equations [4]. The orbitals, which are now molecular orbitals, are expanded in a linear combination of atomic orbitals or basis functions, χ_i , which are centered on the nuclei

$$\phi_{i} = \sum_{j=1}^{\infty} \chi_{j}C_{ji}$$
 (26)

where the C's should not be confused with configurations. In a matrix representation, equation (26) becomes $\phi_i = \vec{\chi} \vec{C}_i$ and the total transformation is $\vec{\phi} = \vec{\chi} C$ where $\vec{\phi}$ and $\vec{\chi}$ are row vectors and \vec{C}_i is a column vector. Practical considerations require a truncation of the set of basis functions. For a system with N₀ occupied orbitals and M basis functions, C is an M X N₀ matrix of expansion coefficients and M > N₀. By substituting equation (26) into equation (25) and writing the result in a matrix notation, we obtain the Hartree-Fock-Roothaan open shell selfconsistent field (HFR-OS-SCF) equations

$$\mathbf{r}\mathbf{\tilde{c}}_{i} = \Delta \mathbf{\tilde{c}}_{i} \mathbf{\varepsilon}_{i} . \tag{27}$$

The following definitions are used

$$\begin{split} \Lambda_{ij} &= \langle \chi_i | \chi_j \rangle \\ \mathbf{F} &= \mathbf{H} + \mathbf{P} - \mathbf{Q} + \mathbf{R} = \mathbf{M} \times \mathbf{M} \text{ matrix} \\ \mathbf{H}_{ij} &= \langle \chi_i | \hat{\mathbf{H}} | \chi_j \rangle \\ \mathbf{P} &= 2 \mathbf{J}_{T} - \mathbf{K}_{T} \\ \mathbf{Q} &= 2 \alpha \mathbf{J}_{0} - \beta \mathbf{K}_{0} \end{split}$$

The matrices J_T or K_T , J_0 or K_0 , are distinguished by the density matrix, p^T or p^0 , that is used in their definition. In the following definitions, $\sigma = T$ or 0:

$$(\mathbf{J}_{\sigma})_{ij} = \sum_{k,1}^{M} \rho_{kl}^{\sigma} < \chi_{i}(1) \chi_{k}(2) \left| \frac{1}{r_{12}} \right| \chi_{j}(1) \chi_{l}(2) >$$

$$(\mathbf{K}_{\sigma})_{ij} = \sum_{k,1}^{M} \rho_{kl}^{\sigma} < \chi_{i}(1) \chi_{j}(2) \left| \frac{1}{r_{12}} \right| \chi_{k}(1) \chi_{l}(2) >$$

$$\rho_{kl}^{T} = \sum_{r}^{closed} c_{rk}^{*} c_{rl} + \rho_{kl}^{0}$$

and

.

$$\rho_{kl}^{0} = f \sum_{r}^{0} C_{rk}^{*}C_{rl} .$$

The energy may now be written as

$$E = trace \{ (H + F) \rho^{T} - Q[\rho^{T} + (f - 1)\rho^{0} \}$$

The constraint, $\langle \phi | \phi \rangle = 1$ = unit matrix results in the constraint, $\mathbf{C}^{\dagger} \Delta \mathbf{C} = 1$. This constraint allows us to rewrite FC = $\Delta C\epsilon$, which is another form of equation (27), as

$$\mathbf{C}^{\dagger}\mathbf{F}\mathbf{C} = \boldsymbol{\varepsilon} \quad . \tag{28}$$

Equation (28) is solved by an iterative process:

- 1) an initial estimate is made for the C matrix
- 2) ρ^{T} and ρ^{0} are constructed
- 3) **F** is assembled
- 4) F is diagonalized to yield a new C and ε matrix (C is a M X M matrix whose first N₀ columns define the occupied orbitals and whose remaining M - N₀ columns define the virtual orbitals; ε is a diagonal matrix whose diagonal elements are the ε_i)
- 5) a new ρ^{T} and ρ^{0} are constructed from the first N₀ columns of C.
- 6) the new ρ^{T} and ρ^{0} are compared with the old ones: if they have not changed, self-consistency has been solved; if they have changed, it is necessary to go back to step 3 and repeat steps 3 to 6.

APPENDIX II

COMPUTATIONAL TECHNIQUES FOR THE POTENTIAL ENERGY SURFACES

The Basis Set

In this study we employed a minimal basis set, <u>i.e.</u>, ls, 2s, $2p_X$, $2p_Y$, and $2p_Z$ orbitals for C and N⁺ and a ls orbital for H. Each of these orbitals was represented by a linear combination of 3 nuclear centered gaussian functions

$$\chi_{i} = \sum_{j=1}^{3} d_{ji}g_{ij}$$

where $g_{ij} = x^{l} y^{m} z^{n} e^{-\alpha} i j^{r^{2}}$ (unnormalized). The angular dependence of these nuclear centered gaussian functions is determined by $x^{l} y^{m} z^{n}$. An stype function implies l = m = n = 0, while a p_{X} type function implies l = 1and m = n = 0. The expansion coefficients, d_{ji} , and the exponents, α_{ij} , which are those given by Ditchfield, Hehre and Pople [5], were determined by minimizing the energy of the ${}^{3}P$, ${}^{4}S$ and ${}^{2}S$ states of C, N, and H, respectively. These are collected in Table 5.

	·j = 1	j = 2	j = 3
C _{ls}	.d.;= .06960382	.3936907	.6658730
	$\alpha_{j} = 155.2622$	23.28926	4.948442
C _{2s}	$d_{j} =08215337$.6034712	.4736710
	$\alpha_{j} = 5.793223$.4472592	.1440200
с _{2р}	$d_{j} = .1124423$.4657363	.6227623
•	$\alpha_{j} = 4.152398$.8464664	.1981786
N ls	d _j = .06913578	. 3934835	.6657830
	$\alpha_{j} = 214.1064$	32.15723	6.866035
N _{2s}	$d_{j} =08165721$.5980757	.5802935
	$\alpha_{j} = 8.394697$.6465681	.2050868
N _{2D}	d ₁ = .1164253	.4705657	.6176643
	α ₁ = 6.085492	1.252070	.2896766
Hls	d ₁ = .07047866	.4078893	.6476689
	$\alpha_{j} = 4.500225$.6812745	.1513748

Table 5.--The coefficients (d_j) and exponents (α_j) of the gaussian functions which represent the C, N, and H atomic orbitals.

The CH_2 and NH_2^+ orientations in C_{2V} and $C_{\infty V}$ geometries are given in Figure 31. We will, for convenience, define AH_2 as representing CH_2 and NH_2^+ when no distinction is to be made between them. We will also let AH and A represent CH and NH^+ , and C and N^+ , respectively.



Figure 31.--The CH_2 and NH_2^+ orientations in C_{2V} and $C_{\infty V}$ geometries.

Our basis set for AH_2 in C_{2V} symmetry was composed of four a_1 functions

$$\chi_{1s}, \chi_{2s}, \chi_{2p_7}, \text{ and } \chi_{H1} + \chi_{H2};$$

two b₂ functions, $\chi_{2p_{Y}}$ and $\chi_{H1} - \chi_{H2}$; one b₁ function, $\chi_{2p_{X}}$; and no a₂ functions. Our basis set for AH₂ in C_{∞V} symmetry was composed of five σ functions

$$x_{1s}$$
, x_{2s} , x_{2p_z} , x_{H1} , x_{H2}

and two π functions χ_{2p_X} and χ_{2p_Y} .

An orthonormal set of 7 orbitals was constructed by applying the Gram-Schmidt technique [7] to our 7 basis functions and then normalizing the resultant orbitals. The forms of the unnormalized orbitals for C_{2V} and $C_{\infty V}$ geometries are given in Tables 6 and 7, respectively. The coefficients a_1 through a_{11} should not be confused with configuration expansion coefficients. For C_{2V} geometries, ϕ_1 through ϕ_4 were a_1 orbitals, ϕ_5 and ϕ_6 were b_2 orbitals, and ϕ_7 was of b_1 symmetry. For $C_{\infty V}$ geometries, we obtained five σ orbitals, ϕ_1 through ϕ_5 , and two π orbitals, ϕ_6 and ϕ_7 .

At this point, it is appropriate to discuss the rationale for our use of orthogonalized symmetry orbitals as the basis. The orbitals (and therefore the electrons in them) in AH_2 systems may be divided into two subsets, core and valence orbitals. The core orbitals are those which are essentially unaffected in the reactions, <u>i.e.</u>, the ls orbital of N⁺ and C. Since these core electrons are not involved in the electronic redistribution, their correlation energy should be relatively constant. And, since our main concern is with energy differences and not absolute energies, we froze the core orbitals in the CI expansion. This means that all determinants which were used contained a
Table 6.--Orthogonal Gram-Schmidt Molecular Orbitals in C_{2V} Geometries

 $\phi_{1} = \chi_{1s}$ $\phi_{2} = \chi_{2s} - a_{1} |\phi_{1}\rangle$ $\phi_{3} = (\chi_{H1} + \chi_{H2}) - a_{2} |\phi_{1}\rangle - a_{3} |\phi_{2}\rangle$ $\phi_{4} = \chi_{2p_{2}}$ $\phi_{5} = \chi_{2p_{2}}$ $\phi_{6} = (\chi_{H1} - \chi_{H2}) - a_{4} |\phi_{5}\rangle$ $\phi_{7} = \chi_{2p_{2}}$

Table 7.--Orthogonal Gram-Schmidt Molecular Orbitals in $C_{\infty V}$ Geometries

```
\phi_{8} = \chi_{18}
\phi_{9} = \chi_{28} - a_{1} | \phi_{8} \rangle
\phi_{10} = \chi_{2p_{Z}}
\phi_{11} = \chi_{H1} - a_{5} | \phi_{8} \rangle - a_{6} | \phi_{9} \rangle - a_{7} | \phi_{10} \rangle
\phi_{12} = \chi_{H2} - a_{8} | \phi_{8} \rangle - a_{9} | \phi_{9} \rangle - a_{10} | \phi_{10} \rangle - a_{11} | \phi_{11} \rangle
\phi_{13} = \chi_{2p_{X}}
```

doubly occupied is orbital on the heavy atom. By selecting the first orbital in the Gram-Schmidt process to be the is orbital of C or N, we were assured that there were no components of the valence orbitals in the core orbital. This insured that the full CI (<u>i.e.</u>, all possible arrangements of 6 valence electrons using the remaining 6 spatial orbitals or 12 spin-orbitals were allowed for) within the valence orbitals completely spanned that subspace.

The Determinants and Configurations

In this section we will discuss the number and type of configurations which were used in our CI wave functions. The specific details of constructing configurations from determinants will be discussed in the next section.

