A Model Study in Chemisorption: Atomic Hydrogen on Beryllium Clusters

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Abstract

The interaction between atomic hydrogen and the (0001) surface of Be metal has been studied by ab initio electronic structure theory. Self-consistent-field (SCF) calculations have been performed using minimum, optimized minimum, double zeta and mixed basis sets for clusters as large as 22 Be atoms. The binding energy and equilibrium geometry (the distance to the surface) were determined for 4 sites. The minimum basis sets give results that differ from the double zeta predictions by about 20 percent. Both spatially restricted (the wavefunction was constrained to transform as one of the irreducible representations of the molecular point group) and unrestricted SCF calculations were performed; different results were obtained in several cases. The cause of this symmetry breaking is discussed in detail for Be_3H . In this case, as in the others studied, the difference is in large part a result of not having computed the correct high symmetry state. The dependence on symmetry is, therefore, a tool in helping to detect unexpected ground states of the chemisorbed system.

Using only the optimized minimum basis set, clusters containing as many as 22 beryllium atoms have been investigated. From a variety of considerations, this cluster is seen to be nearly converged within the model used, providing our most reliable results for chemisorption. For this cluster all four distinct sites were considered. Three of the sites

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87

have similar characteristics, producing bond energies of ~ 50 kcal/mole and bond lengths (surface-hydrogen distance) of $1 \text{ \AA}$. The directly overhead site (H directly above a surface Be atom) is qualitatively different, its bond length being $\sim 1.4 \text{ \AA}$ and bond energy ~ 30 kcal/mole. The vibrational frequency, which the SCF formalism is known to predict accurately, was calculated for the chemisorbed hydrogen. The open and eclipsed sites have very similar results (1220 cm^{-1} and 1230 cm^{-1} respectively). The bond midpoint was found to have a frequency of 1360 cm^{-1} , while the directly overhead site was found to be very different (2060 cm^{-1}). The site dependence of the frequency is shown to be a geometrical effect depending on the number and angle of the bonds. The diffusion of atomic hydrogen through a perfect beryllium crystal is predicted to be energetically unfavorable.

The cohesive energy, the ionization energy and the singlet-triplet separation were computed for the clusters without hydrogen. These quantities can be seen as a measure of the total amount of edge effects. The chemisorptive properties are not related to the total amount of edge effects, but rather the edge effects felt by the adsorbate bonding berylliums. This lack of correlation with the total edge effects illustrates the local nature of the bonding, further strengthening the cluster model for chemisorption.

A detailed discussion of the bonding and electronic structure is included. The remaining edge effects for the Be_{22} cluster are discussed.

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Table of Contents

I. Introduction	1
A. General Remarks	1
B. Considerations and Limitations of a Cluster Model	5
C. The Choice of the $\text{Be}_n\text{-H}$ System	6
D. Theoretical Considerations	9
II. Results	14
A. Basis Set Tests	14
B. Computational Aspects	25
C. Symmetry Considerations	29
D. Mixed Basis Sets	35
E. Properties of the Cluster without Hydrogen	39
F. Summary of Results for Chemisorption	54
III. Bonding, Electronic Structure and Edge Effects	67
Analyzed from the Properties of the Charge Distribution	
IV. Conclusions	62
Appendix I.	87
Appendix II.	102
Appendix III.	118

I. Introduction

A. General Remarks

There has been a great deal of interest in the problem of chemisorption¹. The binding energies of various adsorbed atoms and molecules are known for a variety of materials and there exists a wealth of data on adsorbed molecular species by various spectroscopies: ESCA, XPS, LEED, and others. A great deal has been learned by these experiments, but there are some questions which are not easily answered by experiment; the nature and extent of the bond, site preference, the step by step mechanism of dissociative adsorption and the changes in charge distributions between the separated and chemisorbed states of the cluster and the adsorbate species. Ab initio molecular orbital theory has shown itself capable of answering these types of questions for many small molecules.² Application of the same techniques to the surface of solids could add to the understanding of chemisorption and aid in the interpretation of the experimental results.

The large number of degrees of freedom in molecular chemisorption make it extremely difficult to handle, and because of this difficulty, we decided to initially investigate the more restricted problem of atomic chemisorption. This problem has less degrees of freedom and can be used to answer many of the questions about the feasibility and interpretation of doing surface calculations using molecular orbital theory.

Within the past five years many semi-empirical calculations on small metal clusters and chemisorption have been performed³⁻¹⁶. It is clear that many systems of interest are outside the range of current ab initio techniques and semi-empirical methods must be used. It is therefore, hoped that this work and other ab initio¹⁷⁻²⁴ calculations will help to calibrate and evaluate existing semi-empirical methods for surface calculations.

The introduction is divided into four subsections: A. General Remarks, this section, B. Considerations and Limitations of the Cluster Model, which discusses the philosophy of the cluster model for a molecular orbital approach, C. The Choice of Be_nH , where the reasons for choosing beryllium, i.e., its small size, the success of the SCF formalism, accuracy of the minimum basis description, a closed shell ground state and covalent nature of the bond, are discussed. D. Theoretical considerations. In this section we discuss the lack of reconstruction leading to the study of the (0001) face, the use of a single configuration SCF wavefunction. The four sites where chemisorption were investigated are described.

The next section is II. Results. First, extensive basis set tests are described, leading to the conclusion that the minimum basis set gives results within 20 percent of the double zeta and bond lengths which are $\sim 0.1\text{\AA}$ too long. Computational details such as convergence problems and techniques, along with problems and methods used to determine the ground state for the bare cluster and the cluster plus hydrogen, are discussed in section IIB. Section C, Symmetry Considerations, discusses the differing results for the spatially restricted (the wavefunction is constrained to transform as one of the irreducible representations of the molecular point group) and spatially unrestricted wavefunctions. Be_3H is used as an example and the difference is shown, in large part, to be a result of having considered the wrong high symmetry state. Configuration interaction results are reported for Be_3H . The SCF and CI results are seen to be very similar.

The testing of mixed basis sets is reported in section IID. These basis sets involve double zeta atoms at the binding site and minimum basis atoms around the double zeta atoms. These basis sets are shown to

be as good as double zeta in most cases, and no worse than an all minimum basis atom treatment.

Section IIE presents a variety of properties of the cluster without hydrogen. These properties, the ionization potential, the cohesive energy and the singlet-triplet separation, are a measure of the edge effects. These cluster properties are shown not to correspond to the chemisorptive properties, since the cluster properties sample the total edge effects, while the fluctuations in the chemisorption are a result of edge effects existing at the bonding site. This corresponds to the bonding being local in nature, thus allowing the use of the cluster model.

Chemisorptive results are discussed in IIF. It is shown that when all the berylliums involved in bonding to the adsorbate molecule have all their nearest neighbors, a reasonable description of the chemisorption is obtained. The $\text{Be}_{22}(14,8)$ cluster meets this nearest neighbor criteria for all 4 sites, and is assumed to be converged within the model of a minimum basis and SCF formalism, leading to the conclusion that 3 sites are very similar with bond lengths of $\sim 1 \text{ \AA}$ and binding energies of $\sim 50 \text{ kcal/mole}$. The fourth site, the directly overhead site, is different producing a bond length of $\sim 1.4 \text{ \AA}$ and a bonding energy of $\sim 30 \text{ kcal/mole}$. The vibrational frequency of the chemisorbed hydrogen is computed. The open and eclipsed sites have frequencies of $\sim 1225 \text{ cm}^{-1}$. The bond midpoint site has a slightly different value of 1360 cm^{-1} , while the directly overhead site is very different, 2060 cm^{-1} . A very simple spring model is applied to the vibration, and the computed frequencies are shown to be a geometrical effect. The dissociative adsorption of H_2 is considered. The $\sim 50 \text{ kcal/mole}$ hydrogen-beryllium bond energy is probably too small as a result of using a minimum basis; also a region large enough for 2 strong Be-H bonds to form without having to

stretch the H_2 greatly is seen to exist. The results point to the possibility of dissociative chemisorption of H_2 . The diffusion of atomic hydrogen through a perfect beryllium crystal is considered and predicted to be energetically unfavorable.

In the next major section, III Bonding, Electronic Structure and Edge Effects Analysed from the Properties of the Charge Distribution, looks at the non-uniform distribution of the charge. It is shown that edge effects exist even for the Be_{22} cluster. The hybridization of the beryllium atoms in the cluster is shown to depend on the number of nearest neighbors. Density difference plots show the covalent nature of the bond.

The last section includes our concluding remarks. The appendices contain a variety of useful numerical data on the clusters and the cluster geometries are shown.

B. Considerations and Limitations of a Cluster Model

We will never be able to rigorously describe 10^{23} metal atoms with a cluster molecular orbital approach. We will therefore be restricted to a cluster of about 30 metal atoms for even our most optimistic choice of the metal (light atoms, such as Be or Li which can be described by a small number of basis functions). Although 30 atoms are not expected to have metallic properties, it is still possible to study chemisorption, since we are not interested in the bulk properties of the metal, but are primarily interested in what occurs at the surface during chemisorption.

If one considers the bonding to be local in nature, what is needed is a sufficient number of neighbors that the atoms directly involved in the bonding do not feel large "edge effects". If this can be achieved, a molecular orbital approach would be preferred, with its ability to accurately describe the nature and extent of the bonding. Of course, how large a number is needed is one of the questions we have attempted to answer.

C. The Choice of the $\text{Be}_n\text{-H}$ System

There has not been a great deal of experimental work on beryllium chemisorption, possibly due to the toxicity of beryllium metal. The experimental work is possible and recently there has been some work on beryllium. In fact one group in Berkeley has begun to investigate the chemisorption of O_2 on beryllium surfaces.²⁵ LEED experiments²⁶ have shown no surface reconstruction for the (0001) surface. Therefore, we will not be forced to optimize the beryllium atom positions in the cluster, but will be able to use the bulk structure positions of the atoms. In addition to saving a great deal of work, it eliminates the problem of edge effects distorting the small clusters into unreasonable geometries as a optimization of the cluster geometry was performed. Finally, we note that Be surfaces have been studied by Auger electron spectroscopy²⁷

From a strictly theoretical point of view, there are five reasons for choosing beryllium.

1). The Be atom has only 4 electrons. This makes Be one of the two smallest metals (from a basis set size point of view), Li being the other small metal. This will allow us to treat very large clusters.

2). Be is a closed shell 1^1S ground state and the metal is known to have no magnetic properties²⁸. This means that the larger clusters would be expected to have a closed-shell singlet ground states. Any open shells would result in a local unpaired spin density and a measurable paramagnetic property. This simplifies our theoretical treatment since we are never concerned with coupling of unpaired electrons to get the proper eigenfunction of S^2 .

3). The Hartree-Fock approximation is very accurate for BeH , the

simplest Be_n-H system. Cade and Huo's near Hartree-Fock calculations²⁹ produce a dissociation energy of 50.3 kcal/mole. This value compares well with both the experimental value of Colin et. al.³⁰ (49.8 ± 0.2 kcal/mole) and the extensive configuration interaction (CI) results of Bagus et. al.³¹ (D_e=48.4 ± 0.7 kcal/mole). The fact that the near Hartree-Fock dissociation energy differs from the exact D_e by only 1.5 ± 0.7 kcal/mole is encouraging as to the accuracy of SCF calculations for this system.

4). The minimum basis result for BeH (where the Be basis set included a 2p function) are in excellent agreement with the exact results (see Table I). The near Hartree-Fock dissociation energy is within 10 percent of the exact value³¹. The double zeta result is also within 10 percent of the exact D_e value. Further the bond length is only 0.009 Å longer than experiment. It is fortuitous that the dissociation energy for the minimum basis is closer to the exact than the double zeta value, but the bond length for the minimum basis is in error by 0.012 Å.

5). The electron affinity of hydrogen (0.7542 eV⁴²) is smaller than the ionization potential of beryllium (9.22eV³³). This leads one to predict a covalent bond and to the anticipation that no additional basis functions will be needed on hydrogen. If the system were ionic, the minimum basis set would be unable to describe H⁻ and even the double zeta basis set might have to be augmented with additional functions to describe the anion accurately. The fact that it is covalent allows the use of the neutral atom optimized basis sets and indicates that a minimum basis might be suitable for the description of the chemisorption.

Table I. Theoretical results for the BeH molecule; a comparison
between basis sets, methods and experiment.

<u>Method</u>	<u>r_e ($\text{\AA}$)</u>	<u>D_e (kcal/mole)</u>
Present work		
Minimum Basis I	1.420	46.4
Double Zeta I	1.352	44.5
Near Hartree-Fock ^a	1.338	50.3
Large Configuration Interaction ^b	1.345	48.8 ± 0.7
Experiment	1.343 ^c	49.8 ± 0.2 ^d

^aReference 29.

^bReference 31.

^cReference 46.

^dReference 30.

D. Theoretical Considerations

It would seem helpful at this point to clearly state what we plan to do and how we intend to go about it.

If a perfect beryllium crystal is cleaved, the (0001) surface is the one which is most likely to be stable with respect to reconstruction. In fact LEED studies²⁶ have shown this to be true. Experimentalists will most likely use the (0001) surface, because of this stability. We obviously want to investigate the chemisorption on this surface to allow for a better comparison between experimental and theoretical studies. Figure 1 shows the Be_{22} cluster we used, illustrating the hexagonal close packed structure of interest.

We will assume the precise structure of the metal for all our cluster calculations. For the (0001) surface, this implies that each surface atom will have nine nearest neighbors, 6 in the same layer and 3 in the layer below. The nearest neighbor distance a_0 within a layer is $2.2866 \text{ \AA}$, while the distance between the surface atoms and their neighbors below is shorter, being only $2.2555 \text{ \AA}$ ³⁴.

All our calculations will employ single configuration SCF theory. A few calculations were performed with two-configuration SCF methods, but the results were qualitatively similar.

As we noted in section IC. (the choice of $\text{Be}_n\text{-H}$), beryllium metal has no magnetic properties. This leads to the prediction of no unpaired electrons, or a closed shell ground state. Because of this we refer to the lowest closed shell state of the cluster as the ground state. Edge effects for the finite clusters cause open shell configurations to sometimes lie lower than the closed shell state. We have computed these open shell configurations and have used them as a measure of the edge effects,

but still refer to the closed shell as the ground state and use it as our description of the cluster when the hydrogen is moved to infinite separation. Similarly we restricted the chemisorbed system to a doublet state, the closed shell cluster interacting with the doublet hydrogen.

It would also be helpful at this time to explain our naming scheme for the clusters. Since all of our clusters have one or two layers, we have therefore enclosed the number in each layer in parentheses. For example a six atom cluster with all the atoms in one layer would be $\text{Be}_6(6,0)$, while one with 3 atoms in the first layer and 3 in the second would be $\text{Be}_6(3,3)$.

There are at least four important distinct sites with symmetry on the (0001) surface of beryllium.

1). If the hydrogen approaches the center of a triangle formed by 3 surface atoms and there is no beryllium in the second layer, we call this the open site. An example would be an approach to the center of the triangle formed by atoms 5,6, and 9 in Figure 1.

2). If the hydrogen approaches a threefold site with a beryllium atom in the second layer, we call this the eclipsed site. An example is the triangle formed by 6,9, and 10 with the atom labeled e being the second layer beryllium.

3). An approach bisecting the line joining two beryllium atoms has been labeled the bond midpoint site. An example is an approach between atoms 6 and 9.