As pointed out earlier, the AH_2 determinants were generated by keeping the lowest energy or first orbital doubly occupied. The determinants generated were all possible electron occupations within this constraint. The determinants for the C, N⁺, CH, NH⁺, and NH systems were generated by using the same constraint.

All possible occupations of the 12 valence spinorbitals with 6 electrons results in $\frac{12!}{(12-6)!6!} = 924$ determinants for AH₂. If we consider only the M_S = 0 components of the higher spin multiplets, we have three a spin electrons to be placed in six α spin-orbitals and three β spin electrons to be placed in six β spin-orbitals. The result is $(\frac{61}{3131})$ $(\frac{61}{3131}) = 400 M_S = 0 AH_2$ determinants. By taking the appropriate linear combinations of these 400 determinants, we may construct 175 singlet, 189 triplet, 35 quitet and 1 septet $M_S = 0 AH_2$ configurations. The 189 triplet configurations may be further broken down by considering their symmetry with respect to the reflection plane, σ_v (YZ). There are 99 triplet configurations which are antisymmetric with respect to σ_v (YZ). These 99 triplets are characterized by a single electron in the b_1 (C_{2V}) or π_x ($C_{\infty V}$) orbital.

In C_{2V} geometries we generated 51 ${}^{3}B_{1}$ configurations from the 99 triplets by selecting only those which were symmetric with respect to σ_{v} (XZ). The remaining 48 triplets, which were ${}^{3}A_{2}$ configurations, were not considered. The ${}^{3}B_{1}$ surfaces for the insertion reactions were represented by a 51 configuration wave function.

The abstraction reactions, which are characterized by $C_{\infty V}$ symmetry, were represented by configurations whose form was not determined as easily. While the orbitals in C_{2V} geometries transform according to the symmetry operations of C_{2V} , the orbitals in $C_{\infty V}$ geometries do not transform according to the symmetry operations of $C_{\infty V}$. The π orbitals, ϕ_X and ϕ_Y , do not have definite symmetry with respect to the infinite number of reflections and

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and rotations containing the molecular axis. The π orbitals are not eigenfunctions of the \hat{L}_Z operator. The angular dependence of gaussian p_X and p_Y functions is a real representation of the $Y_1^{\pm 1}$ spherical harmonics. Aside from normalization constants, we may write the angular dependence of ϕ_X and ϕ_Y as

$$\phi_{X} = \frac{1}{2} (\phi_{+} + \phi_{-})$$

$$\phi_{Y} = \frac{1}{2} (\phi_{+} - \phi_{-}) , \qquad (29)$$

$$\phi_{+} = Y_{1}^{\pm} .$$

For convenience, let $\phi_X^1 \phi_Y^1$ represent the Slater determinant A $[\phi_1 \overline{\phi}_1 \dots \phi_X \phi_Y]$, where all the orbitals before ϕ_X are doubly occupied. The ϕ_X^1 , ϕ_Y^1 , $\phi_X^1 \phi_Y^1 \phi_Y^1$, and $\phi_X^1 \overline{\phi}_X^1 \phi_Y^1$ determinants are not eigenfunctions of \hat{L}_Z and thus are not strictly Π determinants. Since the potential is cylindrically symmetric and independent of M_L , our Π determinants are just unitary transformations of the eigenfunctions of \hat{L}_Z and therefore are equivalent representations.

where

A p^2 configuration gives rise to, among other possibilities, the following determinants and terms,



When equations (29) are substituted into equations (30) and linear combinations are taken, so as to create real functions, we obtain

$$\begin{aligned} & \phi_{\mathbf{X}} \overline{\phi}_{\mathbf{X}} - \phi_{\mathbf{Y}} \overline{\phi}_{\mathbf{Y}} & \mathbf{1}_{\Delta} \\ & \phi_{\mathbf{X}} \overline{\phi}_{\mathbf{Y}} - \overline{\phi}_{\mathbf{X}} \phi_{\mathbf{Y}} & \mathbf{1}_{\Delta} \\ & \phi_{\mathbf{X}} \overline{\phi}_{\mathbf{Y}} + \overline{\phi}_{\mathbf{X}} \phi_{\mathbf{Y}} & \mathbf{3}_{\Sigma^{-}} (\mathbf{M}_{\mathbf{S}} = \mathbf{0}) \\ & \phi_{\mathbf{X}} \overline{\phi}_{\mathbf{X}} + \phi_{\mathbf{Y}} \overline{\phi}_{\mathbf{Y}} & \mathbf{1}_{\Sigma^{+}} \end{aligned}$$

The Δ states are not eigenfunctions of $\hat{L}_{\mathbf{Z}}$, while the Σ states are.

For the linear AHH system, we considered the ${}^{3}\Pi_{\chi}$ and the ${}^{3}\Sigma^{-}$ (M_S = 0) states. The $\phi_{\chi}, \phi_{\chi}\phi_{\chi}\phi_{\chi}, \phi_{\chi}\overline{\phi}_{\chi}$, and $\overline{\phi}_{\chi}\phi_{\chi}$ classes of determinants required to represent these states resulted in the 99 triplet configurations described earlier. Our ${}^{3}\Sigma^{-}$ (M_S = 0) and ${}^{3}\Pi_{\chi}$ states were represented by 51 and 48 configuration wave functions, respectively. The states of AH which we characterized were the lowest doublet and lowest quartet states. Since two electrons were in the core orbital, there were 5 electrons to be placed in 5 valence orbitals. The placement of three α spin electrons in five α spin-orbitals and two β spin electrons in five β spin-orbitals resulted in $(\frac{51}{2131})$ $(\frac{51}{3121}) = 100 M_{\rm S} = +\frac{1}{2}$ determinants, from which one may construct 75 doublet, 24 quartet, and 1 sextet configurations. Of the 75 doublets, only 18 we were required to completely describe the ${}^{2}\Pi_{\rm Y}$ state. Only 10 of the 24 quartets were required to complete describe the lowest quartet state, ${}^{4}\Sigma^{-}$.

Of the possible 100 $M_S = 0$ determinants for NH, there are 45 triplet configurations of which only 12 are of ${}^3\Sigma^-$ symmetry.

For C and N⁺, 36 M_S = 0 configurations completely characterized the ${}^{3}P$, ${}^{1}D$, and ${}^{1}S$ states.

Tables 8 through 14 list the fifty-one ${}^{3}B_{1}$ AH₂, forty-eight ${}^{3}\Pi_{X}$ AHH, fifty-one ${}^{3}\Sigma^{-}$ AHH, eighteen ${}^{2}\Pi_{Y}$ AH, ten ${}^{4}\Sigma^{-}$ AH, twelve ${}^{3}\Sigma^{-}$ NH, and thirty-six ${}^{3}P$, ${}^{1}D$ and ${}^{1}S$ A configurations which were used, respectively.

Spin Eigenfunctions

In this section the construction of configurations, which are eigenfunctions of the \hat{S}^2 operator, will be detailed. If we had used determinants, they would have

CONFIG- URATION	DETER- MINANT	M.O ORB	. OC	CUPA	FIRS	I(ALP T)	PHA S	PIN-	WFIGHT
		1a ₁	2a ₁	^{3a} 1	4a ₁	^{1b} 2	^{2b} 2	1b ₁	
ĺ	1	11	11	11	10	00	00	01	.707107
	2	11	11	11	01	00	00	10	.707107
2	1	11	11	10	11	00	00	01	.707107
	2	11	11	01	11	00	00	10	.707107
3 ·	1	11	11	10	00	11	00	01	.707107
	2	11	11	01	00	11	00	10	.707107
4	1	11	11	00	10	11	00	01	.707107
	2	11	11	00	01	11	00	10	.707107
5	1	11	11	10	00	00	11	01	.707107
	2	11	11	01	00	00	11	10	.707107
6	1	11	11	00	10	00	11	01	.707107
	2	11	11	00	01	00	11	10	.707107
7	1	11	10	11	11	00	00	01	.707107
	2	11	01	11	11	00	00	10	.707107
8	1	11	10	11	00	11	00	01	.707107
	2	11	01	11	00	11	00	10	.707107
9	1	11	00	11	10	11	00	01	.707107
	5	11	00	11	01	11	00	10	.707107
10	1	11	10	11	00	00	11	01	.707107
_	2	11	01	11	00	00	11	10	.707107
11	1	11	00	11	10	00	11	01	.707107
	2	11	00	11	01	00	11	10	.707107
12	1	11	10	00	11	11	00	01	.707107
	2	11	01	00	11	11	00	10	707107
13	1	11	00	10	11	11	00	01	707107
	2	11	00	01	11	11	00	10	.707107
14	1	11	10	00	11	00	11	01	.707107
	2	11	01	00	11	00	11	10	.707107
15	1	11	00	10	11	00	11	01	.707107
	2	11	00	01	11	00	11	10	.707107
16	1	11	10	00	00	11	11	01	.707107
	2	11	01	00	00	11	11	10	.707107
17	1	11	00	10	00	11	11	01	.707107
	2	11	00	01	00	11	11	10	.707107
18	1	11	00	00	10	11	11	01	.707107
	2	11	00	00	01	11	11	10	.707107
19	1	11	11	10	00	10	01	01	.707107
	2	11	11	01	00	01	10	10	- 707107
20	1	11	11	00	10	10	01	01	.707107
	2	11	11	00	01	01	10	10	- 707107
21	1	11	10	11	00	10	01	01	.707107
	2	11	01	11	00	01	10	10	707107
22	1	11	00	11	10	10	01	01	.707107
	2	11	00	11	01	01	10	10	707107
							-		•••••

TABLE 8. THE FIFTY-ONE 3B1 CONFIGURATIONS FOR ANH(C2V).