4). Finally the hydrogen can approach straight on top of one surface beryllium, and we have called this the directly overhead site.

It is clear that we want to investigate all four sites. The question of site preference is one we can hopefully answer.

Figure 1. The $\text{Be}_{22}(14,8)$ cluster. This cluster illustrates the (0001) surface used in our studies of hydrogen adsorption on beryllium. The cluster has C_s symmetry with and without hydrogen. The open site was studied by the approach of an H to the center of the triangle formed by atoms 5, 6, and 9. the eclipsed site by the approach to the center of the triangle formed by atoms 6, 9, and 10, with the atom labeled e being the second layer beryllium. The bond midpoint is the bisector of the line joining atoms 6 and 9. The directly overhead site is the approach to atom 10.

From a practical point of view, the first thing we have to do is calculate the chemisorption for the small clusters using both the double zeta and the minimum basis. Does the minimum basis work well for the small clusters or is the Bell result anomalous? If the minimum basis sets give reasonable results, the obvious next step is to increase the cluster size and look for convergence for the chemisorption at each site.

The possibility also exists to investigate other cluster properties and look for a correlation between these properties and the chemisorption. They may help us independently determine the quality of some of the clusters.

The final goal is a detailed analysis of the chemisorption on the largest clusters. The remaining edge effects, charge movement and the nature of the bonding will be investigated in detail.

II. Results

A. Basis Set Tests

In any ab initio calculation the choice of the basis set is extremely important in order to be able to accurately describe the system. This is especially true when a minimum basis set is used. It is for this reason that several different basis sets were used in the course of this work. Many of the basis set tests were designed to answer specific questions which arose as the work proceeded, but all the basis set comparisons were used to test the quality of the minimum basis set model, for both the chemisorption and cluster properties. Although the basis set tests are not as complete as would have been desired, we believe they do support the reliability of the minimum basis set used for our larger clusters.

The basis sets are described below and tabulated in Appendix III. A comparison of the results for the different basis sets on various clusters is made and conclusions on the quality of the basis sets are made.

The basis sets are:

a). minimum basis set I. Here 1s, 2s and 2p functions on Be were used, while a single 1s function was centered on hydrogen. Each function was a three-gaussian expansion³⁵ of a Slater function. The Slater function orbital exponents were those of Clementi and Raimondi:³⁶ $\zeta(1s)=3.685$, $\zeta(2s)=0.956$. Although the 2p orbital is not occupied in the Be atom, we believed it would be very important in the clusters. Therefore $2p_x$, $2p_y$, and $2p_z$ functions were included. The exponent ($\zeta(2p)=0.890$) was optimized³⁷ for the $^3P(1s^2 2s 2p)$ state of Be. Finally, for the hydrogen atom, $\zeta(1s)=1.15$ was adopted. The atomic SCF energies obtained with this

basis were -14.3919 hartrees (Be) and -0.4839 hartrees (H) compared to the Clementi minimum basis result for Be ($1s$), $E_{SCF} = -14.5567$.

b). Minimum basis set IIa. The hydrogen basis set remained the same, as did the beryllium $1s$ function. The beryllium $2s$ and $2p$ Slater exponents were constrained to be equal and optimized for the $Be_{13}(10,3)$ A cluster (figure 12 Appendix II). The optimum Slater exponent was found to be 1.00. An additional constraint imposed, as a computational convenience was that the $2s$ and $2p$ Slater functions be fit to the same 3 gaussian functions.

c). Minimum basis IIb. This basis set is the same as minimum basis set IIa, except the $2s$ and $2p$ functions were fit separately to the best 3 gaussian fit. The choice between using IIa or IIb depended on which system of programs were being used, since for some programs the constrained fit offered no computational advantage.

d). Minimum basis III. The beryllium $2s$ and $2p$ functions were optimized separately. This optimization was carried out for the $Be_{10}(10,0)$ cluster. The optimum Slater exponents were found to be $\zeta(2s)=1.01$ and $\zeta(2p)=0.98$.

e). Double zeta I. This basis is a contracted gaussian set of size $Be(9s\ 2p/4s\ 2p)$, $H(4s\ 1p/2s\ 1p)$. The beryllium primitive gaussian set of s functions was that of van Duijneveldt³⁸, contracted 6111 to yield an SCF energy of -14.5704 hartrees, compared to the true Hartree-Fock energy³⁹ -14.5730. The two Be $2p$ primitive gaussians, with exponents $\alpha=0.509$ and 0.118 , were taken from a previous study⁴⁰ on BeF_2 . For the hydrogen atom, van Duijneveldt's primitive $(4s)$ set was contracted 31 to $(2s)$ and a scale factor of 1.2 was applied. For the H atom, this basis yields an energy of -0.4977 Hartrees. A set of $2p$ functions with

$\alpha=1.0$ was added to the hydrogen since Roos and Siegbahn⁴¹ have pointed out the importance of having a set of 2p functions on hydrogen.

f). Double Zeta II. The hydrogen basis set and the beryllium s functions are unchanged, but a set of four 2p functions replaced the previous set of p functions. The functions were optimized for Be (³p)⁴², and were contracted 31.

Tables II through VI summarize the basis set tests for the small clusters. In general the minimum basis description of the chemisorption is very reasonable. The bond energies are within 20 percent of the double zeta results, excluding the Be₅(4,1) open site where the minimum basis I yields only 75 percent of the double zeta I value for the chemisorption. The bond lengths are uniformly too long by from 0.05 Å to 0.16 Å.

Whenever a minimum basis set is used careful testing is required, especially when unexpected results are obtained. The quality of our minimum basis set first came into question when the ground state of the Be₇(7,0) was computed. If 7 beryllium atoms with an occupancy of 1s² 2s² are used to construct the Be₇(7,0) cluster, the expected occupancy is (in D_{6h} symmetry)

$$\dots 3a_{1g}^2 \quad 2e_{1u}^4 \quad 2e_{2g}^4 \quad 2b_{1g}^2 \quad 4a_{1g}^2$$

but the actual ground state was found to be

$$\dots 3a_{1g}^2 \quad 2e_{1u}^4 \quad 2e_{2g}^4 \quad 1b_{2u}^2 \quad 4a_{1g}^2.$$

The 1b_{2u} orbital cannot be constructed from s orbitals on the berylliums.

The concern arose that the minimum basis I might be favoring the p functions in such a way as to predict the wrong ground state. The cluster ground state was recomputed using both the double zeta I and double zeta II basis sets. The ground state was found to be the same one as predicted by the minimum basis. The same problem was noted for the Be₁₀(10,0) cluster. As in the case of Be₇(7,0), the double zeta basis sets

Table II. Chemisorption of hydrogen on the clusters of three and four beryllium atoms. The various clusters are illustrated in the figures in Appendix II. The $\text{Be}_3(3,0)$ cluster was used to study the open site. The cluster has D_{3h} symmetry, and with the hydrogen the symmetry is C_{3v} . The $\text{Be}_4(3,1)$ cluster has C_{3v} symmetry, both with and without the hydrogen. The eclipsed site was studied using this cluster. The other four atom cluster, $\text{Be}_4(4,0)$ has D_{2h} symmetry which is reduced to C_{2v} with the addition of hydrogen. The site of interest on this cluster is the bond midpoint.

<u>Cluster</u>	<u>Basis Set</u>	<u>r_e (Å)</u>	<u>E (kcal/mole)</u>
$\text{Be}_3(3,0)$	Minimum Basis I	1.25	19.1
	Minimum Basis IIb	1.17	22.5
	Double Zeta I	1.10	22.0
$\text{Be}_4(3,1)$	Minimum Basis I	1.24	28.7
	Double Zeta I	1.17	33.0
$\text{Be}_4(4,0)$	Minimum Basis I	1.26	70.1
	Double Zeta I	1.19	65.4

Table III. Chemisorption of hydrogen on the $\text{Be}_5(4,1)$ cluster. The cluster was C_{2v} symmetry. The hydrogen approaches in such a way as to retain this symmetry. The open, eclipsed and bond midpoint were all studied using this cluster.

<u>Site</u>	<u>Basis Set</u>	<u>r_e (Å)</u>	<u>E (kcal/mole)</u>
Open	Minimum Basis I	1.02	23.2
	Double Zeta I	0.91	31.9
Eclipsed	Minimum Basis I	1.15	30.1
	Double Zeta I	1.06	36.4
Bond Midpoint	Minimum Basis I	1.14	32.4
	Double Zeta	1.06	38.1

Table IV. Chemisorption of hydrogen at the directly overhead site on the $\text{Be}_7(7,0)$ cluster. The cluster has D_{6h} symmetry and with the hydrogen adsorbed the total system has C_{6v} symmetry.

<u>Basis Set Used</u>	<u>r_e ($\text{\AA}$)</u>	<u>E (kcal/mole)</u>
Minimum basis I	1.43	71.3
Minimum Basis IIb	1.39	73.9
Double Zeta I	1.39	60.9
Double Zeta II	1.38	64.0

Table V. The chemisorption of hydrogen at the bond midpoint site on the Be₁₀(10,0) cluster. The cluster has D_{2h} symmetry and with the addition of hydrogen the symmetry of the total system is reduced to C_{2v}. The results presented in this table are spatially restricted.

<u>Basis Set Used</u>	<u>r_e (Å)</u>	<u>E (kcal/mole)</u>
Minimum Basis I	1.16	31.5
Minimum Basis III	1.11	32.9
Double Zeta I	1.10	38.4
Double Zeta II	1.06	35.8

Table VI. The chemisorption of hydrogen on the two Be_6 clusters and the $\text{Be}_7(6,1)$ cluster. All three clusters with hydrogen have a total symmetry of C_{3v} . The $\text{Be}_6(6,0)$ and $\text{Be}_6(3,3)$ clusters have D_{3h} symmetry when the hydrogen is removed. The open site was investigated on the two Be_6 clusters, while the $\text{Be}_7(6,1)$ cluster was used to study the eclipsed site.

<u>Cluster</u>	<u>Basis Set Used</u>	<u>r_e ($\text{\AA}$)</u>	<u>E (kcal/mole)</u>
$\text{Be}_6(6,0)$	Minimum Basis I	1.18	47.3
	Double Zeta II	1.06	45.9
$\text{Be}_6(3,3)$	Minimum Basis I	1.11	55.3
	Double Zeta II	1.03	60.6
$\text{Be}_7(6,1)$	Minimum Basis I	1.11	40.8
	Double Zeta II	1.02	47.8

predicted the same ground state as the smaller basis set. From this we conclude the importance of the p functions is not a result of the basis set but reflects some real effect in the cluster.

The environment of the berylliums in the cluster is extremely different from that of the atom. The Mulliken populations per atom show 2p populations as large as 1.48 electrons ($\text{Be}_{10}(10,0)$) in the cluster. This high p electron population along with the unexpected ground state lead to the optimization of the 2s and 2p functions for the $\text{Be}_{10}(10,0)$ cluster. The optimum Slater exponents were found to be $\zeta(1s)=1.01$ and $\zeta(2p)=0.98$. This optimization increased the cohesive energy (the binding energy per atom for the cluster) of the cluster from 8.94 kcal/mole (Minimum basis I) to 12.23 kcal/mole. This basis set was labeled minimum basis III, and using this basis set the chemisorption on the $\text{Be}_{10}(10,0)$ cluster was recomputed (see Table V). The difference between the two minimum basis sets is very small. The bond length changes by 0.07 Å and the bond energy by only 1.4 kcal/mole out of a total of ~30 kcal/mole.

The optimum 2s and 2p exponents for the $\text{Be}_{10}(10,0)$ are nearly equal (1.01 and 0.98). Clearly, constraining the exponents to be equal would not result in a serious reduction in the quality of the basis set, but would greatly reduce the work required to optimize the basis set for the other clusters. This restriction, along with the constraint that the 2s and 2p Slater functions be fit to the same 3 gaussian functions (a computational convenience, which dramatically reduces the integral calculation time) was applied to the exponent optimization for the $\text{Be}_{13}(10,3)$ A cluster (see figure 12, Appendix II). The result of this calculation was similar to the $\text{Be}_{10}(10,0)$ results. The optimum exponent was $\zeta(2s=2p)=1.00$ as compared to $\zeta(2s)=1.01$ and $\zeta(2p)=0.98$. The cluster cohesive energy increased, relative to minimum basis I, by 3.04 kcal/mole to 14.03 kcal/mole. No comparisons of the chemisorption

were made for the Be_{13} (10,3) A cluster; rather the results of this optimization were applied to the chemisorption for the Be_7 (7,0) cluster. The results are listed in Table IV under minimum basis IIb (the constrained gaussian fit was dropped). As with the two previous clusters, the cohesive energy increased by 3.01 kcal/mole. The bond length became 0.04 Å shorter and the bond energy increased from 71.3 kcal/mole to 73.9 kcal/mole. Although the optimized minimum basis set improves the cohesive energy of the cluster it makes a small change in the chemisorption properties. The bond length shortens to lie between the minimum basis set I and the double zeta basis set. The bond energy changes by less than 5 percent.

The high 2p populations which prompted the additional minimum basis set tests also lead to a double zeta basis test. Two uncontracted functions had been initially used, but this was increased to four function which were optimized⁴² for $\text{Be } 3\text{P}$ and were contracted 31. This increase allowed a better description of the Be 2p orbital, which was clearly important in the bonding within the cluster. Tables IV and V contain the results of both double zeta basis sets for Be_7 (7,0) and Be_{10} (10,0). In both cases the difference between the two basis sets is small, the bond energy changes by less than 4.0 kcal/mole and the bond length by less than 0.05 Å. Both basis sets were flexible enough to describe the chemisorption. Although the increase in the number of primitive 2p functions decreases the total energy of the system, it made little difference on the chemisorption properties.

Extensive tests have been performed on the quality of the minimum basis set used. All the tests showed that the minimum basis set gives a reasonable description to the chemisorption properties. The bond energy is within 20 percent of the double zeta result, usually being too small, although $\text{Be}_7(7,0)$ and $\text{Be}_4(4,0)$ are exceptions to this. It is shown later that these clusters

have large edge effects which cause anomalous binding energies. For all of the larger clusters the minimum basis binding energy is, therefore expected to be too small. The bond lengths are too long by about $0.1 \text{ \AA}$. Optimization of the minimum basis set increases the cohesive energy, but makes a small difference in the chemisorptive properties. The bond length is a little shorter (by $\sim 0.05 \text{ \AA}$) and the bond energy remains essentially unchanged.

B. Computational Aspects

Whenever an iterative scheme, such as SCF is used, the question of convergence problems arise. For most molecules with a closed shell ground state, chemical intuition gives a reasonable starting guess and rapid convergence follows. In fact a bad starting guess usually leads to convergence of a closed shell ground state. The lowest open shell states, while not as easy as the closed shells, usually present no serious problems.

The first step in the calculation of the chemisorption for a specific cluster was to calculate the wavefunction for the lowest closed shell state. The hydrogen was then added and the lowest doublet computed. For the small clusters no problems of convergence arose, but the larger clusters presented several different problems.