CONFIG- URATION	DETER- MINANT	M.O ORB	• OC	CUPA IS	WEIGHT				
	•	la _l	2a1	^{3a} 1	4a ₁	^{1b} 2	^{2b} 2	^{lb} 1	
23	1	11	10	00	11	10	01	01	.707107
	2	11	01	00	11	01	10	10	707107
24	1	11	00	10	11	10	01	01	.707107
	2	11	00	01	11	01	10	10	707107
25	1	11	10	10	01	11	00	01	.707107
	2	11	01	01	10	11	00	10	707107
26	1	11	10	10	01	00	11	01	.707107
	2	11	01	01	10	00	11	10	707107
27	1	11	11	10	00	01	10	01	.707107
	2	11	11	01	00	10	01	10	707107
28	1	11	11	00	10	01	10	01	.707107
	2	11	11	00	01	10	01	10	707107
29	1	11	10	11	00	01	10	01	.707107
	2	īī	01	ii	00	ĺŌ	01	10	707107
30	1	11	00	11	10	01	10	01	.707107
	2	11	00	11	01	10	01	10	707107
31	1	11	10	00	11	01	10	01	.707107
	2	11	01	00	11	10	01	10	-,707107
32	1	11	00	10	11	01	10	01	.707107
	2	11	00	01	11	10	01	10	707107
33	1	11	10	01	10	11	00	01	.707107
	2	11	01	10	01	11	00	10	-,707107
34	1	11	10	01	10	00	11	01	.707107
	2	11	01	10	01	00	11	10	707107
35	1	11	11	10	00	01	01	10	.707107
	2	11	11	01	00	10	10	01	707107
36	ī	11	11	00	10	01	01	10	.707107
	2	11	11	00	01	10	10	01	707107
37	1	11	10	11	00	01	01	10	.707107
	2	11	01	īī	00	10	10	01	707107
38	1	ĨĪ	00	11	10	01	01	10	.707107
	Ž	11	00	11	01	10	10	01	707107
39	ī	11	10	00	11	01	01	10	.707107
•	2	ii	01	00	11	10	10	01	707107
40	ī	11	00	10	ii	01	01	10	.707107
•••	2	11	00	01	11	10	10	01	707107
41	ī	ii	10	01	01	11	00	10	.707107
• •	2	11	01	10	10	ii	00	01	707107
42	1	11	10	01	01	00	11	10	_707107
-7 L	2	11	01	10	i n	00	11	01	- 707107
47	1	11	in	10	10	01	01	01	670820
7.)	2	11	01	01	01	۱ <u>۸</u>	10	10	- 67020
	2	11	10	10	01	10	01	01	
	.J	11	10	10	U I	IU	V I	U I	+U1#330

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CONFIG- URATION	DETER- MINANT	M.O ORB). OC BITAL	CUP/	FIRS	I(ALP St)	PHA S	SPIN-	WEIGHT
		la _l	2a ₁	3a ₁	4a ₁	^{1b} 2	^{2b} 2	^{1b} 1	
43	4	11	01	01	10	01	10	10	.074536
	5	11	10	10	01	01	10	01	.074536
	6	11	01	01	10	10	01	10	.074536
	7	11	10	10	01	01	01	10	.074536
	8	11	01	01	10	10	10	01	.074536
	9	11	10	01	10	10	01	01	.074536
	10	11	01	10	01	01	10	10	.07453 6
	11	11	10	01	10	01	10	01	.074536
	12	11	01	10	01	10	01	10	.074536
	13	11	10	01	10	01	01	10	.074536
	14	11	01	10	01	10	10	01	.074536
	15	11	10	01	01	01	10	10	.074536
	16	11	91	10	10	10	01	01	.074536
	17	11	10	01	01	10	01	10	074536
	18	11	01	10	10	01	10	01	.074536
	19	11	10	01	01	10	10	01	.074536
	20	11	01	10	10	01	01	10	.074536
44	1	11	10	10	01	10	01	01	666667
	2	11	01	01	10	01	10	10	666667
	3	11	10	10	01	01	10	01	.083333
	4	11	01	01	10	10	01	10	.083333
	5	11	10	10	01	01	01	10	.083333
	6	11	01	01	10	10	10	01	.083333
	7	11	10	01	10	10	01	01	.083333
	8	11	01	10	01	01	10	10	.083333
	9	11	10	01	10	01	10	01	.083333
	10	11	01	10	01	10	01	10	.083333
	11	11	10	01	10	01	01	10	.083333
	12	11	01	10	01	10	10	01	.083333
	13	11	10	01	01	01	10	10	.083333
	14	11	01	10	10	10	01	01	.083333
	15	11	10	01	01	10	01	10	.083333
	16	11	01	10	10	01	10	01	.083333
	17	11	10	01	01	10	10	01	.083333
	18	11	01	10	10	01	01	10	.083333
45	1	11	10	10	01	01	10	01	661438
	2	11	01	01	10	10	01	10	661438
	3	11	10	10	01	01	01	10	.094491
	4	11	01	01	10	10	10	01	.094491
	5	11	10	01	10	10	01	01	.094491
	6	11	01	10	01	01	10	10	.094491
	7	11	10	01	10	01	10	01	.094491
	8	11	01	10	01	10	01	10	.094491
									-

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	CONFIG- URATION	DETER- MINANT	M.n ORB	ITAL	CUPA	TION FIPS	I(ALP St)	HA S	SPIN-	WFIGHT
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			la ₁	^{2a} 1	^{3a} 1	4a ₁	^{1b} 2	^{2b} 2	^{1b} 1	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	45	9	11	10	01	10	01	01	10	.094491
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		10	11	01	10	01	10	10	01	.094491
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		11	11	10	01	01	01	10	10	.094491
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		12	11	01	10	10	10	01	01	.094491
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		13	11	10	01	01	10	01	10	.094491
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		14	11	01	10	10	01	10	01	.094491
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		15	11	10	01	01	10	10	01	.094491
46 1 11 10 10 01 01 10 10 $$		16	11	01	10	10	01	01	10	.094491
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	46	1	11	10	10	01	01	01	10	- .654654
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2	11	01	01	10	10	10	01	654654
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		3	11	10	01	10	10	01	01	.109109
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		4	11	01	10	01	01	10	10	.109109
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		5	11	10	01	10	01	10	01	.109109
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		6	11	01	10	01	10	01	10	.109109
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		7	11	10	01	10	01	01	10	.109109
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		8	11	01	10	01	10	10	01	. 109109
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		9	11	10	01	01	01	10	10	.109109
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		10	11	01	10	10	10	01	01	.109109
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		11	11	10	01	01	10	01	10	.109109
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		12	11	01	10	10	01	10	01	.109109
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		13	11	10	01	01	10	10	01	.109109
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		14	11	01	10	10	01	01	10	.109109
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	47	1	11	10	01	10	10	01	01	645497
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2	11	01	10	01	01	10	10	- .645497
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		3	11	10	01	10	01	10	01	.129099
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		4	11	01	10	01	10	01	10	.129099
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		5	11	10	01	10	01	01	10	.129099
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		6	11	01	10	01	10	10	01	.129099
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		7	11	10	01	01	01	10	10	.129099
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		8	11	01	10	10	10	01	01	. 129099
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		9	11	10	01	01	10	01	10	. 129099
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		10	11	01	10	10	01	10	01	.129099
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		11	11	10	01	01	10	10	01	•129099
48 1 11 10 01 10 01 10 01 632456 2 11 01 10 01 10 01 10 632456 3 11 10 01 10 01 10 .158114 4 11 01 10 01 10 01 .158114 5 11 10 01 01 10 .158114 5 11 10 01 01 10 .158114 6 11 01 10 10 .158114 7 11 10 01 01 10 .158114 8 11 01 10 10 01 .158114 8 11 01 10 01 10 .158114 9 11 10 01 10 .158114		12	11	01	10	10	01	01	10	. 1290 9 9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	48	1	11	10	01	10	01	10	01	632456
3 11 10 01 10 01 10 .158114 4 11 01 10 01 10 01 .158114 5 11 10 01 01 10 10 .158114 5 11 10 01 01 10 10 .158114 6 11 01 10 10 01 01 .158114 7 11 10 01 01 10 .158114 8 11 01 10 01 10 .158114 9 11 10 01 10 01 .158114 9 11 10 01 10 01 .158114		2	11	01	10	01	10	01	10	632456
4 11 01 10 01 10 01 .158114 5 11 10 01 01 10 10 .158114 6 11 01 10 10 10 .158114 6 11 01 10 10 01 .158114 7 11 10 01 10 01 .158114 8 11 01 10 01 10 .158114 9 11 10 01 01 .158114		3	11	10	01	10	01	01	10	.158114
5 11 10 01 01 10 10 .158114 6 11 01 10 10 01 01 .158114 7 11 10 01 01 10 .158114 8 11 01 01 10 01 .158114 9 11 10 01 10 01 .158114		4	11	01	1.0	01	10	10	01	.158114
6 11 01 10 10 01 01 .158114 7 11 10 01 01 10 10 .158114 8 11 01 10 01 10 01 .158114 9 11 10 10 01 10 01 .158114		5	11	10	01	01	01	10	10	. 158114
7 11 10 01 10 01 10 .158114 8 11 01 10 01 10 01 .158114 9 11 10 01 10 01 .158114		6	11	01	10	10	10	01	01	<u>,</u> 158114
8 11 01 10 01 10 01 .158114 9 11 10 01 10 10 01 .158114		7	11	10	01	01	10	01	10	.158114
9 11 10 01 01 10 10 01 •158114		8	11	01	10	10	01	10	01	. 158114
		9	11	10	01	01	10	10	01	. 158114

TABLE	8.	CONT	INUED
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CONFIG- URATION	DETER- MINANT	M.C ORE	D. OC	WEIGHT					
		'la _l	2a ₁	^{3a} 1	4a ₁	^{1b} 2	^{2b} 2	1b ₁	
48	10	11	01	10	10	01	01	10	.158114
49	1	11	10	01	10	01	01	10	612372
	2	11	01	10	01	10	10	01	- 612372
	3	11	10	01	01	01	10	10	204124
	4	11	01	10	10	10	01	01	204124
	5	11	10	01	01	10	01	10	204174
	6	11	01	10	10	01	10	01	.204124
	7	11	10	01	01	10	10	01	204124
	8	11	01	10	10	01	01	10	.204124
50	1	11	10	01	01	01	10	10	- 577350
	2	11	01	10	10	10	01	01	- 577350
	3	11	10	01	01	10	01	10	288675
	4	11	01	10	10	01	10	01	288675
	5	11	10	01	01	10	10	01	288675
	6	11	01	10	10	01	01	10	288675
51	1	11	10	01	01	10	01	10	500000
	2	11	01	10	10	01	10	01	500000
	3	11	10	01	01	10	10	01	.500000
	4	11	01	10	10	01	01	10	.500000