The technique used for the clusters calculations was to start with an occupancy of $1s^2 2s^2$ for each of the n beryllium atoms in the cluster, then pick the occupied orbitals for the following iterations as the eigenvectors associated with the $2n$ lowest eigenvalues of the Fock matrix. The initial convergence proved poor for the larger clusters. The poor starting guess is the cause of this slow convergence. The beryllium atoms in the cluster look more like $1s^2 2s 2p$, than the $1s^2 2s^2$ occupancy of the atom. The $Be_{13}(10,3)$ A cluster proved impossible to converge until the 16 a' (the highest occupied orbital) and the 17 a' (the lowest unoccupied orbital) were switched. The initial calculation had been attempting to converge to an excited state, The result of a poor starting guess combined with two orbitals having very similar orbital energies. Whichever one of the orbitals was occupied had a lower eigenvalue of the Fock matrix and continued to be occupied throughout the calculation. Switching of virtual orbitals and occupied

orbitals was used to ensure that the ground state has been found.

A second technique which helped convergence and in finding the ground state was to first occupy only the 1s orbitals, converge this problem, then add a few more electrons and converge the system again. This was continued until all the electrons were added. This improved the convergence since the virtual orbitals of the n-m electron case proved to be a good guess for the n electron case orbitals. Also the choice of which orbitals within the same symmetry to occupy was made by eigenvalue of the fewer electron case and proved correct.

At infinite separation, the open shell orbital is the hydrogen orbital, but becomes a beryllium orbital in the chemisorbed system, with the hydrogen orbital becoming involved in the bonding orbitals. This change in the open shell orbital caused some problems, but we were able to overcome them by heavy damping (averaging of the output vectors with the input vectors). Although convergence for the first point was slow, the following points were started from the nearby converged vectors and showed good convergence.

The most serious problem was encountered for the calculation of the ionization potential of the Be_{22} cluster. The convergence problem was further complicated by the long time per iteration and the large core requirements for the SCF. The technique used to converge this case was as follows: first the integrals were transformed to integrals over the molecular orbitals of the closed shell ground state. We restricted ourselves to the occupied orbitals plus 15 virtual orbitals in the a' symmetry (the system has C_g symmetry) and 10 virtuals in the a'' symmetry. This transformed basis set contained fewer basis functions, and the reduction in basis functions reduced the time per

iteration and core requirements greatly. We were then able to experiment with shifting of orbital eigenvalues and damping the eigenvectors until convergence was obtained. The solution of the reduced basis was then expanded to the full basis set with the aid of the molecular orbitals in terms of the original basis functions. The same shift and damping were applied and convergence was achieved.

In addition to convergence problems, the determination of the ground state proved to be a non-trivial matter. The configuration predicted for a cluster, Be_n on the basis of n beryllium atoms with an occupancy of $1s^2 2s^2$ is not necessarily the ground state. In the cluster the beryllium atoms look more like $1s^2 2s 2p$. As we noted above this makes the selection of the trial vectors hard, but it also makes predicting the ground state impossible. We were forced to compute many states with different occupations in order to determine the ground state.

The problem was reduced in size by the same method as we used to improve convergence. First the $1s$ orbitals were occupied, then more and more electrons were added until the correct number of electrons were in the system.

This technique of adding electrons a few at a time using the virtual orbitals with the lowest eigenvalues, while excellent in choosing orbitals of the same symmetry, was not foolproof in deciding between two orbitals (in different symmetries) which had approximately the same eigenvalues. Both possibilities had to be tested. This technique reduced the number of states which had to be calculated in order to find the ground state.

The final method used, was a test of the ground state. This was

done by running a small CI consisting of all singly excited configurations from the highest occupied orbitals into the lowest unoccupied orbitals. The several lowest roots were examined in detail; the occupancy of any low lying state was determined and an SCF calculation with this occupancy was run as a check.

Although convergence problems were non-trivial, we were able to overcome them with existing methods or by developing others well suited for these cluster calculations. These same methods helped determine the ground state.

C. Symmetry Considerations

One of the most puzzling aspects of the early work was a large change in the chemisorptive bond energy when we changed from a spatially restricted (the wavefunction is constrained to transform as one of the irreducible representations of the molecular point group) wavefunction to a spatially unrestricted wavefunction.

One cluster to show this effect was $\text{Be}_3(3,0)$, as the binding energy of the hydrogen on this cluster changed by 16.32 kcal/mole, corresponding to a 265 percent

increase. In this cluster the 3 berylliums are positioned at the corners of an equilateral triangle. The cluster itself has D_{3h} symmetry. The hydrogen approaches the center of the triangle on a line perpendicular to the plane of the three berylliums, giving the entire system C_{3v} symmetry.

The ground state of the cluster was computed to be $1a_1^2 1e^4 2a_1^2 2e^4$. The hydrogen orbital transforms as a_1 , so at infinite separation the orbital occupancy is $1a_1^2 2e^4 2a_1^2 2e^4 3a_1^1$. We assumed that this would also be the occupancy of the chemisorbed system. Using minimum basis IIb ($\zeta(2s,2p)=1.0$), the chemisorption was computed. The bond length was 1.02 Å and a bond energy of 6.16 kcal/mole was obtained (see Table VII). The symmetry constraint was reduced to C_s for the wavefunction and the chemisorption recomputed. The results were very different, the bond energy had increased by more than a factor of 3 to 22.48 kcal/mole and the bond length had increased by 0.15 Å to 1.17 Å. Initially we were unable to understand this effect by looking at the wavefunctions with C_{3v} symmetry and those with C_s symmetry. This problem was overcome by the following procedure. The wavefunction was computed in C_{3v} symmetry. The integrals were transformed to integrals over the C_{3v} molecular orbitals. The symmetry

constraint was eliminated and the C_s wavefunction computed with the transformed integrals. The results of this calculation are shown in Table VIII. If no "symmetry breaking" had occurred, the $1a'$, $3a'$, and $5a'$ orbitals (in C_s symmetry) would correspond to a_1 orbitals in C_{3v} and the $2a'$ and $4a'$ orbitals would correspond to e_x orbitals in C_{3v} . The a'' orbitals in C_s would have been the e_y orbitals in C_{3v} . The C_s occupancy is therefore $1a'^2 2a'^2 3a'^2 4a'^2 5a'^1 1a''^2 2a''^2$. The $3a'$ orbital is seen to be mostly $2a_1$ (C_{3v}) orbital. The $4a'$ orbital is mostly the $3a_1$ orbital, while the $5a'$ orbital is mostly the $2e_x$ orbital. The $4a''$ orbital is doubly occupied while the $3a_1$ had been the open shell in the C_{3v} symmetry case. The C_{3v} state most closely related to the C_s calculation is the 2E ($\dots 3a_1^2 2e^3$) state and not the expected 2A ($\dots 2e^4 3a_1^1$) state. The 2E state was then computed, yielding 19.23 kcal/mole and a bond length of 1.21 Å in good agreement with the C_s , differences of 0.05 Å and 3.25 kcal/mole were observed.

It is clear that most of the "symmetry breaking" was a result of not having treated the Be_3H ground state. Reducing the symmetry constraints allowed for a reorganization of the orbitals, producing the correct ground state. In Be_3H the use of C_s symmetry allowed the doubly occupied orbital to become an a_1 orbital where before it was constrained to be an e orbital. There are some small additional effects that account for the remaining difference between the C_s symmetry and the 2E state. They can be viewed as a localization to help account for correlation effects.

In the cases where we did not accurately determine the correct high symmetry ground state, we used the low symmetry results. It is felt that they transform approximately as one of the irreducible representations of the high symmetry and are a ground state calculation. In these cases,

Table VII. A summary of the Be_3H (3,0) results for chemisorption.

Minimum basis IIb was used. The system has C_{3v} symmetry.

The CI calculations used the interacting space⁴³ in C_s symmetry.

<u>Type of Calculation and State</u>	<u>r_e (Å)</u>	<u>E (kcal/mole)</u>
SCF 2A_1 ($2e^4$ $3a_1^1$) C_{3v}	1.02	6.16
SCF 2E ($3a_1^2$ $2e^3$) C_{3v}	1.21	19.23
SCF C_s symmetry	1.17	22.48
CI 2A_1 C_{3v}	1.06	17.72
CI 2E C_{3v}	1.22	23.59

Table VIII. C_s ($^2A'$) molecular orbitals in terms of the C_{3v} (2A_1) molecular orbitals for Be_3H . The system has C_{3v} symmetry. The hydrogen is 1.93 bohr above the plane of the Be_3 cluster. Only the a' valence orbitals are shown. The orbital occupancy in C_s is $1a'^2 2a'^2 3a'^2 4a'^2 5a'^1 1a''^2 2a''^2$.

orbital in C_{3v} sym.	C_s		
	$3a'$	$4a'$	$5a'$
Orbital energy	<u>-0.605764</u>	<u>-0.277515</u>	<u>-0.31677</u>
1 $1a_1$	-0.000200	0.000402	-0.000009
2 $2a_1$	0.998107	0.024417	0.05573
3 $1e_x$	-0.000187	-0.000256	-0.000491
4 $2e_x$	-0.033131	-0.472879	0.834815
5 $3a_1$	0.045813	-0.880248	-0.449881
6 $4a_1$	-0.011992	0.0142669	0.183542
7 $3e_x$	0.019221	0.024215	-0.239100
8 $4e_x$	0.008069	-0.001640	-0.073923
9 $5e_x$	0.002566	0.003439	0.012311
10 $5a_1$	-0.000052	0.012185	0.033337

the high symmetry calculations are dealing with an excited state and therefore less meaningful. This symmetry dependence is a powerful tool in helping to determine the correct ground state of the adsorbed system.

CI calculations were also performed for the $\text{Be}_3(3,0)\text{H}$ system. The beryllium $1s$ orbitals were frozen and only excitations from the valence orbitals were allowed. The configurations were restricted to the interacting space⁴³, that is all singly and doubly excited configurations with a non-zero matrix elements with the reference state were included (due to the nature of the computer programs used, the calculations were performed in C_s symmetry). The results of the CI computations are summarized in Table VII. The 2E state CI result is very similar to the C_s symmetry SCF result. This small correlation effect is a good sign as to the accuracy of our single configuration description. Unlike the 2E state, the 2A_1 state has an extremely large correlation effect. Analysis of the 2A_1 wavefunction showed that all the important configurations (excluding the reference configuration) were $2e$ to $3a_1$ and/or $4a_1$ or $2e$ to $3e$ or $4e$ excitations (see Table IX). The system clearly favors having fewer electrons in the $2e$ orbital. This large correlation effect resulting from moving electrons out of the $2e$ orbital also indicates that the wrong high symmetry state was initially considered. Unlike repeating the SCF in lower symmetry, the CI calculations are of limited use in detecting unexpected ground states, because of their complexity.

Table IX. The important configurations (coefficients larger than 0.07) and the coefficients for the 2A_1 state (occupancy is $1a_1^2 2a_1^2 1e^4 2e^4 3a_1^1$) of Be_3H . $R=1.930$ bohr (the 2A_1 CI computed minimum)

<u>Coefficient</u>	<u>Occupation</u>
0.89834	$2e_x^2 2a_1^2 3a_1^1 2e_y^2$ (SCF reference)
-0.09762	$2e_x$ to $3a_1$ and $2e_y$ to $3e_y$
0.08809	$2e_y$ to $4e_y$
0.07354	$2e_y$ to $3e_y$
0.07587	$2e_x$ to $4a_1$
-0.07971	$2e_y^2$ to $3a_1$
-0.07603	$2e_y^2$ to $3e_x^2$
-0.09663	$2e_y^2$ to $4a_1^2$
-0.07532	$2e_y^2$ to $3e_y^2$
0.07971	$2e_x^2$ to $3a_1 4a_1$
-0.07603	$2e_x^2$ to $4a_1^2$
-0.07828	$2e_x$ to $3e_x$ and $2e_y$ to $3e_y$
-0.09063	$2e_x^2$ to $3e_y^2$

D. Mixed Basis Sets

The hydrogen adsorption on beryllium surfaces is reasonably well described by a minimum basis set. This is not true for all systems of interest. A minimum basis description would fail for any system in which the adsorption was ionic in nature, since the same minimum basis set would be totally unable to describe both the neutral atom at infinite separation and the chemisorbed ion equally well. Alterations would have to be made to a double zeta basis set, as well, to accurately describe the anion. After realizing that the adsorbate atom or molecule must use at least a double zeta basis set, it is clear that the cluster must also use a double zeta basis set to prevent the anomalous results associated with unbalanced basis sets. Unfortunately, the large basis set on the cluster atoms imposes the restriction of using only small clusters, and small clusters can give bad results due to large edge effects. There is a way out of this dilemma. A double zeta basis set is used for the adsorbate and for the cluster atoms directly involved in the bonding. The remaining cluster atoms use a minimum basis set. This should allow an accurate description of the bonding and also provide a potential around the double zeta atoms which can change, if necessary, during the chemisorption. In this way the cluster can be large enough to eliminate edge effects and still accurately describe the chemisorption. Since some of the systems we are interested in present this type of problem, we decided to investigate such a basis set using Be_nH where a large variety of basis set data already exists.

The mixed basis set used is a combination of double zeta II for the hydrogen and the adsorbate bonding berylliums and minimum basis set IIb ($\zeta(2s=2p)=1.00$) for the remaining berylliums.

The results of these calculations are summarized in Table X, along

Table X. Comparison between Mixed basis sets, double zeta and minimum basis sets. For the Mixed basis set the number of double zeta atoms is listed after the label "mixed".

<u>Cluster</u>	<u>Basis Set</u>	<u>r_e (Å)</u>	<u>E (kcal/mole)</u>
Be ₇ (7,0)	Minimum Basis IIb	1.39	73.9
Directly overhead	Double Zeta II	1.38	64.0
site C _{6v}	Mixed (1 DZ atom)	1.38	69.9
Be ₁₀ (10,0)	Minimum III	1.11	32.9
Bond Midpoint	Double Zeta II	1.06	35.8
site C _{2v}	Mixed (2 DZ atoms)	1.05	30.6
	Mixed (4 DZ atoms)	1.05	31.1
Be ₆ (6,0)	Minimum Basis I	1.18	47.3
open site	Double Zeta II	1.06	45.9
C _{3v}	Mixed (3 DZ atoms)	1.06	46.6
Be ₆ (3,3)	Minimum Basis I	1.11	55.3
open site	Double Zeta II	1.03	60.0
C _{3v}	Mixed (3 DZ atoms)	1.03	60.9
Be ₇ (6,1)	Minimum Basis I	1.11	40.8
Eclipsed site	Double Zeta II	1.02	47.8
C _{3v}	Mixed (4 DZ atoms)	1.02	48.4

with the minimum basis set and double zeta II results for comparison. The $\text{Be}_7(7,0)$ cluster was used to study the directly overhead site, in which the central atom was involved in the bonding. One double zeta beryllium was therefore used for this cluster. The bond midpoint site was investigated using the $\text{Be}_{10}(10,0)$ cluster. Initially two double zeta atoms were used, but the number was then increased to 4. Both of the Be_6 clusters ((6,0) and (3,3)) had been used to study the 3 fold coordinated open site; 3 double zeta atoms were used for these clusters. The 3 fold coordinated eclipsed site had been studied using the $\text{Be}_7(6,1)$ cluster and 4 double zeta atoms were used, 3 on the top layer and one on the second layer.

In all cases the bond length was the same as that of the double zeta (actually the $\text{Be}_{10}(10,0)$ differed by $0.01 \text{ \AA}$). The bond energies, however, vary somewhat. The results for both Be_6 clusters and $\text{Be}_7(6,1)$ are extremely good, the largest difference being only 0.7 kcal/mole in the case of $\text{Be}_6(6,0)$. The $\text{Be}_7(7,0)$ cluster has a bond strength (69.9 kcal/mole) between the double zeta II (64.0 kcal/mole) and the minimum basis IIb (73.9 kcal/mole). The worst case is the $\text{Be}_{10}(10,0)$ where the mixed basis set results (30.6 kcal/mole for 2 double zeta atoms or 31.1 kcal/mole for 4 double zeta atoms) lie outside the minimum basis set III (32.9 kcal/mole) and the double zeta II result (35.8 kcal/mole), but all 3 results are in good agreement. The small change due to the addition of the two additional double zeta atoms is surprising when the change (8.2 kcal/mole) between the bond midpoint results for the $\text{Be}_{10}(10,0)$ and $\text{Be}_{14}(14,0)$ are considered, where the addition of the nearest neighbors to these two berylliums makes a sizable difference, but an increase in basis set makes little change. As we will discuss later, edge effects may be responsible for some of the problems with this cluster.

The mixed basis sets give geometry predictions in excellent

agreement (within $0.01 \text{ \AA}$) with the double zeta results. The bond energies vary from agreement with the double zeta to agreement with the minimum basis in the worst case. Such mixed basis sets appear to be ideally suited for cluster calculations, giving both good results and limited number of basis functions. The final step is to test these basis sets out on an ionic system where charge transfer takes place.

E. Properties of the Cluster without Hydrogen

Edge effects are certainly responsible for the large variation in the adsorptive energies of the small clusters. Furthermore, the nature of the bonding in the Be metal prevents simple saturation of the edge bonds as done by Cartling and coworkers⁴⁴ for silicon. However, other properties of the cluster without hydrogen are also expected to reflect these edge effects. Therefore, another measure of the importance of edge effects might be gained by looking at several bulk properties as a function of cluster size. It should be pointed out that these cluster properties are only used as a measure of the edge effects and are not an attempt to get accurate cluster properties with a very limited number of atoms. It is hoped that we will then be able to identify anomalous chemisorptive properties with large edge effects, thus simplifying the interpretation of our data. And we further note that chemisorption involves only differences between the cluster plus an atom at infinite separation and the bound cluster-atom. Thus we expect the theoretical description of chemisorption to converge much more rapidly as a function of cluster size than do the cluster properties.

The first cluster property investigated was the ionization potential. The energy calculated for the removal of one electron from the cluster is related to the work function of the metal. Whenever a calculation and an experiment are compared, one must be careful that the same quantities are being compared. The experiment does not measure the removal of one electron from the crystal, but a sufficient number to be detectable by the apparatus. Also the experiment is able to measure different work functions for the various faces of a crystal, while the calculation does not restrict the electron loss to a specific face. It is clear

that the calculation will not reproduce the work function even for an infinite cluster, but we can reasonably expect to see a trend from the ionization of the atom (9.32 eV^{45}) toward the work function of the metal (3.22 eV^{33}). The variation in this trend should be a measure of the edge effects.

The absence of observed magnetic properties²⁵ guarantees a closed shell ground state. From the fact that beryllium is a conductor, we can infer that the separation between the ground state and the lowest excited states will be small. Also, the separation between a triplet and open shell singlet, with the same occupation, will become small as the "pairing energy" goes to zero with the increased delocalized nature of the "conduction" orbital with an increase in the metallic nature of the cluster. The lowest triplet, and for some of the larger clusters the open shell singlet, were computed to measure the edge effects and metallic properties of the cluster.

The cohesive energy is easily calculated and is expected to show two effects for large clusters. The cluster should be bound with respect to the atoms and the addition or repositioning of one atom should not greatly effect the results. The first is a statement of the existence of Be metal at room temperature and the second is to be expected for any stable, large crystal lattice. If an arbitrary restriction to lattices of only 2 layers or less is adopted, it is clear that one will not obtain the correct value for the cohesive energy since the ratio of bulk to face and edge atoms is incorrect. But we can expect convergence to some fixed value.

Chemical intuition also shows that these cluster properties should relate to the chemisorptive properties. The ionization potential can be seen as a measure of how strongly the electrons are bound and therefore

how willing the cluster will be to donate electrons to the bonding site and the hydrogen atom. The unstable cluster views bonding with the hydrogen as a method of spreading its electrons over a larger region of space, thus helping to reduce the beryllium-beryllium repulsive interaction. The bonding of the hydrogen to the surface might be considered as a two step process. First the cluster is excited from the singlet ground state to the triplet, then the hydrogen bonds with an open shell of the cluster. This would predict that a smaller singlet-triplet separation would be expected to produce a stronger cluster-hydrogen bond. Unfortunately, this is an oversimplification of the problem, since the hydrogen actually interacts most strongly with the low lying molecular orbitals of the beryllium cluster, those with approximately the same orbital energy as the hydrogen orbital.

Spatially unrestricted single-configuration wavefunctions were computed for the clusters with 13 or less beryllium atoms. Spatially restricted wavefunctions were computed for the Be_{14} and Be_{22} clusters. Considered were the closed shell singlet, the lowest triplet, and the positive ion (a doublet state). The ionization potential reported here is the energy difference between the closed shell singlet and the positive ion. The cohesive energy is calculated as the per-atom energy difference between the singlet and n Be atoms, where n is the number of atoms in the cluster. The singlet-triplet separation is self-explanatory. A negative singlet-triplet separation in Tables XI and XII indicates the triplet is lower in energy than the singlet.

We should note that the Be_5 minimum basis set triplet state was done in C_s symmetry. This was due to convergence problems with the no symmetry calculations.

One indication of the size of the edge effects is the calculation of

the singlet-triplet separation. The calculation is not a measure of the conduction ability of the cluster, but a measure of the edge effects. This is best viewed by an example; in the case of $\text{Be}_{13}(10,3) \text{ A}$, the triplet orbitals were plotted (Figures II and III). The plot is through the top plane of the cluster. The positions of the ten atoms in the top surface are marked by x's. The orbitals are not delocalized over the cluster, but "dangle" off the end of the cluster. It is clear that this property is very sensitive to edge effects.

A frozen orbital approximation was made and the low lying triplets and singlets recomputed. Freezing the excited state orbitals was imposed to prevent relaxation of the orbitals, which increase the edge effects. In this way a more reasonable measure of the conduction ability of the cluster could be obtained. A list of singly excited configurations was generated; we restricted the configurations to those excitations from the five or ten highest occupied orbitals into the lowest five or ten virtual orbitals per symmetry, then a CI was run and the diagonal elements of the H matrix printed. This approach was used, since it computed all the excited states with the same symmetry and spin in one run.

The procedure is not a self-consistent one, so the choice of the orbitals will effect the results. The original choice of the orbitals for the Be_{14} cluster was the closed shell ground state. The results of this calculation are summarized in Table XI. The calculations for this cluster were repeated with the virtual orbitals (the orbitals not occupied in the closed shell ground state) coming from the positive ion calculation. The results for the lowest excited singlet and triplet of each symmetry in the second calculation differ from the

Figure II. The $16 a'$ orbital density of the $\text{Be}_{13}(10,3)A, {}^3A$ state. The plane of the plot is the top layer of the beryllium cluster. The x's mark the positions of the beryllium atoms.

XBL 769-10461

Figure III. The $17 a'$ orbital density of the $\text{Be}_{13}(10,3)A, {}^3A$ state. The plane of the plot is the top layer of the beryllium cluster. The x's mark the positions of the beryllium atoms.

XBL 79-10462

Table XI. The separation between the ground state and several excited states using a frozen orbital approximation. The term "improved" orbitals implies that the virtual orbitals were taken from the positive ion calculation. The excitation energies are reported in eV.

Cluster	State	Excitation Energy (eV)	The number of excited states within 1 eV of first excited state
Be ₂₂ (14,8)	¹ A'	1.29	9
	¹ A"	1.48	12
	³ A'	0.76	9
	³ A"	0.96	9
Be ₁₄ (14,0)	¹ A'	1.27	3
improved	¹ A'	1.27	3
	¹ A"	0.07	1
improved	¹ A"	0.06	1
	³ A'	1.18	5
improved	³ A'	1.18	5
	³ A"	-0.07	2
improved	³ A"	-0.08	2

first by a maximum of 0.01 eV (see Table XI). The choice of the virtual orbitals has little effect on the excitation energies, and therefore only the ground state orbitals were used for the Be_{22} cluster.

Several interesting points are observed for this series of calculations. The first is the striking difference in the results between the Be_{22} and Be_{14} clusters. The Be_{22} cluster has a larger excitation energy and a larger separation between the excited singlets and excited triplets, than the corresponding Be_{14} cluster values. The Be_{14} cluster has 2 closed shell occupancies which differ by only 1.11 kcal/mole. The occupancies in C_s are $\dots 15a'^2 16a'^2 \dots 10a''^2 11a''^2 12a''^2$ and the nearby excited state $\dots 15a'^2 16a'^2 17a'^2 \dots 10a''^2 11a''^2$. It is the obvious why the singlet and triplet states with the occupation $\dots 15a'^2 16a'^2 17a' \dots 10a''^2 11a''^2 12a''$ lie so low in energy. On this basis, Be_{14} would appear to give a better description of a metal; but if the number of excited states within 1 eV of the first excited state (see Table XI) are considered, Be_{22} would appear to give a better description of the metal. Clearly, even our largest clusters are too small to completely describe a metal, and edge effects can cause a large variation in results for the two largest clusters considered.

A complete summary of the cluster and chemisorptive properties is located in Table XII. The limited data seems to indicate some convergence on the ionization potential, the singlet-triplet separations are not unreasonable for the large clusters, and the cohesive energy is positive and increasing as the number of bonds increases, in fact the cohesive energies per "bond" are: $\text{Be}_{10}(10,0)$ 6.44*, $\text{Be}_{13}(10,3)$ A 5.93, $\text{Be}_{13}(10,3)$ B 5.88, $\text{Be}_{14}(14,0)$ 6.93, and $\text{Be}_{22}(14,8)$ 6.76 kcal/mole.

* $\text{Be}_{10}(10,0)$ cohesive energy was computed using Minimum basis III.

All of these factors point to a reduction in edge effects and the beginning of convergence for some of the cluster properties, but (as the singlet-triplet separation illustrated) not an accurate description of a metal.

A close inspection of Table XII shows that no simple correlation exists which connects any of the cluster properties with the chemisorptive properties. For any of the cluster properties, two clusters can be found with the same cluster property, but very different chemisorptive results. There are several examples of this for the cohesive energy; $\text{Be}_4(4,0)$ has a negative cohesive energy (-9.78 kcal/mole) as does $\text{Be}_3(3,0)$ (-5.03 kcal/mole), but the $\text{Be}_4(4,0)$ gives a very unreasonable description of the chemisorption at the bond midpoint site, while the $\text{Be}_3(3,0)$ result is reasonable result for the size of the cluster. The two Be_7 clusters show this result even more clearly. $\text{Be}_7(7,0)$ has an anomalous chemisorption result and has a low cohesive energy (3.64 kcal/mole), but the $\text{Be}_7(6,1)$ gives a reasonable description of the chemisorption and has an even lower value of the cohesive energy. The ionization potential is even more puzzling. $\text{Be}_{14}(14,0)$ and $\text{Be}_{22}(14,8)$ have the same ionization potential (4.73 ev and 4.71 ev, respectively). The results for the chemisorption at the open and bond midpoint sites are the same for both clusters, but the results for the directly overhead site are very different (59.0 kcal/mole vs. 31.4 kcal/mole).

This lack of correlation between the cluster and the chemisorption properties is understandable on the basis of our original statements on the cluster model. The cluster properties are a measure of the total amount of edge effects for a specific cluster, while the chemisorption is very local in nature and only those edge effects which the adsorbate

Table XII. A comparison between some properties of the cluster without hydrogen with the chemisorption results for the same cluster with hydrogen. Results in parentheses were obtained using double zeta I, all others used a minimum basis set.

Site	Description	Ionization Potential (eV)	Singlet-Triplet Separation (eV)	Cohesive Energy (kcal/mole)	Chemisorbed Bond energy (kcal/mole)
Directly	Be	8.44 (8.04)	1.78 (2.02)	— (—)	46.4 (44.5)
Overhead	Be ₇ (7,0)	5.21	-0.73	3.64	71.3
	Be ₁₀ (7,3)	6.05	0.04	8.98	27.3
	Be ₁₃ (10,3)B	4.70	-0.62	14.03	31.3
	Be ₁₄ (14,0)	4.73	-0.39	14.44	59.0
	Be ₂₂ (14,8)	4.71	n.c.	20.59	31.4
Open	Be ₃ (3,0)	6.97 (6.47)	0.73 (-.98)	-5.03 (-3.24)	19.1 (22.0)
	Be ₅ (4,1)	5.73 (5.11)	-0.68 (-0.40)	0.23 (1.68)	23.2 (31.9)
	Be ₆ (6,0)	5.58	-0.24	-1.53	47.3
	Be ₆ (3,3)	5.30	-0.43	3.51	55.3
	Be ₉ (6,3)	4.81	-1.56	3.53	50.2
	Be ₁₃ (10,3)A	4.32	-0.62	14.15	39.0
	Be ₁₄ (14,0)	4.73	-0.39	14.44	56.1
	Be ₂₂ (14,8)	4.71	n.c.	20.59	55.1
Eclipsed	Be ₄ (3,1)	7.18 (6.68)	1.15 (1.08)	4.07 (4.84)	28.7 (33.0)
	Be ₅ (4,1)	5.73 (5.11)	-0.68 (-0.40)	0.23 (1.62)	30.1 (36.4)
	Be ₇ (6,1)	5.58	-0.24	1.49	40.8
	Be ₁₃ (10,3)A	4.32	-0.62	14.15	57.2
	Be ₁₃ (10,3)B	4.70	-0.62	14.03	58.3
	Be ₂₂ (14,8)	4.71	n.c.	20.59	51.9

Table XII. continued

Bond	Be ₄ (4,0)	5.13 (4.94)	-1.18 (-0.79)	-9.78 (-6.69)	70.1 (65.4)
Midpoint	Be ₅ (4,1)	5.73 (5.11)	-0.68 (-0.40)	0.23 (1.62)	32.4 (38.1)
	Be ₁₀ (10,0)	5.17	0.02 .	8.94	45.3
	Be ₁₃ (10,3)A	4.32	-0.62	14.15	44.8
	Be ₁₄ (14,0)	Δ.73	-0.39	14.44	53.1
	Be ₂₂ (14,8)	4.71	n.c.	20.59	53.3

bonding berylliums feel affect the chemisorption. Although the measure of the edge effects supplied by these cluster calculations have not helped in the understanding of the fluctuation in the chemisorption results, they have verified the local nature of the bonding and strengthened the use of the cluster model for chemisorption studies.

Although the cluster properties do not give us an a priori method of evaluating a cluster as a model for chemisorption, they are not totally worthless with respect to understanding chemisorption. All three cluster properties, taken along with the chemisorption data help to explain some of the results for the smaller clusters, where the total edge effects and the local edge effects are expected to be similar. The $\text{Be}_4(4,0)$ cluster has a negative cohesive energy (-9.78 kcal/mole), and ionization potential lower than would be expected for such a small cluster (5.13 ev), and the triplet state 1.18 ev lower than the closed shell singlet state. These 3 facts help to explain the $\text{Be}_4(4,0)\text{H}$ results.