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CONFIG- URATION	DETER- MINANT	M.O ORB	• OC	CUPA IS	TION	(ALP	HA S	PIN-	WEIGHT
		. <u>σ</u> 1	σ2	σ3	σ 4	σ 5	^π Y	^π x	
i	1	11	11	11	10	00	00	01	.707107
	2	11	11	11	01	00.	00	10	.707107
2	1	11	11	10	11	00	00	01	.707107
	2	11	11	01	11	00	00	10	.707107
3	1	11	11	10	00	11	00	01	.707107
	2	11	11	01	00	11	00	10	.707107
4	1	11	11	00	10	11	00	01	.707107
	2	11	11	00	01	11	00	10	.707107
5	1	11	11	10	00	00	11	01	.707107
	2	11	11	01	00	00	11	10	.707107
6	1	11	11	00	10	00	11	01	.707107
	2	11	11	00	01	00	11	10	.707107
7	1	11	10	11	11	00	00	01	.707107
-	2	11	01	11	11	00	00	10	,707107
8	1	11	10	11	00	11	00	01	.707107
•	6	11	01	11	00	11	00	10	,707107
9	1	11	00	11	10	11	00	01	.707107
	2	11	00	11	01	11	00	10	.707107
10	1	11	10	11	00	00	11	01	./0/10/
• •	2	11	01	11	00	00	11	10	./0710/
11	1	11	00	11	10	00	11	10	,/0/10/
12	e J	11	00	11	01	. 00	11	10	, /0/10/
12	1	11	10	00	11	11	00	10	•/0/10/
12	2.	11	01	10	11	11	00	10	• / 0 / 1 0 / 707107
13	2	11	00	01	11	11	00	10	•/0/10/
14	1	11	10	00	11	00	11	01	•/0/10/ 707107
* -	2	11	01	00	11	00	11	10	707107
15	1	11	00	10	11	00	11	01	707107
• 5	2	11	00	01	11	00	11	10	.707107
16	1	11	10	00	00	11	ii	01	.707107
10	2	ii	01	00	00	ii	ii	10	.707107
17	ī	ii	00	10	00	ii	īī	01	.707107
	2	ii	00	01	00	11	11	10	.707107
18	1	11	00	00	10	ii	ii	01	.707107
	Ž	11	00	00	01	ii	11	10	.707107
19	1	ĨĪ	10	10	01	11	00	01	.707107
-	2	11	01	01	10	11	00	10	707107
20	1	11	10	10	01	00	11	01	.707107
-	2	11	01	01	10	00	11	10	707107
2i	1	11	10	01	10	11	00	01	.707107
-	2	11	01	10	01	11	00	10	707107
22	1	11	10	01	10	00	11	01	.707107
	2	11	01	10	01	00	11	10	707107

TABLE 9.THE FOURTY-EIGHT TRIPLET-PI-X CONFIGURATIONS
FOR LINEAR AHH.

	M.O. OCCUPATION(ALPHA SPIN- ORBITAL IS FIRST)								
$\sigma_1 \sigma_2 \sigma_2$	3 ⁰ 4	^σ 5 ^π Υ	^π x						
23 1 11 10 0	1 01	11 00	10	.707107					
2 11 01 1	0 10	11 00	01	707107					
24 1 11 10 0	1 01	00 11	10	.707107					
2 11 01 1	0 10	00 11	01	- 707107					
25 1 11 11 1	1 00	10 00	01	707107					
2 11 11 1	1 00	01 00	10	.707107					
26 1 11 11 0	0 11	10 00	01	707107					
2 11 11 0	0 11	01 00	10	707107					
27 1 11 11 0	0 00	10 11	01	707107					
2 11 11 0	0 00	01 11	10	.707107					
28 1 11 00 1	1 11	10 00	01	707107					
2 11 00 1	1 11	01 00	10	.707107					
29 1 11 00 1	1 00	10 11	01	707107					
2 11 00 1	1 00		10	707107					
30 1 11 00 0			01	.707107					
2 11 00 0	0 11	01 11	10	707107					
31 1 11 1	0 10	01 00	01	.707107					
2 11 11 0		10 00	10	- 707107					
32 1 11 10 1	1 10		01	707107					
	1 01		10	- 707107					
37 1 11 10 1	0 11		01	707107					
			10	- 707107					
	0 00		0)	707107					
			10	- 707107					
			0)	-,107107					
		10 11	10	- 707107					
			10	-,707107					
				. 707107					
			10	/0/10/					
				.707107					
			10	/0/10/					
			10	. 707107					
			10	/U/1U/ 707107					
				./0/10/					
			10	/0/10/					
			01	./0/10/					
	0 00		10	/0/10/					
	0 01		01	./0/10/					
2 11 01 0	0 10	01 11	10	707107					
42 1 11 00 1	U 01	10 11	UI 20	.707107					
2 11 00 0	1 10	01 11	10	707107					
43 1 11 11 1	0 01	01 00	10	.707107					
2 11 11 0	1 10	10 00	01	707107					
44 1 11 10 1	1 01	01 00	10	.707107					
2 11 01 1	1 10	10 00	01	707107					

T	ABL	E	9.	CONT	INUED
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CONFIG- URATION	DETER- MINANT	M.O ORB). OC	WEIGHT					
		σι	σ 2	σ3	σ4	σ5	^π y	^π x	
45	1	11	10	01	11	01	00	10	.707107
	2	11	01	10	11	10	00	01	707107
46	1	11	10	01	00	01	11	10	.707107
	2	11	01	10	00	10	11	01	707107
47	1	11	10	00	01	01	11	10	.707107
	2	11	01	00	10	10	11	01	707107
48	1	11	00	10	01	01	11	10	.707107
	2	11	00	01	10	10	11	01	707107

CONFIG- URATION	DETER- MINANT	M.O Orb	. OC	CUPA IS	TION	(ALP	HA S	PIN-	WEIGHT
		σι	σ 2	σ ₃	σ 4	^σ 5	^π Υ	^π x	
i	1	11	11	10	0.0	10	01	01	. 707107
-	2	ii	11	01	00	01	10	10	- 707107
2	ī	11	11	00	10	10	01	01	.707107
	2	11	11	00	01	01	10	10	- 707107
3	1	11	10	11	00	10	01	01	.707107
	2	11	01	11	00	01	10	10	707107
4	1	11	00	11	10	10	01	01	.707107
	2	11	00	11	01	01	10	10	-,707107
5	1	11	10	00	11	10	01	01	707107
	2	11	01	00	11	01	10	10	707107
6	1	11	00	10	11	10	01	01	.707107
	2	11	00	01	11	01	10	10	-,707107
7	1	11	11	10	00	01	10	01	.707107
	2	11	11	01	00	10	01	10	707107
8	1	11	11	00	10	01	10	01	.707107
	2	11	11	00	01	10	01	10	707107
9	1	11	10	11	00	01	10	01	•707107
	2	11	01	11	00	10	01	10	707107
10	1	11	00	11	10	01	10	01	.707107
	2	11	00	11	01	10	01	10	707107
11	1	11	10	00	11	01	10	01	.707107
	2	11	01	00	11	10	01	10	707107
12	1	11	00	10	11	01	10	01	•707107
	2	11	00	01	11	10	01	10	707107
13	1	11	11	10	00	01	01	10	.707107
	2	11	11	01	00	10	10	01	707107
14	1	11	11	00	10	01	01	10	.707107
	2	11	11	00	01	10	10	01	707107
15	1	11	10	11	00	01	01	10	.707107
	2	11	01	11	00	10	10	01	707107
16	1	11	00	11	10	01	01	10	.707107
	2	11	00	11	01	10	10	01	707107
17	1	11	10	00	11	01	01	10	.707107
-	2	11	01	00	11	10	10	01	707107
18	1	11	00	10	11	01	01	10	.707107
	2	11	00	01	11	10	10	01	707107
19	1	11	10	10	10	01	01	01	670820
	2	11	01	01	01	10	10	10	670820
	3	11	10	10	01	10	01	01	.074536
	4	11	01	01	10	01	10	10	.074536
	5	11	10	10	01	01	10	01	.074536
	6	11	01	01	10	10	01	10	•074536
	7	11	10	10	01	01	01	10	. 074536

TABLE 10.	THE FIFTY-ONE TRIPLET-SIGMA-MINUS	CONFIGURATIONS
	FOR LINEAR AHH.	

TAB	LE	10	1	CONT	INL	IED
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CONFIG- URATION	DETER- MINANT	M.O ORB	O. OC	CUPA IS	TION FIRS	(ALP T)	HA S	PIN-	WFIGHT
		σ1	^σ 2	^σ 3	^σ 4	^σ 5	^π y	^π x	
19	8	11	01	01	10	10	10	01	.074536
	9	11	10	01	10	10	01	01	.074536
	10	11	01	10	01	01	10	10	.074536
	11	11	10	01	10	01	10	01	.074536
	12	11	01	10	01	10	01	10	.074536
	13	11	10	01	10	01	01	10	.074536
	14	11	01	10	01	10	10	01	.074536
	15	11	10	01	01	01	10	10	.074536
	16	11	01	10	10	10	01	01	.074536
	17	11	10	01	01	10	01	10	.074536
	18	11	01	10	10	01	10	01	.074536
	19	11	10	01	01	10	10	01	.074536
	20	11	01	10	10	01	01	10	.074536
20	1	11	10	10	01	10	01	01	666667
	2	11	01	01	10	01	10	10	666667
	3	11	10	10	01	01	10	01	•083333
	4	11	01	01	10	10	01	10	.083333
	5	11	10	10	01	01	01	10	.083333
	6	11	01	01	10	10	10	01	.083333
	7	11	10	01	10	10	01	01	.083333
	8	11	01	10	01	01	10	10	•083333
	9	11	10	01	10	01	10	01	•083333
	10	11	01	10	01	10	01	10	•083 3 33
	11	11	10	01	10	01	01	10	•083333
	12	11	01	10	01	10	10	01	•083333
	13	11	10	01	01	01	10	10	•083333
	14	11	01	10	10	10	01	01	. 083333
	15	11	10	01	01	10	01	10	.083333
	16	11	01	10	10	01	10	01	•083333
	17	11	10	01	01	10	10	01	.083333
-	18	11	01	10	10	01	01	10	.083333
21	1	11	10	10	01	01	10	01	661438
	2	11	01	01	10	10	01	10	661438
	3	11	10	10	01	01	01	10	.094491
	4	11	01	01	10	10	10	01	.094491
	5	11	10	01	10	10	01	01	.094491
	6	11	01	10	01	01	10	10	.094491
	7	11	10	01	10	01	10	01	.094491
	8	11	01	10	01	10	01	10	•094491
	9	11	10	01	10	01	01	10	.094491
	10	11	01	10	01	10	10	01	.094491
	11	11	10	01	01	01	10	10	•094491
	12	11	01	10	10	10	01	01	.094491