The cluster properties show that even the largest clusters do not describe a metal, and edge effects still remain for the large clusters, but have shown signs that some of the cluster properties have begun to converge. This is encouraging since the chemisorption is expected to converge more rapidly than the cluster properties, since the chemisorption involves the difference between the cluster with and without the adsorbing atom or molecule. The lack of correlation between the cluster properties and the chemisorption indicates the local nature of the bonding. All of these results verify the use of the cluster model for the study of chemisorption and the feasibility of getting converged results with a limited number of atoms. All that remains is a method of determining the edge effects felt by the adsorbate

bonding berylliums. This is done in the next section on the basis of nearest neighbor considerations.

F. Summary of Results for Chemisorption

The minimum basis set was tested extensively and shown to give a reasonable description of the chemisorption. The cluster without hydrogen was investigated and these properties compared with the chemisorptive properties. This comparison and these cluster properties indicate the workability of the cluster model. With the model tested, it seems safe to proceed to the chemically interesting problem of chemisorption.

The clusters were chosen to be a part of the (0001) surface and designed for specific sites, and therefore most of the small clusters were used to study only one site. Designing the clusters with the site of interest at the center was an attempt to reduce the edge effects at the binding site. For example, the $\text{Be}_3(3,0)$ cluster was used for the open site; bond midpoint and directly overhead sites exist, but were not used since they would have been on the edge of the cluster.

The most important question to be answered is the number of atoms needed to get convergence in chemisorptive properties. Until this is answered no chemically interesting conclusions on chemisorption of hydrogen on beryllium surfaces can be made. In addition to the number of atoms, considerations of geometry and the number of nearest neighbors are extremely important for an understanding of the edge effects at the binding site, and ultimately the extension to other systems.

The most relevant properties which we can compute are the binding energy and the equilibrium geometry (the distance of the hydrogen above the plane of the cluster) for the four sites of interest. This will answer the question of site preference for the chemisorption. The possibility of dissociative chemisorption of H_2 can be considered on

the basis of the computed binding energy and geometrical considerations. Finally the experimentally measurable quantities, such as the vibrational frequency of the chemisorbed hydrogen and the diffusion of the hydrogen through the beryllium cluster, can be considered.

A complete summary of the chemisorption is contained in Table XIII. All of the results reported in Table XIII use a minimum basis set. The clusters with 10 or less beryllium atoms use minimum basis I, the two Be_{13} clusters use minimum basis IIa, and the Be_{14} and Be_{22} clusters use minimum basis IIb (these basis sets are described in section IIA. Basis Set Tests and are tabulated in Appendix III).

Initially, the convergence of the chemisorption with cluster size is discussed by site.

The directly overhead site. Looking down the column, there appears to be no convergence of results with cluster size, however if one strikes out the $\text{Be}_7(7,0)$ and $\text{Be}_{14}(14,0)$ results, this is no longer the case. Both of these clusters contain only one layer, and it would appear as if this has a large effect on the chemisorption. This is very reasonable since the atom most directly involved with the bonding is missing three of its nearest neighbors, the three atoms below it. Once this fact is recognized, it is safe to conclude that this site is fairly well converged with a bond length of approximately $1.4 \text{ \AA}$ and a bond energy of about 30 kcal/mole.

The eclipsed site. The two 13 atom clusters have about the same binding energy (57.2 kcal/mole and 58.3 kcal/mole) and bond lengths ($0.90 \text{ \AA}$ and $0.94 \text{ \AA}$). This is reasonable since, one would expect that the movement of one atom not directly involved in the bonding should have only a small effect on the chemisorption. The Be_{22} result is somewhat different (~ 57.5 kcal/mole vs. 51.9 kcal/mole) indicating

Table XIII. A summary of hydrogen chemisorption on beryllium listed by site. The results were obtained using a minimum basis sets. Bond distances r_e are in Å and chemisorptive bond energies D_e in kcal/mole.

Open site			Eclipsed site			Bond midpoint site			Directly overhead site		
Model	r_e	D_e	Model	r_e	D_e	Model	r_e	D_e	Model	r_e	D_e
Be ₃ (3,0)	1.25	19.1	Be ₄ (3,1)	1.24	28.7	Be ₄ (4,0)	1.26	70.1	Be ₁ (1,0)	1.42	46.4
Be ₆ (6,0)	1.18	47.3	Be ₅ (4,1)	1.15	30.1	Be ₁₀ (10,0)	1.17	45.3	Be ₇ (7,0)	1.43	71.3
Be ₁₄ (14,0)	1.11	56.1	Be ₇ (6,1)	1.11	40.8	Be ₁₄ (14,0)	1.17	53.1	Be ₁₄ (14,0)	1.40	59.0
Be ₅ (4,1)	1.02	23.2	Be ₁₃ (10,3)A	0.90	57.2	Be ₅ (4,1)	1.14	32.4	Be ₁₀ (7,3)	1.43	27.3
Be ₆ (3,3)	1.11	55.3	Be ₁₃ (10,3)B	0.94	58.3	Be ₁₃ (10,3)A	1.05	44.8	Be ₁₃ (10,3)B	1.41	31.1
Be ₉ (6,3)	1.13	50.2	Be ₂₂ (14,8)	0.97	51.9	Be ₂₂ (14,8)	1.04	53.4	Be ₂₂ (14,8)	1.39	31.4
Be ₁₃ (10,3)A	0.99	39.0									
Be ₂₂ (14,8)	0.94	55.1									

that we may not have reached convergence with respect to cluster size.

The bond midpoint site. The interesting thing to note is that $\text{Be}_{14}(14,0)$ and $\text{Be}_{10}(10,0)$ (one layer clusters) have longer bond lengths than the large two layer clusters, $1.17 \text{ \AA}$ for the one layer clusters as compared to $\sim 1.05 \text{ \AA}$ for the two layer clusters. In spite of this difference, both large clusters $\text{Be}_{14}(14,0)$ and $\text{Be}_{22}(14,8)$ have the same binding energy $\sim 53 \text{ kcal/mole}$.

The open site. As in the case of the bond midpoint site, the $\text{Be}_{14}(14,0)$ has a longer bond length than the two layer $\text{Be}_{22}(14,8)$ ($1.11 \text{ \AA}$ vs. $0.94 \text{ \AA}$), but similar binding energies (56.1 kcal/mole vs. 55.1 kcal/mole). We should also note the very low value for the Be_{13} cluster (39.0 kcal/mole).

Unlike the other 3 sites, the results for the directly overhead site appear convincingly converged. It appears that reasonable results are obtained when all of the atoms involved in the adsorbate bond have all their nearest neighbors, and this occurs for the $\text{Be}_{10}(7,3)$ cluster. Additional atoms would be needed in order to get completely converged results, for the directly overhead site the addition of 3 atoms to form $\text{Be}_{13}(10,3)\text{B}$ changes the results from 27.3 kcal/mole (the $\text{Be}_{10}(7,3)$ result) to 31.1 kcal/mole . The even larger $\text{Be}_{22}(14,8)$ has virtually the same result (31.4 kcal/mole).

Based on this criteria, a cluster of $\text{Be}_{18}(12,6)$ would be needed for the open site. The minimum cluster size for the eclipsed site would be $\text{Be}_{19}(12,7)$ (this assumes the atom on the second layer does not need its neighbors on the third layer). The bond midpoint could be studied with a cluster of $\text{Be}_{15}(10,5)$ if the bond midpoint site is two fold coordinated and a cluster of $\text{Be}_{22}(14,8)$ if the bond midpoint is four fold coordinated.

Inspection of the results show that $\text{Be}_{14}(14,0)$ and $\text{Be}_{22}(14,8)$ have the same bond energies (to within 1 kcal/mole) for both the open and bond midpoint sites. Convergence for these sites is more dependent upon the first layer, than the second layer. This lack of importance of the second layer explains the very similar results for open (55.1 kcal/mole) and the eclipsed site (51.9 kcal/mole). Although the binding energy converges for the one layer clusters, the bond lengths are too long for the single layer clusters by $\sim 0.1 \text{ \AA}$, and the vibrational frequency for the hydrogen adsorbed on the surface changes by ~ 4 to 6 percent (Table XVI) with the addition of the second layer.

The single layer $\text{Be}_{10}(10,0)$ and the two layer $\text{Be}_{13}(10,3)\text{A}$ have very similar binding energies (45.3 kcal/mole and 44.8 kcal/mole respectively). This is the same one-two layer effect as the $\text{Be}_{14}(14,0)$ and $\text{Be}_{22}(14,8)$ show. The interesting point is the Be_{10} - Be_{13} results are ~ 9 kcal/mole lower than the Be_{14} - Be_{22} . If the bond midpoint site was a two fold coordinated site this effect would not have been observed, it is clear that the bond midpoint site is a four fold site. If the hydrogen is $1.01 \text{ \AA}$ above the surface, its distance to the nearest bonding berylliums is $1.522 \text{ \AA}$ and the distance to the two additional berylliums is $2.221 \text{ \AA}$. At the open site the similar distances are $1.659 \text{ \AA}$ to the bonding berylliums and $3.635 \text{ \AA}$ to the next set of beryllium atoms. Both the results and distance consideration indicate the bond midpoint site should be treated as a four fold coordinated site, making $\text{Be}_{22}(14,8)$ the minimum cluster to give reasonable results.

This nearest neighbor analysis also helps to explain the low (39.0 kcal/mole) result for the open site on the $\text{Be}_{13}(10,3)\text{A}$ cluster.

Table XIV. The vibrational frequencies for the hydrogen adsorbed on the beryllium surface. The results are given in cm^{-1} .

Cluster	Site			
	directly overhead	open	eclipsed	bond midpoint
$\text{Be}_{22}(14,8)$	2060	1220	1230	1360
$\text{Be}_{13}(10,3)\text{A}$	----	1190	1190	1360
$\text{Be}_{13}(10,3)\text{B}$	2070	----	1190	----
$\text{Be}_{14}(14,0)$	1960	1150	----	1300

This site was chosen so that one of the bonding berylliums is on the edge. It is missing 3 of its nearest neighbors, two on the top layer and one on the second layer. The other two bonding berylliums have 8 out of a possible 9 nearest neighbors. Large edge effects at the binding site can give poor results, this was not an ideal site for the study of the open site.

Different chemisorption properties converge at different rates for the various sites, but it appears that all the chemisorption properties give reasonable results when all the adsorbate bonding berylliums have all their nearest neighbors. The $\text{Be}_{22}(14,8)$ cluster meets this nearest neighbor criteria for all four sites, and we can take these $\text{Be}_{22}(14,8)$ results as being nearly converged within the model used (i.e. minimum basis, cluster model and SCF formalism). We draw the following conclusions about chemisorption of hydrogen on beryllium. The directly overhead site is different from the other three sites with a bond energy of ~ 30 kcal/mole and a bond length of ~ 1.4 Å. The other three sites are very similar, all having bond energies of approximately 50 kcal/mole and bond lengths on the order of 1 Å.

An important property of the adsorbed hydrogen is its vibrational stretching frequency. For BeH , this property is described well within the Hartree-Fock approximation. The near Hartree-Fock result²⁹, $\omega_e = 2147 \text{ cm}^{-1}$ is very close to the extensive CI of Bagus et.al.³¹, $\omega_e = 2143 \text{ cm}^{-1}$. The minimum basis set result, $\omega_e = 2174 \text{ cm}^{-1}$ is in fortuitously good agreement with the more extensive calculations and with experiment⁴⁶, $\omega_e = 2061$.

Using the largest clusters, $\text{Be}_{13}(10,3)\text{A}$ and B , $\text{Be}_{14}(14,0)$ and

$\text{Be}_{22}(14,8)$, we computed the vibrational frequency of the hydrogen stretching. Three points near the minimum were fit to a parabola, determining the force constant. The mass of the cluster was assumed to be infinite, and thus the reduced mass of the system was the mass of hydrogen. These results are reported in Table XIV. Note that the results are very similar among the four clusters. The $\text{Be}_{14}(14,0)$, which gave poor binding for the directly overhead site, gives reasonable results for the stretching frequency, differing by 5 percent from the two layer clusters. This difference in the vibrational frequency is the same as noted above for the one vs. two layer clusters at the open and bond midpoint sites.

The vibrational frequencies for the open and eclipsed sites are the same ($\sim 1225 \text{ cm}^{-1}$) falling at the lowest energy. The bond midpoint site is somewhat higher in frequency falling at 1350 cm^{-1} . The directly overhead site is very different (2060 cm^{-1}), being almost twice that of the open and eclipsed sites. This result is qualitatively easy to understand. When the hydrogen moves perpendicular to the surface at the open or eclipsed site, the change in distance between the hydrogen and the bonding berylliums is less than the change in distance between the hydrogen and beryllium for the equivalent perpendicular movement at the directly overhead site. To be more quantitative, consider the problem with springs replacing the bonds. Let s be the distance from the hydrogen to the beryllium (the length of the spring), let b be the distance from the beryllium to a line normal to the beryllium surface and passing through the hydrogen, and let z be the length of this line (the distance of the hydrogen above the surface). For the directly overhead site, s and z are equal. All other sites have the relationship

$s^2 = z^2 + b^2$ or $s = (z^2 + b^2)^{1/2}$. The change in the spring length for the vertical movement is $ds/dz = (z^2 + b^2)^{-1/2} z = z/s$. The potential energy for a spring, with force constant k , is $E = -1/2 k (\Delta x)^2$. In terms of the movement of the spring, $E = -1/2 k \Delta s^2$. Converting to the movement perpendicular to the surface, $E = -1/2 k (z/s \Delta z)^2$. Regrouping $E = -1/2 (k (z/s)^2) \Delta z^2$ or $E = -1/2 k_{\text{eff}} \Delta z^2$, where k_{eff} is the effective force constant after geometrical considerations, $k_{\text{eff}} = k(z/s)^2$. The frequency is proportional to the square root of the force constant, therefore the geometrical correction to the perpendicular movement is z/s , thus the vibrational frequency at any site should be z/s times the directly overhead site frequency. This assumes the force constant of each spring at the open site (or eclipse) is $1/3$ of the directly overhead site, and the bond midpoint springs have a force constant $1/2$ that of the directly overhead site. The vibrational frequency of the bond midpoint site is the same for the $\text{Be}_{13}(10,3)\text{A}$ cluster and $\text{Be}_{22}(14,8)$, and it is therefore safe to assume it is a two fold site for vibrational analysis, even though it is a four fold site by energy criteria. The force constants were so approximated, to allow the reduction of the problem to one spring with the same force constant as before, the frequency is then just z/s times the directly overhead site (2060 cm^{-1}). Substituting in the appropriate values of s and z , the spring model predicts 1394 cm^{-1} for the bond midpoint ($z=1.968$ bohr and $s=2.922$ bohr), 1229 cm^{-1} at the eclipsed site ($z=1.840$ bohr and $s=3.100$ bohr) and 1201 cm^{-1} for the open site ($z=1.779$ bohr and $s=3.064$ bohr). The simple model clearly illustrates that the observed relationships between the frequencies are just a matter of geometry.