CONFIG- URATION	DETER- MINANT	M.O ORB	PIN-	WEIGHT					
		σι	^σ 2	σ3	σ 4	σ ₅	^π Y	^π x	
21	13	11	10	01	01	10	01	10	.094491
	14	11	01	10	10	01	10	01	094491
	15	11	10	01	01	10	10	01	094491
	16	11	01	10	10	01	01	10	.094491
22	1	11	10	10	01	01	01	10	654654
	2	11	01	01	10	10	10	01	654654
	3	11	10	01	10	10	01	01	.109109
	4	11	01	10	01	01	10	10	.109109
	5	11	10	01	10	01	10	01	.109109
	6	11	01	10	01	10	01	10	.109109
	7	11	10	01	10	01	01	10	.109109
	8	11	01	10	01	10	10	01	.109109
	9	11	10	01	01	01	10	10	.109109
	10	11	01	10	10	10	01	01	.109109
	11	11	10	01	01	10	01	10	.109109
	12	11	01	10	10	01	10	01	.109109
	13	11	10	01	01	10	10	01	.109109
	14	11	01	10	10	01	01	10	.109109
23	1	11	10	01	10	10	01	01	645497
	2	11	01	10	01	01	10	10	645497
	3	11	10	01	10	01	10	01	.129099
	4	11	01	10	01	10	01	10	.129099
	5	11	10	01	10	01	01	10	.129099
	6	11	01	10	01	10	10	01	.129099
	7	11	10	01	01	01	10	10	.129099
	8	11	01	10	10	10	01	01	.129099
	9	11	10	01	01	10	01	10	.129099
	10	11	01	10	10	01	10	01	.129099
	11	11	10	01	01	10	10	01	.129099
• <i>i</i>	12	11	01	10	10	01	01	10	.129099
24	1	11	10	01	10	01	10	01	
	2	11	01	10	01	10		10	-032470
		11	10	01	10	01		10	•158114
	4	11		10	01	10	10		•100114
	5	11					10	10	•100114
	n	11		10	10	10	01		•108114
	1	11	10	01	01	10		10	•158114
	Ø	11	10	10	10	10	10	01	+100114 100114
	9 10	11	10		10	10	10	10	120114
2-	10	11		10	10	01	01	10	_ 4100114
25	I	11	10		10	10	10	01	- 412272
	<i>c</i>	11		10	01	10	10	10	-0163/6 20/124
	د	11	10	υI	01	υI	17	10	• 204124

CONFIG- URATION	DETER- MINANT	M.O ORB). OC Bital	CUPA	WEIGHT				
		σ1	σ2	σ3	σ4	σ5	^π y	^π x	
25	4	11	01	10	10	10	01	01	.204124
	5	11	10	01	01	10	01	10	204124
	6	11	01	10	10	01	10	01	.204124
	7	11	10	01	01	10	10	01	.204124
	8	11	01	10	10	01	01	10	204124
26	1	11	10	01	01	01	10	10	-,577350
	2	11	01	10	10	10	01	01	577350
	3	11	10	01	01	10	01	10	288675
	4	11	01	10	10	01	10	01	288675
	5	11	10	01	01	10	10	01	288675
	6	11	01	10	10	01	01	10	288675
27	1	11	10	01	01	10	01	10	- 500000
	Ž	īī	01	10	10	01	10	01	- 500000
	3	ĨĨ	10	01	01	ĨÕ	10	01	.500000
	. 4	11	01	10	10	01	01	10	.500000
28	1	11	11	11	00	00	10	01	.707107
	2	11	11	11	00	00	01	10	.707107
29	1	11	11	00	11	00	10	01	.707107
	2	11	11	00	11	00	01	10	.707107
30	1	11	11	00	00	11	10	01	.707107
-	2	11	11	00	00	11	01	10	.707107
31	1	11	00	11	11	00	10	01	.707107
	2	11	00	11	11	00	01	10	.707107
32	1	11	00	11	00	11	10	01	.707107
	2	11	00	11	00	11	01	10	.707107
33	1	11	00	00	11	11	10	01	.707107
	5	11	00	00	11	11	01	10	.707107
34	1	11	11	10	10	00	01	01	.707107
	2	11	11	01	01	00	10	10	707107
35	1	11	10	11	10	00	01	01	.707107
	2	11	01	11	01	00	10	10	707107
36	1	11	10	10	11	00	01	01	.707107
	2	11	01	01	11	00	10	10	707107
37	1	11	10	10	00	11	01	01	.707107
	2	11	01	01	00	11	10	10	707107
38	1	11	10	00	10	11	01	01	.707107
	2	11	01	00	01	11	10	10	707107
39	1	11	00	10	10	11	01	01	.707107
	2	11	00	01	01	11	10	10	707107
40	1	11	11	10	01	00	10	01	,707107
•	2	11	11	01	10	00	01	10	-,707107
41	ī	11	10	11	01	00	10	01	707107
• 4	2	11	01	11	10	00	01	10	- 707107
	•		~ .				* *		

CONFIG- URATION	DETER- MINANT	M.O ORB	WFIGHT						
		<u>σ</u> 1	σ 2	σ3	σ 4	σ5	^π y	^π x	
42	1	11	10	01	11	00	10	01	.707107
	2	11	01	10	11	00	01	10	70710
43	1	11	10	01	00	11	10	01	.70710
	2	11	01	10	00	11	01	10	70710
44	1	11	10	00	01	11	10	01	.70710
·	2	11	01	00	10	11	01	10	- 70710
45	1	11	00	10	01	11	10	01	.70710
	2	11	00	01	10	11	01	10	70710
46	ī	īī	ii	ĨŌ	01	00	01	10	.70710
	2	11	11	01	10	00	10	01	70710
47	1	11	10	11	01	00	01	10	.70710
	2	11	01	11	10	00	10	01	70710
48	1	11	10	01	11	00	01	10	.70710
	2	11	01	10	11	00	10	01	70710
49	1	11	10	01	00	11	01	10	.70710
	2	11	01	10	00	11	10	01	70710
50	1	11	10	00	01	11	01	10	.70710
	2	11	01	00	10	11	10	01	70710
51	1	11	00	10	01	11	01	10	.70710
	2	11	00	01	10	11	10	01	70710

CONFIG- URATION	DETER- MINANT	M.O Ore). OC BITAL	CUPA Is	TION	(ALP	HA SPIN-	- WEIGHT
		σι	σ 2	^π x	^π Y	σ3	σ 4	
ĩ	1	11	11	11	10	00	00	1.000000
2	1	11	11	00	10	11	00	1.000000
3	1	11	11	00	10	00	11	1.000000
4	1	11	00	11	10	11	00	1.000000
5	1	11	00	11	10	00	11	1.000000
6	1	11	00	00	10	11	11	1.000000
7	1	11	11	00	10	01	10	1.000000
	2	11	11	00	01	10	10	-1.000000
8	1	11	10	11	01	10	00	1.000000
	2	11	01	11	10	10	00	-1.000000
9	1	11	10	11	01	00	10	1.000000
	5	11	01	11	10	00	10	-1.000000
10	1	11	00	11	10	01	10	1.000000
_	2	11	00	11	01	10	10	-1.000000
11	1	11	10	00	01	11	10	1.000000
	2	11	01	00	10	11	10	-1.000000
12	1	11	10	00	01	10	11	1.000000
	2	11	01	00	10	10	11	-1.000000
13	1	11	11	00	10	10	01	2.000000
	2	11	11	00	10	01	10	-1.000000
	3	11	11	00	01	10	10	-1.000000
14	1	11	10	11	10	01	00	5.000000
	2	11	10	11	01	10	00	-1.000000
	3	11	01	11	10	10	00	-1.000000
15	1	11	10	11	10	00	01	2.000000
	2	11	10	11	01	00	10	-1.000000
	3	11	01	11	10	00	10	-1.000000
16	1	11	00	11	10	10	01	2.000000
	S	11	00	11	10	01	10	-1,000000
	3	11	00	11	01	10	10	-1.000000
17	1	11	10	00	10	11	01	2.000000
	2	11	10	00	01	11	10	-1.000000
	3	11	01	00	10	11	10	-1.000000
18	1	11	10	00	10	01	11	5.000000
	2	11	10	00	01	10	11	-1.000000
	3	11	01	00	10	10	11	-1.000000

TABLE 11. THE EIGHTEEN DOUBLET-PI-Y CONFIGURATIONS FOR AH.

CONFIG- URATION	DETER- MINANT	M.O ORB	O. OC	CUPA IS	TION	(ALP T)	HA SPIN	N- WEIGHT
		σι	σ2	^π x	^π Y	^σ 3	σ 4	
i	1	11	01	01	10	10	10	6,000000
-	2	11	01	10	01	10	10	1,00000
	3	ii	01	īŏ	10	01	10	1,000000
	4	11	01	10	10	10	01	1,000000
	5	11	10	01	01	10	10	1,000000
	6	11	10	01	10	01	10	1.000000
	7	11	10	01	10	10	01	1,000000
	8	11	10	10	01	01	10	-4,000000
	9	11	10	10	01	10	01	-4,000000
	10	11	10	10	10	01	01	-4,000000
2	1	11	01	10	01	10	10	1.000000
-	Ŝ	11	01	10	10	10	01	-1.000000
	3	ĨĪ	10	01	01	ĨÕ	10	1.000000
	4	11	10	01	10	10	01	-1.000000
	5	11	10	10	01	01	10	1.000000
	6	11	10	10	10	01	01	-1,000000
3	1	11	01	10	01	10	10	-1.000000
	2	11	01	10	10	01	10	2.000000
	.3	11	01	10	10	10	01	-1.000000
	4	11	10	01	01	10	10	-1,000000
	5	11	10	01	10	01	10	2.000000
	6	11	10	01	10	10	01	-1.000000
	7	11	10	10	01	01	10	1.000000
	8	11	10	10	01	10	01	-2,000000
	9	11	10	10	10	01	01	1.000000
4	1	11	01	10	01	10	10	1.000000
	2	11	01	10	10	01	10	1.000000
	3	11	01	10	10	10	01	1.000000
	4	11	10	01	01	10	10	-1,000000
	5	11	10	01	10	01	10	-1.000000
	6	11	10	01	10	10	01	-1.000000
5	1	11	11	10	10	01	00	1.000000
	5	11	11	10	01	10	00	1.000000
	3	11	11	01	10	10	00	1.000000
6	1	11	11	10	10	00	01	1.000000
	5	11	11	10	01	00	10	1.000000
	.3	11	11	01	10	00	10	1.000000
7	1	11	10	10	01	11	00	1.000000
	S	11	10	01	10	11	00	1.000000
	3	11	01	10	10	11	00	1.000000
8	1	11	00	10	10	11	01	1.000000
	2	11	00	10	01	11	10	1.000000
	3	11	00	01	10	11	10	1.000000

TABLE 12.THE TEN QUARTET-SIGMA-MINUS CONFIGURATIONS
FOR AH.