The Be_2 cluster is large enough to be able to describe all four sites reasonably well, and it is therefore possible to consider the variation in potential along a path through the several sites. Figure IV shows the variation in potential energy as a function of position on the cluster. The region between the eclipsed and open sites appears to have approximately the same chemisorption energy, which we calculate to be about 50 kcal/mole. This is most probably too small as a result of using a minimum basis. This leads to the interesting possibility of dissociative adsorption of H_2 . The dissociation energy of H_2 ($D_e(\text{H}_2)=109.5 \text{ kcal/mole}^{47}$) is very close to the computed energy returned by the formation of 2 beryllium-hydrogen bonds. The H_2 could approach the surface and (once it is sufficiently close) two hydrogen-beryllium bonds could form. The two H atoms would then be free to move around the surface, since there appears to be a large portion of the surface with the same potential for hydrogen bonding. This analysis is very simple, since it does not account to the change in chemisorption of the hydrogen due to a hydrogen chemisorbed nearby or the possibility of a barrier in breaking the H_2 bond in order to form the hydrogen beryllium bonds. Our purpose is only to point out that the possibility of dissociative adsorption is not unreasonable from our results.

Since hydrogen is known⁴⁸ to be absorbed into the bulk for many metals, this possibility was considered for the open site of Be_{22}H . This would appear to be the most obvious site for absorption to occur. However, the total energy appears to become continuously higher as R is decreased from its equilibrium value $R_e=0.14 \text{ \AA}$. When the H atom is placed on the surface (i.e., $R=0.0 \text{ \AA}$) the relative energy is only 4 kcal/mole below the asymptotic limit of Be_{22} plus H. When the H

Figure IV. The variation in potential energy for the various sites of the $\text{Be}_{22}(14,8)$ cluster. The values are reported in kcal/mole. The open site is labeled O, the eclipsed site E, the bond midpoint BMP, and the directly overhead site is labeled DOH. The arrows point to the location of the site on the cluster. The lines on the bottom of the figure are the binding energies drawn to scale.

12-13-14-15

16-17-18-19

20-21-22-23

24-25-26-27

is halfway between the top and bottom layers (i.e., $R = -0.90 \text{ \AA}$; equidistant from six Be nuclei) the system has a total energy only 2 kcal below the separated surface plus atom limit, and is 53 kcal/mole above the chemisorbed equilibrium value. Thus it appears unlikely that absorption will occur into a perfect beryllium crystal without some deformation of crystal structure, and maybe not even then. Of course the hydrogen could always be absorbed into the crystal through a dislocation, vacancy or impurity in the metallic structure.

III. Bonding, Electronic Structure and Edge Effects Analyzed from the Properties of the Charge Distribution

One way ab initio calculations can aid in the understanding of chemisorption is through their ability to describe the nature and extent of the bonding. These quantities are not easily deduced from experimental data, but are crucial to understanding chemisorption at the molecular level.

Mulliken populations, contour plots of the electron density, and the expectation values with respect to x , y , z (commonly called the dipole), and r^2 give a measure of the charge distributions, which will give some measure of the edge effects. An infinite cluster would have a large number of equivalent atoms, for example, all the (0001) surface atoms would be expected to be the same. The finite cluster has "equivalent" atoms with differing environments--the surface atoms for example, where some are on the edge, having only 2 nearest neighbors, while others have all nine nearest neighbors. The difference between these atoms can be measured by differences in the total charge or the difference in hybridization of the berylliums. Also changes in the charge distributions can give some measure of what happens during bond formation. The density difference plot is extremely helpful for this. A change in the location of the charge can indicate whether the bond is ionic, where a large collection of charge on the adsorbate atom is observed; or covalent, where the increase in density is located between the adsorbate atom and the surface. The movement of the charge within the cluster can indicate how extensive the bonding is, and if the cluster is large

enough to describe this bonding.

We will restrict our discussion to the $\text{Be}_{22}(14,8)$ cluster, since all the smaller clusters suffer from large edge effects.

The first question we should direct ourselves to is, how large are the edge effects for a cluster as large as Be_{22} ?

The cluster without hydrogen was initially considered. The dipole was calculated to give a measure of the charge distribution. Let a line connecting atoms 5 and 10 in figure 1 be the x direction, a line connecting 7 and 10, be the y direction and the z direction is perpendicular to the surface of the cluster. It is clear that there is no dipole in the y direction by symmetry. If we had an infinite two-dimensional cluster (i.e. a cluster with a finite number of layers in the z direction, but infinite in both the x and y directions), a zero dipole in both the z and x direction would also be expected. As it turns out for the finite cluster, there is a dipole. The top layer is more negative than the bottom and the atoms numbered 11 and 14 lie at the more negative end of the cluster. It appears that regions containing more atoms get a greater amount of charge than would be expected; the top layer has more atoms than the bottom and ends up negatively charged, similarly in the x direction.

The expectation value with respect to r^2 was computed, and the nuclear value (3.8×10^3 charge-bohr²) is smaller than the electronic (-4.1×10^3 charge-bohr²), indicating that some of the charge is "dangling" off the edge of the cluster. In fact when the electron is removed from the cluster it comes from the edge of the cluster. Figure V shows the open shell orbital, the plane of the plot is the top surface of the $\text{Be}_{22}(14,8)$ cluster. The positions of the beryllium atoms are marked with x's. The open shell orbital is located almost entirely

on atoms 11 and 14. Figure VI shows a density difference plot between Be_{11} and Be_{22}^+ . The plotter plane is the top layer of the cluster, and the beryllium atoms position are denoted by x's. The solid lines are decreases in charge while the dashed line indicate an increase in charge. There is a great loss of charge at the edge near atoms 11 and 14, but there is also an increase in charge inside the cluster near 11 and 14, in such a way as to spread the loss of charge out over more atoms. The Mulliken populations indicate the charge comes only from the edge atoms. The plot indicates that in addition to this loss at the edge there is some repositioning of charge inside the cluster.

When the hydrogen is adsorbed on the surface at the eclipsed site one would expect local C_{3v} symmetry in the bonding. The overlap population for atom 10 with the hydrogen is 0.267, while the overlap population with 6 or 9 is 0.317. The results for the open site are even more asymmetric. The overlap population with 6 or 9 is 0.398, while with 5, the value is 0.278. Although all the atoms involved in bonding have all their nearest neighbors, some of the nearest neighbors have their nearest neighbors, while others do not. This is enough to produce local asymmetry in the overlap population.

The dipole was calculated for the hydrogen adsorbed at the eclipsed site. The dipole changed in the x direction as the charge repositioned for the bonding. Unlike the x dipole the z dipole produces an unexpected result, switching direction from that of the cluster alone, indicating a build up of charge on the lower layer. Figure VII is a plot of the density difference between Be_{11}^+H and Be_{11}H for the eclipsed site. The plane of the plot is perpendicular to the surface of the beryllium cluster, dividing the cluster in half and therefore also passes through the hydrogen. The solid lines are increases in

Figure V. The 27 a' orbital density of the Be_{22}^+ cluster. The plane of the plot is the top surface of the cluster. The positions of the beryllium atoms in the top layer are marked by x's. This orbital is the open shell orbital, and is located mostly on atoms 11 and 14 (see figure I).

XBL 769 10463

Figure VI. A density difference plot between Be_{22} and Be_{22}^+ . The plane of the plot is the top layer of the cluster. The positions of the atoms is noted with x's. Solid lines are areas of charge loss, while dotted lines indicate areas of charge gain.

XBL 769 10464

Figure VII. A density difference plot for Be_{22}H at the eclipsed site $R=1.7$ bohr above the surface and $\text{Be}_{22} + \text{H}$. The plane of the plot divides the cluster in half and passes through the hydrogen. The solid lines indicate areas of charge gain, while the dotted lines are areas of charge loss. The centers marked with x's are in the plane of the plot, while those marked with x's enclosed in circles are above and below the plane of the plot. The numbering of the centers is the same as in Figure I.

XBL 709 10465

charge, while the dashed lines are areas of charge loss. The increase in charge between the hydrogen and beryllium is the formation of the covalent bond, but on the lower layer opposite the hydrogen is an even larger increase in charge, causing the dipole's unexpected direction, but even more important, the "reverse" dipole indicates an edge effect due to the 2 layer restriction.

An additional measure of the edge effects can be obtained from the Mulliken populations. One would reasonably expect all the atoms in the same layer to have the same populations. In Be_{22} the range of values for the top layer is 3.94 to 4.05. For comparison, the $\text{Be}_{13}(10,3)\text{A}$ cluster has a range of values from 3.90 to 4.16, while the other Be_{13} cluster has a range in value of 3.94 to 4.05. Even more interesting then the total charge on the atoms is the "hybridization". For $\text{Be}_{13}(10,3)\text{A}$ (figure 12 in Appendix II) atom 4 has a 2p population of 1.46 electrons, while its 2s population is only 0.57. This corresponds to a "hybridization" of $\text{sp}^{2.56}$. Atoms 1 and 2 (both edge atoms) have hybridizations of $\text{sp}^{1.12}$ and $\text{sp}^{1.04}$ respectively, while atom 3, also an edge atom, but having more nearest neighbors, including one on the lower layer, has a hybridization of $\text{sp}^{1.70}$. The results for the Be_{22} cluster Figure I are even more interesting. Atoms 5, 9, and 10, which have all their nearest neighbors have a hybridizations of $\text{sp}^{2.37}$, $\text{sp}^{2.34}$, and $\text{sp}^{2.21}$. Edge atoms 8 and 13 are $\text{sp}^{1.54}$ and $\text{sp}^{1.83}$, while edge atoms 4, 12, and 14, who have fewer neighbors are hybridized to $\text{sp}^{1.13}$, $\text{sp}^{1.11}$, and $\text{sp}^{1.19}$. It is clear that the hybridization is dependent upon the number of nearest neighbors. The wide variation in the small cluster results is easy to understand; depending upon the shape and number of atoms, the berylliums involved in the bonding

could be in very different electronic configurations.

Above we stated that the bonding is covalent, and both the Mulliken populations and the density difference plot (Figure V) support this conclusion. For all our clusters the hydrogen populations have been about one, but the plot is even more convincing; the build up in charge is between the hydrogen and the beryllium surface, which can only mean a covalent bond.

The bonding of the hydrogen with the surface falls into two different types. The first is the bonding at the directly overhead site. The total population for atom 10 on the Be_{22} cluster increases from 3.98 to 4.30 electrons (see Table XV for the relevant populations). All of this change occurs in the 2p population, which increases by 0.34 electrons. The second type of bonding is exhibited by the other 3 sites. The total charge changes by a small amount, the largest being 0.08 electrons for atom 10 at the eclipsed site on the Be_{22} cluster. Accompanying this small change in the gross charge is a small shift of electrons from the 2s to 2p orbitals. This difference in bonding is reflected in the bond strengths of chemisorption. The directly overhead site is very different from the other 3, which are very similar in nature.

Finally, it seems worthwhile to indicate for at least one case, "where" the H atom population resides in the electronic structure of Be_nH . For this purpose the $\text{Be}_{22}(14,\text{S})$ cluster, the open site at $R=1.7$ bohr, was used to construct a histogram (Figure VIII) of, the percent of the total H hydrogen population found in each valence orbital. The total H atom population for this system was 1.01 electrons. The

Table XV. Mulliken populations for relevant berylliums in the Be₂₂ cluster (see Figure I).

Atom	Be ₂₂ + H	Open	Eclipsed	Bond midpoint	Directly Overhead
#5 s	2.61	2.59			
p	1.40	1.48			
total	4.03	4.07			
#6 s	2.61	2.56	2.57	2.56	
or p	1.42	1.46	1.45	1.50	
#9 total	4.03	4.02	4.02	4.06	
#10 s	2.59		2.57		2.58
p	1.39		1.49		1.73
total	3.98		4.06		4.30
H s	1.00	1.02	1.02	1.01	0.96

Figure VIII. A histogram indicating the percent H atom population on each of the valence orbitals. The core orbitals and a'' orbitals have been omitted. The eigenvalues of the valence orbital are given for the cluster with and without the hydrogen. The open site with $R=1.500$ bohr on the Be_{22} cluster was used to generate the histogram.

Histogram of Percent Hydrogen Population in Each Valence Orbital

XBL 769-10466

orbital energies are also given on the histogram. The hydrogen population is dominated by those orbitals with approximately the same orbital energies as the hydrogen orbital (-0.489). In fact, orbitals 16a' and 17a' have orbital energies of -0.5370 and -0.4710 for the bare cluster and they are the two orbitals which most strongly interact with the hydrogen, containing 65 percent of the hydrogen atom population.

IV. Conclusions

It would appear that the minimum number of atoms needed to describe chemisorption, is a cluster in which all atoms involved in bonding have all their nearest neighbors. The Be_{22} cluster we investigated meets this requirement and predicts that 3 sites are very similar with a bond length of $\sim 1.8 \text{ \AA}$ and a bond energy of $\sim 50 \text{ kcal/mole}$, and the fourth site (the directly overhead site) is different, with a bond length of $\sim 1.4 \text{ \AA}$ and a bond energy of $\sim 30 \text{ kcal/mole}$. These numbers are probably low by about 20 percent due to the use of a minimum basis set, leading to the possibility of dissociative adsorption of H_2 on beryllium surfaces. Other properties are seen to converge at different rates. The vibrational frequency of the adsorbed hydrogen was correct for some of the smaller clusters; the shape of the curve was correct, despite the fact that its absolute position was in error. The properties of the cluster without hydrogen converged more slowly than the chemisorption and even the large clusters were not accurate descriptions of a metal. The same cluster properties showed the local nature of the bonding to the hydrogen, supporting the use of a cluster model.

The chemisorption on beryllium is very much like that on the transition metals (experimental data is in the 60-70 kcal/mole range¹), despite the fact that beryllium has no d electrons.

The bond is covalent in nature, with the berylliums shifting charge into the 2p orbital to facilitate bonding.

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Appendix I. The total and relative energies, valence orbital energies, and Mulliken population analyses are tabulated for the cluster with hydrogen at infinite separation and for the chemisorbed equilibrium geometry. The tables run up to and including the two Se_{13} clusters.

TABLE A. Comparison of infinitely separated Be + H with BeH. The first number in each slot comes from a minimum basis calculation, while the second number (in parentheses) arises from the use of the larger basis set. All entries are given in atomic units.

	Be + H	BeH
Total Energy	-14.8757 (-15.0681)	-14.9496 (-15.1391)
Relative Energy	—	- 0.0739 (-0.0710)
r_e	—	2.683 (2.554)
Valence Orbital Energies	$2s_{\text{Be}}$ - 0.310 (-0.308)	2σ - 0.469 (-0.467)
	$1s_{\text{H}}$ - 0.484 (-0.498)	3σ - 0.321 (-0.307)
Populations		
Be s	4.00 (4.00)	3.15 (3.06)
p	0.00 (0.00)	0.81 (0.72)
Total	4.00 (4.00)	3.96 (3.78)
H s	1.00 (1.00)	1.04 (1.22)
p	0.00 (0.00)	-- (0.01)
Total	1.00 (1.00)	1.04 (1.23)

TABLE B. Comparison of $\text{Be}_3 + \text{H}$ with Be_3H . Format is as in Table A.