T	ABL	.E	12	•	CONT	INUED
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CONFIG- DETER URATION MINAN	DETER- MINANT	HA SPIN-	WEIGHT					
		σ1	^σ 2	^π x	^π Y	^σ 3	σ 4	
9	1	11	10	10	01	00	11	1.000000
	2	11	10	01	10	00	11	1.000000
	3	11	01	10	10	00	11	1.000000
10	1	11	00	10	10	01	11	1.000000
	2	11	00	10	01	10	11	1.000000
	3	11	00	01	10	10	11	1.000000

CONFIG- URATION	DETER- MINANT	M.C ORE). OC BITAL	CUPA	WEIGHT			
	•	σι	^σ 2	^σ 3	σ 4	^π Y	^π x	
i	1	11	11	11	00	10	01	1.000000
	2	11	11	11	00	01	10	1.000000
2	•]	11	11	00	11	10	01	1.000000
	2	11	11	00	11	01	10	1.000000
3	1	11	00	11	11	10	01	1.000000
	2	11	00	11	11	01	10	1.000000
4	1	11	11	10	10	01	01	1.000000
	2	11	11	01	01	10	10	-1.000000
5	1	11	11	10	01	10	01	1.000000
-	S	11	11	01	10	01	10	-1.000000
6	1	11	11	10	01	01	10	1.000000
Ū	2	11	11	01	10	10	01	-1.000000
7	1	11	10	11	10	01	01	1.000000
•	2	ii	01	ii	01	ĭõ	10	-1.000000
8	ī	īī	ĨŌ	īī	0Ī	10	01	1.000000
-	2	11	01	11	10	01	10	-1.000000
9	ĩ	11	10	11	01	01	10	1.000000
-	2	11	01	11	10	10	01	-1.000000
10	ī	11	10	10	11	01	01	1.00000
	2	11	01	01	11	10	10	-1.000000
11	1	11	ìò	ői	11	10	01	1.000000
	2	11	01	10	11	01	10	-1.000000
12	1	11	Ĭ	01	11	01	10	1.00000
. <i>C.</i> .	2	11	01	10	11	10	01	-1.000000
	٤.			10		<u> </u>	V L	-1000000

TABLE 13.THE TWELVE TRIPLET-SIGMA-MINUS CONFIGURATIONS
FOR NH.

CONFIG-	DETER-	M_C		CUPA	TION	(AL PHA SPIN-	WFIGHT
URATION	MINANT	ORE	BITAL	IS	FIRS	T)	
		ls	2s	² p _x	2py	² p _Z	
1	1	11	11	11	00	00	1.000000
2	1	11	11	00	11	00	1.000000
3	1	11	11	00	00	11	1.000000
4	1	11	00	11	11	00	1.000000
5	1	11	00	11	00	11	1.000000
6	1	11	00	00	11	11	1.000000
7	1	11	11	10	01	00	.707107
	2	11	11	01	10	00	707107
8	1	11	11	10	00	01	.707107
	2	11	11	01	00	10	707107
9	1	11	11	00	10	01	.707107
	2	11	11	00	01	10	707107
10	1	11	10	11	01	00	.707107
• =	2	11	01	11	10	00	707107
1)	1	11	10	11	00	01	.707107
••	2	11	01	11	00	10	70710/
12	1	11	00	11	10	01	.70710/
	2	11	00	11	01	10	707107
13	1	11	10	01	11	00	.707107
•	2	11	01	10	11	00	/0/10/
14	1	11	10	00	11	01	•/0/10/
15	2	11	01	00	11	10	-,/0/10/
15	1	11	00	10	11		•/U/10/
14	E J	11	10	01	11	10	-,/0/10/
10	1	11	10	10	00		·/U/1U/
17	2	11	10	10	00		/0/10/
17	1	11		00	10		+/U/IU/ - 707107
10	2	11	00	00	10	11	/0/10/
10	1	11	00	01	10	11	- 707107
10	2	11	10	10	01	11	577350
17	2	11	01	01	10	10	577350
	2	11	10	01	10	0)	- 288675
	4	11	10	01	01	10	- 288675
	5	11	01	10	01	10	- 288675
	6	11	01	10	10	0)	- 288675
20	ĭ	11	10	01	10	01	.500000
20	2	ii	01	10	01	10	.500000
	3	ii	10	01	01	10	- 500000
	ů,	ii	01	10	10	01	- 500000
21	i	11	īī	10	01	00	.707107
	- 2	<u>j</u> i	11	01	10	00	.707107
22	ī	īi	īi	10	00	01	.707107
	2	11	11	01	00	10	.707107
				v •			

TABLE 144THE THIRTY-SIX 3P, 1D AND 1S CONFIGURATIONS
FOR A.

TABLE 14. CONTINUED

CONFIG- URATION	DETER- MINANT	M.O ORB	• OC ITAL	CUPA IS	TION FIRS	(ALPHA SPIN- T)	WEIGHT
		· ls	2s	2p _X	2py	² p _z	
23	1	11	11	00	10	01	.707107
	2	11	11	00	01	10	.707107
24	1	11	10	11	01	00	.707107
	2	11	01	11	10	00	.707107
25	1	11	10	11	00	01	,707107
	2	11	01	11	00	10	.707107
26	1	11	00	11	10	01	.707107
	2	11	00	11	01	10	.707107
27	1	11	10	01	11	00	.707107
	2	11	01	10	11	00	.707107
28	1	11	10	00	11	01	,707107
	2	11	01	00	11	10	.707107
29	1	11	00	10	11	01	.707107
	2	11	00	01	11	10	.707107
30	1	11	10	01	00	11	.707107
	2	11	01	10	00	11	.707107
31	1	11	10	00	01	11	.707107
-	2	11	01	00	10	11	.707107
32	1	11	00	10	01	11	.707107
	2	11	00	01	10	11	.707107
33	1	11	10	10	01	01	.707107
	2	11	01	01	10	10	-,707107
34	1	11	10	01	10	01	.707107
	2	11	01	10	01	10	- 707107
35	1	11	10	01	01	10	.707107
	2	11	01	10	10	01	707107
36	ī	11	10	10	01	01	.288675
	2	11	01	01	10	10	288675
	3	11	10	01	10	01	288675
	4	īī	ŌĨ	10	01	10	288675
	5	11	10	01	01	10	288675
	6	11	01	10	10	01	288675

.

spanned the same space as the configurations, and we would have obtained spin eigenfunctions as our final wave functions. The use of spin eigenfunctions reduced the number of terms in the CI expansion. When working with large CI expansions, the diagonalization of the resultant Hamiltonian matrix becomes the major problem.

For systems with an even number of electrons, the $M_S = 0$ component was considered, while systems with an odd number of electrons the $M_S = +\frac{1}{2}$ component was considered. The determinants (D) and the configurations (C) are numbered by their subscripts. The superscripts on the C's denote the spin multiplicity of the configuration. It is assumed that the reader is familiar with required configurations for 0, 1, and 2 unpaired electrons.

The \hat{s}^2 operator operates only within a subspace defined by all determinants which have the same spatial orbitals doubly occupied. The configurations which are generated for one such subspace are applicable to all other subspaces which may be constructed from determinants with the same number of unpaired electrons.

The \hat{S}^2 operator is

$$\hat{S}^{2} = \sum_{\alpha \parallel 1} \hat{\mathcal{O}}_{\alpha\beta} + \frac{1}{4} \left[\left(n_{\alpha} - n_{\beta} \right)^{2} + 2 \left(n_{\alpha} + n_{\beta} \right) \right]$$

where n_{α} equals the number of α spin electrons, n_{β} equals the number of β spin electrons, and $\sum_{\alpha\beta} \hat{\ell}_{\alpha\beta}$ is the sum of all permutations of α with β spin electrons consistent with the Pauli principle. The term $\sum_{\substack{\alpha \\ \alpha \beta}} \hat{\rho}_{\alpha\beta}$ is a comall $\hat{\rho}_{\alpha\beta}$ is a combination of (1) the sum of all permutations of unpaired α spin electrons with unpaired β spin electrons and (2) the sum of all permutations of α with β spin electrons within a doubly occupied spatial orbital, for all of the doubly occupied orbitals. A determinant with 2 unpaired electrons, for example, is not an eigenfunction of \hat{s}^2 :

$$\hat{s}^{2} \not A \ [\phi_{1}\overline{\phi}_{1}\phi_{2}\overline{\phi}_{3}] = \not A \ [\overline{\phi}_{1}\phi_{1}\phi_{2}\overline{\phi}_{3}] + \not A \ [\phi_{1}\overline{\phi}_{1}\overline{\phi}_{2}\phi_{3}]$$
$$+ \frac{1}{4} \ [0 + 2(4)] \not A \ [\phi_{1}\overline{\phi}_{1}\phi_{2}\overline{\phi}_{3}]$$
$$= \not A \ [\phi_{1}\overline{\phi}_{1}\phi_{2}\overline{\phi}_{3}] + \not A \ [\phi_{1}\overline{\phi}_{1}\overline{\phi}_{2}\phi_{3}]$$

The general form for a spin projection operator

$$\hat{\mathfrak{S}}_{\mathbf{k}} = \prod_{\mathbf{i} \neq \mathbf{k}} (\frac{\hat{\mathbf{s}}^2 - \lambda_{\mathbf{i}}}{\lambda_{\mathbf{k}} - \lambda_{\mathbf{i}}})$$

is

where λ_i is the eigenvalue of \hat{s}^2 corresponding to the spin state we wish to project out. The λ_k are the eigenvalues of \hat{s}^2 corresponding to the spin states we wish to annihilate. A determinant with 4 unpaired electonrs, is in general, a mixture of singlet, triplet, and quintet spin. A pure triplet spin state may be obtained by annihilating the singlet and quintet components by using

$$\hat{\Theta}_{T} = (\frac{\hat{s}^{2}-0}{2-0}) (\frac{\hat{s}^{2}-6}{2-6}) = -\frac{1}{8}\hat{s}^{2} (\hat{s}^{2}-6)$$

The result of operating on a determinant with a projection operator is a linear combination of determinants which is a pure spin function. In general, if there are N determinants in the subspace of determinants with the same spatial orbitals singly and doubly occupied, N linearly dependent configurations will result. The M linearly independent configurations were determined by trial-and-error, when M was less than N.

The application of this method to 3 unpaired electrons will be detailed. There are 3 possible $M_S = +\frac{1}{2}$ determinants with 3 unpaired electrons:

$$D_{1} = A \left[\phi_{1} \overline{\phi}_{1} \phi_{2} \phi_{3} \overline{\phi}_{4} \right]$$
$$D_{2} = A \left[\phi_{1} \overline{\phi}_{1} \phi_{2} \overline{\phi}_{3} \phi_{4} \right]$$
$$D_{3} = A \left[\phi_{1} \overline{\phi}_{1} \overline{\phi}_{2} \phi_{3} \phi_{4} \right]$$

If we use the doublet projection operator,

$$\hat{\Theta}_{\rm D} = -\frac{1}{3} (\hat{\rm s}^2 - \frac{15}{4}),$$

we obtain

$$\hat{\Theta}_{D}D_{1} = \frac{7}{4}D_{1} + D_{2} + D_{3}$$
$$\hat{\Theta}_{D}D_{2} = D_{1} + \frac{7}{4}D_{2} + D_{3}$$
$$\hat{\Theta}_{D}D_{3} = D_{1} + D_{2} + \frac{7}{4}D_{3}.$$

Two linearly independent configurations may be generated from these linearly dependent configurations:

$${}^{2}C_{1} = \hat{\Theta}_{D}D_{2} + \hat{\Theta}_{D}D_{3} + 2D_{1} - D_{2} - D_{3}$$

and

$${}^{2}C_{2} = \hat{\mathbb{G}}_{D}D_{2} - \hat{\mathbb{G}}_{D}D_{3} = D_{2} - D_{3}$$
.

If we use the quartet projection operator,

$$\hat{\Theta}_{Q} = \frac{1}{3} (\hat{s}^{2} - \frac{3}{4}),$$

we obtain

$$\hat{\Theta}_{Q}^{D}{}_{1} = \hat{\Theta}_{Q}^{D}{}_{2} = \hat{\Theta}_{Q}^{D}{}_{3} = \frac{1}{3} (D_{1} + D_{2} + D_{3})$$

The linearly independent quartet configuration is

$${}^{4}C_{1} = D_{1} + D_{2} + D_{3}$$
.

The determinants and linearly independent configurations which were used are listed in Tables 15, 16, and 17 for 4, 5, and 6 unpaired electrons, respectively. The configurations given in Tables 15, 16, and 17 are for

Table 15.--Determinants and Configurations Arising From Four Unpaired Electrons (with $M_S = 0$)

D ₁ = A	[\$ ₁ \$ ₂ \$ ₃ \$ ₄]	D ₄ = A	$[\overline{\phi}_1 \overline{\phi}_2 \phi_3 \phi_4]$
D ₂ = A	$[\phi_1 \overline{\phi}_2 \phi_3 \overline{\phi}_4]$	D ₅ = A	$[\overline{\phi}_1 \phi_2 \overline{\phi}_3 \phi_4]$
D ₃ = A	$[\phi_1\overline{\phi}_2\overline{\phi}_3\phi_4]$	D ₆ = 4	$[\overline{\phi}_1 \phi_2 \phi_3 \overline{\phi}_4]$
	${}^{3}C_{1} = D_{1} - D_{4}$ ${}^{3}C_{2} = D_{2} - D_{5}$		
	${}^{3}C_{3} = D_{3} - D_{6}$		

Table 16.--Determinants and Configurations Arising From Five Unpaired Electrons (with $M_S = + 1/2$)

D ₁ = A	$[\overline{\phi}_1\overline{\phi}_2\phi_3\phi_4\phi_5]$	D ₆ = 3	$[\phi_1 \overline{\phi}_2 \phi_3 \overline{\phi}_4 \phi_5]$	
D ₂ = 2	$[\overline{\phi}_1 \phi_2 \overline{\phi}_3 \phi_4 \phi_5]$	D ₇ = 2	$[\phi_1 \overline{\phi}_2 \phi_3 \phi_4 \overline{\phi}_5]$	
D ₃ = A	$[\overline{\phi}_1 \phi_2 \phi_3 \overline{\phi}_4 \phi_5]$	D ₈ = Å	$[\phi_1\phi_2\overline{\phi}_3\overline{\phi}_4\phi_5]$	
D ₄ = (4	$[\overline{\phi}_1 \phi_2 \phi_3 \phi_4 \overline{\phi}_5]$	D ₉ = 🛶	$[\phi_1\phi_2\overline{\phi}_3\phi_4\overline{\phi}_5]$	
D ₅ = 엇	$[\phi_1\overline{\phi}_2\overline{\phi}_3\phi_4\phi_5]$	D ₁₀ = <i>É</i>	$[\phi_1\phi_2\phi_3\overline{\phi}_4\overline{\phi}_5]$	
² c ₁ =	(D ₆ +D ₉) - (D ₇ +D ₈)			
² c ₂ =	$2(D_5+D_{10}) - (D_6+D_7+D_8)$	+D ₉)		
${}^{2}C_{3} = 2(D_{3}-D_{4}) + (D_{7}+D_{9}) - (D_{6}+D_{8})$				
${}^{2}C_{4} = 4D_{2} + 2D_{10} - 2(D_{3}+D_{4}+D_{5}) + (D_{6}+D_{7}) - (D_{8}+D_{9})$				
${}^{2}C_{5} = 3D_{1} + (D_{8}+D_{9}+D_{10}) - (D_{2}+D_{3}+D_{4}+D_{5}+D_{6}+D_{7})$				
${}^{4}C_{1} = (D_{2} + D_{3} + D_{4}) - (D_{5} + D_{6} + D_{7})$				
${}^{4}C_{2} = (D_{2}+D_{5}+D_{8}) - (D_{4}+D_{7}+D_{10})$				
${}^{4}C_{3} = 2(D_{3}+D_{6}-D_{9}) + (D_{8}+D_{10}) - (D_{2}+D_{4}+D_{5}+D_{7})$				
${}^{4}C_{4} = 6D_{1} - 4(D_{8}+D_{9}+D_{10}) + (D_{2}+D_{3}+D_{4}+D_{5}+D_{6}+D_{7})$				

Table 17.--Determinants and Configurations Arising From Six Unpaired Electrons (with $M_S = 0$)

$D_{1} = \mathcal{A} \left[\phi_{1} \phi_{2} \phi_{3} \overline{\phi}_{4} \overline{\phi}_{5} \overline{\phi}_{6} \right]$	$D_{11} = \mathcal{A} \left[\overline{\phi}_1 \overline{\phi}_2 \overline{\phi}_3 \phi_4 \phi_5 \phi_6 \right]$
$D_2 = \mathcal{A} \left[\phi_1 \phi_2 \overline{\phi}_3 \phi_4 \overline{\phi}_5 \overline{\phi}_6 \right]$	$D_{12} = \begin{bmatrix} \frac{1}{2} & [\overline{\phi}_1 \overline{\phi}_2 \phi_3 \overline{\phi}_4 \phi_5 \phi_6] \end{bmatrix}$
$D_3 = \stackrel{*}{\asymp} [\phi_1 \phi_2 \overline{\phi}_3 \overline{\phi}_4 \phi_5 \overline{\phi}_6]$	$D_{13} = 4 \left[\overline{\phi}_1 \overline{\phi}_2 \phi_3 \phi_4 \overline{\phi}_5 \phi_6\right]$
$D_4 = [4] [\phi_1 \phi_2 \overline{\phi}_3 \overline{\phi}_4 \overline{\phi}_5 \phi_6]$	$D_{14} = \cancel{4} \left[\overline{\phi}_1 \overline{\phi}_2 \phi_3 \phi_4 \phi_5 \overline{\phi}_6\right]$
$D_5 = A \left[\phi_1 \overline{\phi}_2 \phi_3 \phi_4 \overline{\phi}_5 \overline{\phi}_6 \right]$	$D_{15} = \begin{bmatrix} \overline{4} & [\overline{\phi}_1 \phi_2 \overline{\phi}_3 \overline{\phi}_4 \phi_5 \phi_6] \end{bmatrix}$
$D_6 = \overset{1}{\not\sim} [\phi_1 \overline{\phi}_2 \phi_3 \overline{\phi}_4 \phi_5 \overline{\phi}_6]$	$D_{16} = \begin{bmatrix} \overline{\phi}_1 \phi_2 \overline{\phi}_3 \phi_4 \overline{\phi}_5 \phi_6 \end{bmatrix}$
$D_7 = \mathcal{A} \left[\phi_1 \overline{\phi}_2 \phi_3 \overline{\phi}_4 \overline{\phi}_5 \phi_6 \right]$	$D_{17} = \begin{bmatrix} \overline{\phi}_1 \phi_2 \overline{\phi}_3 \phi_4 \phi_5 \overline{\phi}_6 \end{bmatrix}$
$D_8 = \mathfrak{P} \left[\phi_1 \overline{\phi}_2 \overline{\phi}_3 \overline{\phi}_4 \phi_5 \phi_6 \right]$	$D_{18} = \frac{\overline{\phi}_{1}\phi_{2}\phi_{3}\phi_{4}\overline{\phi}_{5}\overline{\phi}_{6}}{\overline{\phi}_{6}}$
$D_{9} = \mathcal{H} \left[\phi_{1} \overline{\phi}_{2} \overline{\phi}_{3} \phi_{4} \overline{\phi}_{5} \phi_{6} \right]$	$D_{19} = \frac{1}{2} \left[\overline{\phi}_1 \phi_2 \phi_3 \overline{\phi}_4 \phi_5 \overline{\phi}_6\right]$
$D_{10} = \ddot{A} \left[\phi_1 \overline{\phi}_2 \overline{\phi}_3 \phi_4 \phi_5 \overline{\phi}_6 \right]$	$D_{20} = \begin{bmatrix} \overline{\phi}_1 \phi_2 \phi_3 \overline{\phi}_4 \overline{\phi}_5 \phi_6 \end{bmatrix}$
${}^{3}C_{1} = 9(D_{1}+D_{11}) - (D_{2}+D_{3}+D_{4})$	+ ^D 5 ^{+D} 6 ^{+D} 7 ^{+D} 8 ^{+D} 9 ^{+D} 10 ⁾
- (D ₁₂ +D ₁₃ +	$D_{14}^{+D}_{15}^{+D}_{16}^{+D}_{17}^{+D}_{18}^{+D}_{19}^{+D}_{20})$
${}^{3}C_{2} = 8(D_{2}+D_{12}) - (D_{3}+D_{4}+D_{5})$	5 ^{+D} 6 ^{+D} 7 ^{+D} 8 ^{+D} 9 ^{+D} 10 ⁾
- (D ₁₃ +D ₁₄ +	^{-D} 15 ^{+D} 16 ^{+D} 17 ^{+D} 18 ^{+D} 19 ^{+D} 20 ⁾
${}^{3}C_{3} = 7(D_{3}+D_{13}) - (D_{4}+D_{5}+D_{6})$; ^{+D} 7 ^{+D} 8 ^{+D} 9 ^{+D} 10 ⁾
- (D ₁₄ +D ₁₅ +	^{-D} 16 ^{+D} 17 ^{+D} 18 ^{+D} 19 ^{+D} 20 ⁾