		$\text{Be}_3 + \text{H}$	Be_3H	Spatially Unrestricted	
Total Energy		-43.6356 (-44.1935)	-43.6422 (-44.2032)	-43.6658 (-44.2286)	
Relative Energy		----	- 0.0068 (- 0.0097)	- 0.0304 (- 0.0254)	
r_e		----	2.064 (1.758)	2.363 (2.079)	
Valence	$2a_1'$	- 0.473 (-0.474)	$2a_1$ - 0.616 (- 0.630)	$4a$	- 0.595 (- 0.610)
Orbital	$2e'$	- 0.263 (-0.255)	$2e$ - 0.270 (-0.259)	$5a, 6a$	- 0.301, -0.271 (-0.290, -0.263)
Energies	$1s_H$	- 4.484 (-0.498)	$3a_1$ - 0.341 (-0.326)	$7a$	- 0.322 (- 0.325)
Population:					
Be	s	3.39 (3.60)	3.23 (3.43)	3.41, 3.24, 2.93 (3.59, 2.94, 3.59)	
	p	0.61 (0.40)	0.80 (0.52)	0.64, 0.76, 1.00 (0.41, 0.75, 0.41)	
Total		4.00 (4.00)	4.02 (3.95)	4.05, 4.00, 3.93 (4.00, 3.68, 4.00)	
H	s	1.00 (1.00)	0.93 (1.14)	1.02 (1.31)	
	p	0.00 (0.00)	-- (0.01)	-- (0.01)	
Total		1.00 (1.00)	0.93 (1.16)	1.02 (1.32)	

TABLE C. Comparison of $\text{Be}_4(3,1) + \text{H}$ with Be_4H . Note, in reference 16, that this Be_4 cluster is nearly, but not precisely, tetrahedral.

	$\text{Be}_4 + \text{H}$		Be_4H	
Total Energy	-58.0773 (-58.8102)		-58.1229 (-58.8629)	
Relative Energy	---		- 0.0456 (-0.0527)	
r_e	---		2.352 (2.211)	
Valence	$3a_1$	- 0.544 (-0.535)	$3a_1$	- 0.629 (-0.620)
Orbital	$2e$	- 0.283 (-0.271)	$4a_1$	- 0.406 (-0.395)
Energies	$4a_1$	- 0.277 (-0.265)	$2e$	- 0.296 (-0.281)
	$1s_H$	- 0.484 (-0.498)	$5a_1$	- 0.251 (-0.239)
Populations				
3 Be	s	3.16 (3.41)		3.11 (3.32)
	p	0.83 (0.58)		0.86 (0.58)
Total		3.99 (3.99)		3.97 (3.91)
1 Be	s	3.15 (3.40)		2.92 (3.07)
	p	0.88 (0.62)		1.15 (0.94)
Total		4.03 (4.02)		4.08 (4.01)
H	s	1.00 (1.00)		1.01 (1.26)
	p	0.00 (0.00)		---- (0.01)
Total		1.00 (1.00)		1.01 (1.27)

TABLE D. Comparison of $\text{Be}_4(4,0) + \text{H}$ with Be_4H . The two equivalent Be atoms closest to each other are called the near Be atoms.

	$\text{Be}_4 + \text{H}$		Be_4H		Spatially Unrestricted	
Total Energy	-57.9890 (-58.7367)		-58.0928 (-58.8345)		-58.1006 (-58.8410)	
Relative Energy	----		- 0.1038 (- 0.0978)		- 0.1116 (- 0.1043)	
1σ	----		2.354 (2.212)		2.390 (2.249)	
Valence	$1a_g$	- 0.525 (-0.527)	$3a_1$	- 0.611 (-0.602)	$5a$	- 0.609 (-0.598)
Orbital	$2b_{2u}$	- 0.371 (-0.366)	$2b_1$	- 0.371 (-0.357)	$6a$	- 0.368 (-0.353)
Energies	$2b_{3u}$	- 0.281 (-0.275)	$4a_1$	- 0.331 (-0.320)	$7a$	- 0.331 (-0.318)
	$4a_g$	- 0.208 (-0.196)	$2b_2$	- 0.273 (-0.258)	$8a$	- 0.275 (-0.259)
			$5a_1$	- 0.242 (-0.224)	$9a$	- 0.281 (-0.263)
Populations						
Near Be	s	3.17 (3.32)		3.13 (3.33)	3.12	(3.28)
	p	0.79 (0.58)		0.95 (0.52)	0.95	(0.67)
Total		3.96 (3.90)		4.08 (3.83)	4.07	(3.95)
Far Be	s	3.67 (3.70)		3.52 (3.51)	3.28, 3.15	(3.41, 3.22)
	p	0.57 (0.40)		0.61 (0.46)	0.59, 0.85	(0.46, 0.73)
Total		4.04 (4.10)		3.93 (3.97)	3.88, 4.00	(3.87, 3.96)
H	s	1.00 (1.00)		0.99 (1.15)	0.99	(1.27)
	p	0.00 (0.00)		---- (0.00 ₂)	----	(0.01)
Total		1.00 (1.00)		0.99 (1.15)	0.99	(1.78)

TABLE E. Comparison of $\text{Be}_3 + \text{H}$ with three forms of Be_3H . The "Near Be" atom is the nonequivalent surface atom closer to the atom in second layer, and the "Below Be" atom is just the atom in the second layer (see Figure 4).

	$\text{Be}_3 + \text{H}$	Open Be_3H	Eclipsed Be_3H	Bond Midpoint Be_3H
Total Energy	-72.4451 (-73.3627)	-72.4821 (-73.4136)	-72.4931 (-73.4207)	-72.4967 (-73.4234)
Relative Energy	----	- 0.0370 (-0.0509)	- 0.0480 (-0.0580)	- 0.0516 (-0.0607)
r_e	----	1.934 (1.718)	2.180 (2.009)	2.145 (2.006)
Valence	5a' - 0.579 (-0.572)	5a' - 0.681 (-0.679)	- 0.660 (-0.660)	- 0.673 (-0.661)
Orbital	6a' - 0.390 (-0.383)	6a' - 0.491 (-0.484)	- 0.440 (-0.431)	- 0.446 (-0.435)
Energies	2a'' - 0.294 (-0.285)	7a' - 0.348 (-0.331)	- 0.403 (-0.389)	- 0.392 (-0.379)
	7a' - 0.292 (-0.281)	2a'' - 0.310 (-0.298)	- 0.308 (-0.295)	- 0.309 (-0.295)
	8a' - 0.223 (-0.210)	8a' - 0.236 (-0.224)	- 0.240 (-0.225)	- 0.247 (-0.233)
	1a _H - 0.404 (-0.498)	9a' - 0.296 (-0.285)	- 0.263 (-0.251)	- 0.275 (-0.264)
Populations				
2 Be s	3.04 (3.25)	2.99 (3.14)	3.04 (3.21)	3.02 (3.19)
p	0.98 (0.74)	1.01 (0.73)	0.97 (0.72)	1.04 (0.76)
Total	4.02 (3.99)	4.00 (3.87)	4.01 (3.93)	4.06 (3.95)
Near Be s	3.21 (3.47)	3.34 (3.52)	3.27 (3.53)	3.41 (3.63)
p	0.82 (0.57)	0.64 (0.46)	0.78 (0.52)	0.56 (0.36)
Total	4.03 (4.04)	3.98 (3.98)	4.06 (4.04)	3.97 (4.01)
Far Be s	3.49 (3.64)	3.50 (3.69)	3.46 (3.53)	3.54 (3.63)
p	0.48 (0.36)	0.55 (0.36)	0.44 (0.34)	0.38 (0.29)
Total	3.97 (3.99)	4.05 (4.05)	3.89 (3.86)	3.92 (3.93)
Below Be s	3.08 (3.38)	2.91 (3.07)	2.92 (3.06)	2.94 (3.06)
p	0.86 (0.61)	1.01 (0.82)	1.09 (0.90)	1.04 (0.86)
Total	3.95 (3.99)	3.92 (3.90)	4.01 (3.96)	3.98 (3.92)
H s	1.00 (1.00)	1.06 (1.32)	1.02 (1.27)	1.01 (1.24)
p	0.00 (0.00)	---- (0.01)	---- (0.01)	---- (0.01)
Total	1.00 (1.00)	1.06 (1.33)	1.02 (1.28)	1.01 (1.25)

TABLE F. Comparison of $\text{Be}_6 + \text{H}$ with Be_6H for two different Be_6 clusters.

All calculations employed a minimum basis set.

	$\text{Be}_6(3,3) + \text{H}$	Be_6H	Spatially Unrestricted
Total Energy	-86.8524	-86.9124	-86.9405
Relative Energy	-----	- 0.0600	- 0.0881
r_e	-----	1.947	2.107
Valence	$2a_g - 0.585$	$3a_1 - 0.644$	$7a - 0.642$
Orbital	$2e_u - 0.360$	$4a_1 - 0.479$	$8a - 0.481$
Energies	$2a_u - 0.338$	$3e - 0.363$	$9a, 10a - 0.364, -0.361$
	$2e_g - 0.207$	$4e - 0.210$	$11a, 12a - 0.248, -0.210$
	$1s_H - 0.484$	$5a_1 - 0.294$	$13a - 0.229$
Populations			
Above 3 Be	s 2.78	2.64	2.78, 2.78, 2.74
	p 1.22	1.37	1.24, 1.24, 1.31
Total	4.00	4.01	4.02, 4.02, 4.05
Below 3 Be	s 2.78	2.70	2.73, 2.65, 2.74
	p 1.22	1.28	1.22, 1.31, 1.22
Total	4.00	3.98	3.96, 3.95, 3.96
H	s 1.00	1.01	1.05

TABLE F. Continued

	$\text{Be}_6(6,0) + \text{H}$		Be_6H		Spatially Unrestricted	
Total Energy	-85.8205		-86.8817		-86.8958	
Relative Energy	----		- 0.0612		- 0.0753	
r_e	----		1.958		2.224	
Valence	$3a_1$	- 0.527	$3a_1$	- 0.639	7a	- 0.612
Orbital	$3e$	- 0.407	$3e$	- 0.411	8a, 9a	- 0.410, -0.404
Energies	$4a_1$	- 0.264	$4a_1$	- 0.357	10a	- 0.353
	$4e$	- 0.224	$4e$	- 0.222	11a, 12a	- 0.239, -0.220
	$1s_H$	- 0.484	$5a_1$	- 0.276	13a	- 0.272
Populations						
Inner 3 Be	s	2.92		2.89		2.69, 2.69, 2.92
	p	1.14		1.23		1.39, 1.39, 1.26
Total		4.07		4.12		4.07, 4.08, 4.18
Outer 3 Be	s	3.24		3.15		3.24, 3.26, 3.24
	p	0.69		0.72		0.63, 0.66, 0.63
Total		3.93		3.87		3.87, 3.92, 3.87
H	s	1.00		1.03		1.00

TABLE G. Comparison of $\text{Be}_7(6,1) + \text{H}$ with Be_7H .

	$\text{Be}_7(6,1) + \text{H}$		Be_7H
Total Energy	-101.2435		-101.3085
Relative Energy	---		- 0.0650
r_e	---		2.099
Valence	$4a_1$	- 0.590	- 0.666
Orbital	$3e$	- 0.415	- 0.428
Energies	$5a_1$	- 0.309	- 0.419
	$6a_1$	- 0.263	- 0.305
	$4e$	- 0.223	- 0.230
	$1a_H$	- 0.484	$(7a_1)$ - 0.270
Populations			
Inner 3 Be	s	2.93	2.94
	p	1.26	1.27
	Total	4.19	4.21
Outer 3 Be	s	3.27	3.19
	p	0.61	0.63
	Total	3.88	3.82
Below Be	s	3.22	2.99
	p	0.58	0.90
	Total	3.79	3.89
H	s	1.00	1.02

TABLE H. Comparison of $\text{Be}_7(7,0) + \text{H}$ with Be_7H .

		$\text{Be}_7(7,0) + \text{H}$	Be_7H
Total Energy		-101.2675	-101.3813
Relative Energy		----	- 0.1138
r_e		----	2.694
Valence	$3a_{1g}$	- 0.554	$3a_1$ - 0.584
Orbital	$2e_{1u}$	- 0.447	$2e_1$ - 0.431
Energies	$2e_{2g}$	- 0.302	$2c_2$ - 0.297
	$1b_{2u}$	- 0.235	$1b_2$ - 0.234
	$4a_{1g}$	- 0.217	$4a_1$ - 0.371
	$1s_H$	- 0.484	$5a_1$ - 0.234
Populations			
Six Equivalent Be	s	2.97	2.94
	p	1.04	1.01
	Total	4.01	3.95
Unique Be	s	2.97	2.67
	p	0.97	1.67
	Total	3.94	4.35
H	s	1.00	0.93

TABLE I. Comparison of $\text{Be}_9(6,3) + \text{H}$ with Be_9H .

	$\text{Be}_9(6,3) + \text{H}$	Be_9H	Spatially Unrestricted
Total Energy	-130.0614	-130.1142	-130.1414
Relative Energy	-----	- 0.0528	0.0800
r_e	-----	2.003	2.144
Valence	$4a_1 - 0.663$	- 0.703	$10a - 0.697$
Orbital	$4e - 0.488$	- 0.493	$11a, 12a - 0.501, -0.498$
Energies	$5a_1 - 0.399$	- 0.506	$13a - 0.494$
	$6a_1 - 0.298$	- 0.337	$14a - 0.344$
	$5e - 0.282$	- 0.280	$15a, 16a - 0.281, -0.280$
	$6e - 0.212$	- 0.211	$17a, 18a - 0.245, -0.215$
	$1s_H - 0.484$	$(7a_1) - 0.288$	$19a - 0.268$
Populations			
Inner 3 Be	s 2.90	2.85	2.79, 2.72, 2.79
	p 1.11	1.26	1.32, 1.32, 1.32
	Total 4.00	4.10	4.12, 4.04, 4.12
Outer 3 Be	s 2.92	2.99	3.09, 3.09, 3.00
	p 1.00	0.89	0.83, 0.83, 0.92
	Total 3.92	3.88	3.92, 3.92, 3.92
Below 3 Be	s 3.00	2.93	2.88, 2.88, 2.73
	p 1.07	1.13	1.14, 1.14, 1.25
	Total 4.08	4.05	4.02, 4.02, 3.98
H	s 1.00	0.69	0.94

TABLE J. Comparison of $\text{Be}_{10}(10,0) + \text{H}$ with Be_{10}H . Atoms are labelled according to

		$\text{Be}_{10}(10,0) + \text{H}$	Be_{10}H	Spatially Unrestricted
Total Energy		-144.5449	-144.5951	-144.6172
Relative Energy		----	- 0.0502	- 0.0723
E_e		----	2.182	2.203
Valence	$5a_g$	- 0.545	$5a_1$ - 0.626	$11a$ - 0.627
Orbital	$4b_{3u}$	- 0.490	$4b_1$ - 0.493	$12a$ - 0.500
Energies	$3b_{2u}$	- 0.439	$3b_2$ - 0.456	$13a$ - 0.458
	$6a_g$	- 0.401	$6a_1$ - 0.454	$14a$ - 0.453
	$2b_{1g}$	- 0.386	$2a_2$ - 0.393	$15a$ - 0.394
	$5b_{3u}$	- 0.284	$5b_1$ - 0.293	$16a$ - 0.340
	$4b_{2u}$	- 0.278	$4b_2$ - 0.275	$17a$ - 0.293
	$7a_g$	- 0.249	$7a_1$ - 0.339	$18a$ - 0.283
	$3b_{1g}$	- 0.240	$3a_2$ - 0.240	$19a$ - 0.248
	$1b_{1u}$	- 0.211	$8a_1$ - 0.249	$20a$ - 0.233
	$1s_H$	- 0.484	$9a_1$ - 0.176	$21a$ - 0.227
Populations				
End 2 Be (#1)	s	2.93	2.92	2.91, 2.94
	p	1.09	1.07	1.08, 1.05
Total		4.01	4.00	3.98, 3.98
4 Equivalent Be (#2)	s	2.89	2.87	2.96, 2.87, 2.89, 2.87
	p	1.09	1.08	1.02, 1.14, 1.05, 1.06
Total		3.97	3.96	3.98, 4.01, 3.94, 3.94
2 Above and Below (#3)	s	2.76	2.84	2.80, 2.86
	p	1.23	1.13	1.17, 1.10
Total		3.99	3.98	3.97, 3.96
2 Left and Right (#4)	s	2.57	2.53	2.56, 2.56
	p	1.48	1.59	1.54, 1.59
Total		4.05	4.12	4.10, 4.15
H	s	1.00	0.98	0.98

TABLE K. Comparison of $\text{Be}_{10}(7,3) + \text{H}$ with Be_{10}H .