Table 17.--Continued

$${}^{3}C_{4} = 6 (D_{4}+D_{14}) - (D_{5}+D_{6}+D_{7}+D_{8}+D_{9}+D_{10}) - (D_{15}+D_{16}+D_{17}+D_{18}+D_{19}+D_{20})$$

$${}^{3}C_{5} = 5 (D_{5}+D_{15}) - (D_{6}+D_{7}+D_{8}+D_{9}+D_{10}) - (D_{16}+D_{17}+D_{18}+D_{19}+D_{20})$$

$${}^{3}C_{6} = 4 (D_{6}+D_{16}) - (D_{7}+D_{8}+D_{9}+D_{10}+D_{17}+D_{18}+D_{19}+D_{20})$$

$${}^{3}C_{7} = 3 (D_{7}+D_{17}) - (D_{8}+D_{9}+D_{10}+D_{18}+D_{19}+D_{20})$$

$${}^{3}C_{8} = 2 (D_{8}+D_{18}) - (D_{9}+D_{10}+D_{19}+D_{20})$$

$${}^{3}C_{9} = (D_{9}+D_{19}) - (D_{10}+D_{20})$$

.

subspaces of determinants with 4, 5, and 6 total electrons, respectively. The results were directly applicable to the same subspaces which arose in our A, AH, and AH₂ systems which had 6, 7, and 8 total electrons, respectively.

The Quality of Our Representations

The failures of an SCF description, especially with respect to dissociation products, required that we use a CI description. The major stumbling block to a CI approach is the large number of configurations which can arise, even when spatial and spin symmetry have been fully exploited. There are two methods which can alleviate this problem. A reduction in the basis set size can significantly reduce the size of the CI expansion. If a larger and better basis set is employed, then a truncation of the CI expansion may be required. The quality of our representation is dictated mainly by our choice of a minimal basis set and not the relatively less significant truncation of the CI expansion. Since this was our first experience with potential energy surfaces, the errors which were bound to arise were less costly than if a more extensive basis were used. Since our CI was complete, our description of the reactants, intermediates and products involved in the reactions is at a consistent level of accuracy.

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Previous experience has shown that minimal basis set calculations provide only qualitatively significant absolute energies, but provide a more reliable description of geometries and relative properties such as energy differences.

Characterization of the Reactants and Products

Our basis set (Table 5) is the 3 gaussian representation of the atomic orbitals given by Ditchfield, Hehre, and Pople [5]. As a check or our integral [6], Gram-Schmidt [7], and CI [8] programs and possible input errors, we duplicated their results by computing the energy of the appropriate single determinants. We obtained energies for $C({}^{3}P)$, $N({}^{4}S)$, and $H({}^{2}S)$ of -37.45306, -54.06288, and -.49698 a.u., respectively, in complete agreement with the calculated energies of Ditchfield, Hehre, and Pople.

The energies of the ${}^{3}P$, ${}^{1}D$, and ${}^{1}S$ states of C, calculated using a 36 configuration wave function, are -37.47011, -37.41099, and -37.36966 a.u., respectively. The corresponding N⁺ energies are, with the same quality wave function, -53.5347, -53.46275, and -53.40599 a.u. The energies of the N atom, using the 51 configuration NH₂⁺ wave function at an N-H₂⁺ separation of 1 × 10⁺¹² bohrs, are -54.06288, -53.9550, and -53.91882 a.u. for
the ⁴S, ²D, and ²P states, respectively. These results are compared with experimental results in Table 18. The comparisons are quite reasonable with respect to the quality of representation. There is a certain consistency which seems reasonable. Our results were obtained by using a basis set whose parameters were optimized for only the lowest term.

The $H_2(^{1}\Sigma_{q}^{+})$, $H_2^{+}(^{2}\Sigma_{q}^{+})$, $CH(^{2}\Pi)$, $CH(^{4}\Sigma^{-})$, $NH(^{3}\Sigma^{-})$, $NH^+(^2\Pi)$, and $NH^+(^4\Sigma^-)$ diatomics were characterized by using the CI wave functions described earlier. The minimum energies and the internuclear separation at the minimum, R_e, were determined by interpolation. Except for the H₂ ${}^{1}\Sigma_{\sigma}^{+}$ and ${}^{3}\Sigma_{u}^{+}$ curves, which are shown in Figure 4, the $H_2^+(^2\Sigma_q^+)$, $H_2^+(^2\Sigma_u^+)$, $CH(^2\Pi)$, $CH(^4\Sigma_{-})$, $NH^+(^2\Pi)$, $NH^+(^{4}\Sigma^-)$ and $NH(^{3}\Sigma^-)$ energy curves as a function of the internuclear separation are shown in Figures 32, 32, 33, 34 35, 36, and 37, respectively. A comparison of our results with experiment, when possible, is given in Tables 19 and 20. The $4\Sigma^{-}$ state of CH has not been observed experimentally. We obtained values for R which are predictably and consistently larger (~ 20%). The De values, which we calculated with the assumption that as the diatmoics dissociated, the only maximum in the energy was at infinite internuclear separation, are consistently smaller than the experimental results. These results

Species	$\Delta E(^{1}D-^{3}P)$	Δε(¹ s- ³ p)
C - This work	1.6088	2.7334
C - Moore [9]	1.26387	2.6841
C - % difference	27.3	1.8
N ⁺ - This work	1.9572	3.5017
N ⁺ - Moore [9]	1.89892	4.05272
N ⁺ - % difference	3.1	-13.6
	$\Delta E(^2 D - {}^4 S)$	$\Delta E (^{2}P - ^{4}S)$
N - This work	2.936	3.920
N - Moore [9]	2.3834	3.5757
N - % difference	23.2	9.6

Table 18.--C, N⁺ and N Energy Differences in Electron Volts



Figure 32.--The H_2^+ Σ_g^+ and Σ_u^+ energy curves.



Figure 33.--The CH $(^{2}\Pi)$ energy curve.



Figure 34.--The CH (${}^{4}\Sigma^{-}$) energy curve.



Figure 35.--The NH^+ (²I) energy curve.



Figure 36.--The NH⁺ (${}^{4}\Sigma^{-}$) energy curve.



Figure 37.--The NH (${}^{3}\Sigma^{-}$) energy curve.

State	R (here) e	R (expt.) e	<pre>% difference</pre>
$\frac{1}{H_2(x^1\Sigma_g^+)}$	1.667	1.4008 [10]	19.0
$H_2^+(x^2\Sigma_g^+)$	2.508	2.003 [11]	25.2
сн (х ² п)	2.552	2.116 [12]	20.6
CH ($a^4\Sigma^-$)	2.335		
NH ($x^3 \Sigma^-$)	2.37	1.9614 [11]	20.8
NH ⁺ (x ² Π)	2.477	2.0428 [13]	21.3
$NH^+(a^4\Sigma^-)$	2.481	2.088 [13]	18.8

Table 19.--Diatomic R_e Values in Bohrs

Table 20.--Diatomic D_e Values in Electron Volts

State	Dissociation Products	D (here) e	D _e (expt.)	% dif- ference
$H_2(x^{1}\Sigma_q^+)$	H(² S), H(² S)	3.243	4.747 [14]	31.7
$H_{2}^{+}(x^{2}\Sigma_{g}^{+})$	$H(^{2}S), H^{+}$	1.814	2.788 [11]	34.9
сн (х ² п)	C(³ P), H(² S)	1.838	3.63 [12]	49.4
$CH(a^{4}\Sigma^{-})$	C(³ P), H(² S)	1.477		
NH ($x^3 \Sigma^-$)	$N(^{4}S)$, $H(^{2}S)$	1.474	3.41 [15]	56.8
$NH^{+}(x^{2}\Pi)$	$N^{+}(^{3}P)$, $H(^{2}S)$	2.903	3.90 [16]	25.6
$\mathrm{NH}^+(\mathbf{a}^4\Sigma^-)$	$N(^{4}S)$, H^{+}	2.559		

provide a useful yardstick by which our results for the reactions may be measured. Our bond distances can be estimated to be about 10 to 30% too large. Our ΔH and energy barrier for a reaction may be estimated to be about 25 to 50% too small and too large, respectively.

We will compare our ${}^{3}B_{1}$ geometries for CH_{2} and NH_{2}^{+} with the "best" <u>ab</u> <u>initio</u> results available. Our criterion for "best" is the common although not always justified criterion of lowest energy.

For the lowest ${}^{3}B_{1}$ surface of CH_{2} , we obtained a global minimum at $R_{CH} = 2.32$ bohrs and $\theta_{HCH} = 126^{\circ}$, where E = -38.64563 a.u. A high quality calculation by Langhoff and Davidson [17] on CH_{2} (${}^{3}B_{1}$) predicted $R_{CH} =$ 2.07 bohrs and $\theta_{HCH} = 132^{\circ}$. Our value of R_{CH} is 12.1% larger than the value given by Langhoff and Davidson.

For the lowest ${}^{3}B_{1}$ surface of NH₂⁺, we obtained a global minimum at R_{NH} = 2.27 bohrs and $\theta_{\rm HNH}$ = 160°, where E = -54.81995 a.u. The NH₂⁺ ion is characterized by a lack of pertinent experimental results and <u>ab initio</u> calculations of the same quality as may be found for CH₂. There appears to be no previously reported calculation which optimized the value of R_{NH} for the ${}^{3}B_{1}$ state of NH₂⁺. Lee and Morokuma [18] have done the best calculations to date on NH₂⁺ (${}^{3}B_{1}$). They obtained $\theta_{\rm HNH}$ = 180° and a very flat potential energy curve (energy vs. $\theta_{\rm HNH}$) around $\theta_{\rm HNH} = 180^{\circ}$. They did not indicate their bond length, however. Chu, Siu, and Hayes [19] obtained $\theta_{\rm HNH} = 140^{\circ}$ with $R_{\rm NH}$ fixed at 2.0 bohrs. Harrison and Eakers [20] used $R_{\rm NH} = 1.9055$ bohrs for their ${}^{3}B_{1}$ state calculations. Their value was obtained by minimizing the SCF energy of the ${}^{1}A_{1}$ state. They obtained $\theta_{\rm HNH} =$ 150° and a very low barrier to linearity. A very high quality calculation is needed to give a good prediction of $\theta_{\rm HNH}$, due to the extreme flatness of the surface around $\theta_{\rm HNH} = 180^{\circ}$.

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