	<u>$\text{Be}_{10}(7,3) + \text{H}$</u>		<u>Be_{10}H</u>	<u>Spatially Unrestricted</u>
Total Energy	-144.5456		-144.5725	-144.5690
Relative Energy	----		- 0.0269	- 0.0434
r_e	----		2.695	2.710
Valence	$4a_1$	- 0.673	$4a_1$	- 0.678 $11a$ - 0.681
Orbital	$4e$	- 0.518	$4e$	- 0.519 $12a, 13a$ - 0.522, -0.519
Energies	$5a$	- 0.409	$5a_1$	- 0.491 $14a$ - 0.492
	$5e$	- 0.331	$5e$	- 0.336 $15a, 16a$ - 0.346, -0.341
	$6a_1$	- 0.290	$6a_1$	- 0.329 $17a$ - 0.332
	$7a_1$	- 0.240	$7a_1$	- 0.243 $18a$ - 0.259
	$6e$	- 0.239	$6e$	- 0.232 $19a, 20a$ - 0.248, -0.231
	$8a_1$	- 0.484	$8a_1$	- 0.288 $21a$ - 0.258
Populations				
6 Be	s	2.88	2.89	2.92, 2.87, 2.89, 2.89, 2.87, 2.93
	p	1.09	1.05	1.03, 1.06, 1.05, 1.05, 1.06, 1.03
	Total	3.97	3.94	3.95, 3.93, 3.94, 3.94, 3.93, 3.95
3 Be	s	2.93	2.90	2.95, 2.84, 2.96
	p	1.13	1.15	1.07, 1.15, 1.07
	Total	4.05	4.05	4.02, 3.99, 4.03
1 Be	s	2.74	2.71	2.73
	p	1.26	1.68	1.69
	Total	4.00	4.39	4.41
H	s	1.00	0.86	0.89

TABLE 1. Comparison of $\text{Be}_{13}(10,3)$ Cluster A (see Figure 1) with three different chemisorbed species Be_{13}H .
 Energies are given in hartrees (1 hartree = 627.5 kcal/mole) and bond distances r_e in bohrs (1 bohr = 0.5292 Å).

	Be ₁₃ + H		Open Site	Eclipsed Site	Bond Midpoint Site	
Total Energy	-187.8713		-187.9334	-187.9624	-187.9427	
Relative Energy	0.0000		- 0.0621	- 0.0911	- 0.0714	
r _e	---		1.868	1.708	1.981	
Valence	9a _u ^{''}	-0.613	9a _u ^{''}	-0.659	9a _u ^{''}	-0.652
Orbital	6a _u ^{''}	-0.502	6a _u ^{''}	-0.512	10a _u ^{''}	-0.512
Energies	10a _u ^{''}	-0.477	10a _u ^{''}	-0.507	6a _u ^{''}	-0.508
	11a _u ^{''}	-0.415	11a _u ^{''}	-0.425	11a _u ^{''}	-0.455
	7a _u ^{''}	-0.390	12a _u ^{''}	-0.419	12a _u ^{''}	-0.421
	12a _u ^{''}	-0.349	7a _u ^{''}	-0.392	7a _u ^{''}	-0.393
	13a _u ^{''}	-0.289	13a _u ^{''}	-0.299	13a _u ^{''}	-0.309
	8a _u ^{''}	-0.285	8a _u ^{''}	-0.288	8a _u ^{''}	-0.289
	14a _u ^{''}	-0.265	14a _u ^{''}	-0.283	14a _u ^{''}	-0.283
	9a _g ^{''}	-0.227	9a _g ^{''}	-0.259	15a _g ^{''}	-0.244
	10a _g ^{''}	-0.216	13a _g ^{''}	-0.228	9a _g ^{''}	-0.230
	15a _g ^{''}	-0.208	10a _g ^{''}	-0.218	10a _g ^{''}	-0.218
	16a _g ^{''}	-0.182	16a _g ^{''}	-0.198	16a _g ^{''}	-0.187
	1a _u	-0.484	17a _u ^{''}	-0.208	17a _u ^{''}	-0.218
Populations						
Be #1	s	2.93	2.96	2.94	2.97	
	p	1.04	1.01	1.02	1.00	
	Total	3.97	3.97	3.96	3.97	
Be #2	s	2.94	2.96	2.95	2.95	
	p	0.98	0.97	0.97	0.99	
	Total	3.92	3.93	3.92	3.94	
Be #3	s	2.80	2.80	2.79	2.80	
	p	1.36	1.32	1.36	1.27	
	Total	4.16	4.12	4.15	4.07	
Be #4	s	2.57	2.50	2.51	2.49	
	p	1.46	1.56	1.52	1.60	
	Total	4.03	4.06	4.03	4.09	
Be #5	s	2.88	2.96	2.88	2.92	
	p	1.13	1.04	1.13	1.09	
	Total	4.01	4.00	4.01	4.01	
Be #6	s	2.78	2.65	2.71	2.69	
	p	1.29	1.49	1.40	1.40	
	Total	4.07	4.14	4.11	4.09	
Be #7	s	2.79	2.78	2.76	2.73	
	p	1.11	1.08	1.13	1.15	
	Total	3.90	3.86	3.89	3.88	
Be #8	s	2.84	2.79	2.90	2.86	
	p	1.16	1.18	1.08	1.13	
	Total	4.00	3.97	3.98	3.99	
Hydrogen	s	1.00	1.00	1.02	0.95	

TABLE M. Comparison of $\text{Be}_{13}(10,3)$ Cluster B (see Figure 2) with two models for Be_{13}H . All entries are given in atomic units.

	$\text{Be}_{13} + \text{H}$		Directly Overhead Site	Eclipsed Site
Total Energy		-187.3688	-187.9183	-187.9617
Relative Energy		0.0000	- 0.0495	- 0.0929
r_e		---	2.66	1.77
	14a	-0.621	-0.633	-0.662
Valence	15a	-0.508	-0.515	-0.553
Orbital	16a	-0.477	-0.483	-0.496
Energies	17a	-0.426	-0.458	-0.455
	18a	-0.381	-0.427	-0.428
	19a	-0.374	-0.391	-0.391
	20a	-0.282	-0.321	-0.312
	21a	-0.272	-0.291	-0.287
	22a	-0.260	-0.276	-0.273
	23a	-0.240	-0.251	-0.263
	24a	-0.214	-0.228	-0.241
	25a	-0.204	-0.217	-0.211
	26a	-0.193	-0.198	-0.200
	27a	-0.484	-0.221	-0.228
Populations				
Be #1	s	2.97	2.96	2.97
	p	1.02	1.02	1.00
	Total	3.99	3.98	3.97
Be #2	s	2.92	2.92	2.91
	p	1.02	1.01	1.01
	Total	3.94	3.93	3.92
Be #3	s	2.81	2.80	2.79
	p	1.22	1.19	1.24
	Total	4.03	3.99	4.03
Be #4	s	2.61	2.58	2.55
	p	1.39	1.38	1.45
	Total	4.00	3.96	4.00
Be #5	s	2.95	2.87	2.97
	p	1.02	1.04	0.97
	Total	3.97	3.93	3.94
Be #6	s	2.78	2.62	2.75
	p	1.27	1.19	1.33
	Total	4.05	4.01	4.08
Be #7	s	2.68	2.66	2.63
	p	1.31	1.68	1.43
	Total	3.99	4.34	4.06
Be #8	s	2.89	2.98	2.94
	p	1.10	0.97	1.06
	Total	3.99	3.95	4.00
Be #9	s	2.83	2.92	2.92
	p	1.16	1.03	1.07
	Total	3.99	3.98	3.99
Be #10	s	2.88	2.91	2.97
	p	1.09	1.02	1.02
	Total	3.97	3.93	3.99
Be #11	s	3.00	3.04	2.97
	p	1.06	0.98	1.06
	Total	4.06	4.02	4.03
Be #12	s	2.82	2.86	2.73
	p	1.17	1.13	1.22
	Total	3.99	3.99	3.95
Be #13	s	2.92	2.91	2.90
	p	1.13	1.12	1.14
	Total	4.05	4.03	4.04
Hydrogen	s	1.0	0.94	1.01

Appendix II. Geometries of the metal clusters studied. The figure captions describe the site or sites studied on each cluster. The $\text{Be}_{22}(14,8)$ cluster is pictured and described in the text (see Figure I). A separate figure of Be_{14} was not included. The Be_{14} cluster is merely the top layer of the $\text{Be}_{22}(14,8)$ and the Be_{22} figure and site description should be used.

Figure Captions

- Figure 1. $\text{Be}_3(3,0)$ a model for the open site for chemisorption. The system with hydrogen has C_{3v} symmetry.
- Figure 2. $\text{Be}_4(3,1)$ a model for the eclipsed site for chemisorption. The system with hydrogen has C_{3v} symmetry.
- Figure 3. $\text{Be}_4(4,0)$ a model for the bond midpoint site. The system with hydrogen has C_{2v} symmetry.
- Figure 4. $\text{Be}_5(4,1)$ a model used to study the open, eclipsed and bond midpoint sites for chemisorption. The system with hydrogen has C_s symmetry.
- Figure 5. $\text{Be}_6(6,0)$ a model for the open site. C_{3v} symmetry is present for the system with hydrogen.
- Figure 6. $\text{Be}_6(3,3)$ a model used to study the chemisorption at the open site. The system with hydrogen has C_{3v} symmetry.
- Figure 7. $\text{Be}_9(6,3)$ a model used to study the open site. The cluster with hydrogen has C_{3v} symmetry.
- Figure 8. $\text{Be}_7(6,1)$ a model for the eclipsed site for chemisorption. The cluster with hydrogen has C_{3v} symmetry.
- Figure 9. $\text{Be}_{10}(10,0)$ a model for the bond midpoint site. The cluster with hydrogen has C_{2v} symmetry.
- Figure 10. $\text{Be}_7(7,0)$ a model for the directly overhead site. The cluster with the hydrogen has C_{6v} symmetry.
- Figure 11. $\text{Be}_{10}(7,3)$ a model for the directly overhead site. The cluster with the hydrogen has C_{3v} symmetry.

Figure 12. $\text{Be}_{13}(10,3)\text{A}$, a model for the open, eclipsed, and bond midpoint sites for chemisorption. The cluster with and without hydrogen has C_s symmetry. The open site is the center of the triangle formed by 4, its symmetry equivalent partner and 6. The eclipsed is the center of the triangle formed by 4, its symmetry equivalent partner and 3; with 7 the atom on the second layer. The bond midpoint site is the bisector of the bond between atom 4 and its symmetry equivalent partner.

Figure 13. $\text{Be}_{13}(10,3)\text{B}$, the system has no symmetry. The directly overhead site is studied by the approach of hydrogen to atom 7, while the eclipsed site was studied by the approach of a hydrogen to the center of the triangle formed by 4, 7, and 6, where 12 is the atom in the second layer.

NOT TO SCALE

Fig. 1

XBB 746.3875

Fig. 2

NO. 100-100000

NOTES

Fig. 3

XBB 746-3880

Fig. 6

XBB 746 3874

Fig. 8

XRD FILE 001

Fig. 19

Appendix III. A tabulation of basis sets used in the present work.

Minimum basis set I

A three gaussian fit^a to a Slater 1s function with $\zeta=3.685^b$

exponent	coefficient
30.249896	0.154029
5.510036	0.535328
1.491243	0.444635

A three gaussian fit to a Slater 2s function with $\zeta=0.956^b$

exponent	coefficient
2.359399	-0.039945
0.143270	0.596039
0.055003	0.458179

A three gaussian fit to a Slater 2p function with $\zeta=0.89^c$

exponent	coefficient
0.728128	0.162395
0.186871	0.566171
0.063446	0.422307

^aReference 35.

^bReference 36.

^cReference 37.

Minimum Basis IIa

The 1s function is the same as Minimum basis set I a three gaussian expansion of a 1s Slater function with $\zeta=3.685$

exponent	coefficient
30.249996	0.154329
5.510056	0.535328
1.491243	0.444635

The 2s and 2p functions are a constrained 3 gaussian fit^a. The same three gaussians were used to fit a Slater 2s and Slater 2p function with $\zeta=1.00$

exponent	2s coefficient	2p coefficient
0.994203	-0.099672	0.155916
0.231031	0.399513	0.607684
0.0751386	0.700115	0.391957

^aW. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. 51, 2657 (1969).

Minimum Basis IIb

The 1s function is the same 3 gaussian expansion of a Slater 1s with $\zeta=3.685$ as minimum basis I and IIa.

exponent	coefficient
30.249896	0.154329
5.519056	0.535328
1.491243	0.444635

The 2s and 2p are 3 gaussian expansions of 2s and 2p Slater functions with $\zeta=1.00$ as in minimum basis IIa, except each is fit separately to the best 3 gaussians.

The 2s function.

exponent	coefficient
2.581580	-0.059945
0.156762	0.596039
0.060133	0.455179

The 2p function

exponent	coefficient
0.919238	0.162395
0.235919	0.566171
0.080098	0.422307

Minimum Basis Set III

The 1s function is a three gaussian expansion of a Slater 1s function with $\zeta=3.685$. This is the same 1s function as the other 3 minimum basis sets.

exponent	coefficient
30.249396	0.154329
5.510056	0.535328
1.491243	0.444635

The 2s function is a 3 gaussian expansion of a 2s Slater function with $\zeta=1.01$.

exponent	coefficient
2.633470	-0.059945
0.159913	0.596039
0.061393	0.458179

The 2p function used is a 3 gaussian expansion of a 2p Slater function with $\zeta=0.98$

exponent	coefficient
0.892836	0.162395
0.226577	0.596171
0.076926	0.422307

Hydrogen Minimum Basis Set

A three gaussian fit to a Slater 1s function with $\zeta=1.15$

exponent	coefficient
2.94608	0.154329
0.536632	0.535328
0.145234	0.444635

Hydrogen Double Zeta Basis Set

The four 1s functions of van Duijneveldt^a scaled by 1.2 and contracted
31 to form 2s contracted functions.

exponent	coefficient
18.73925	0.019678
2.825994	0.137952
<u>0.540179</u>	<u>0.478313</u>
<u>0.175612</u>	<u>1.000000</u>

The one uncontracted 2p function.

exponent	coefficient
1.00000	1.000000

^aReference 33.

Double Zeta I

The nine 1s function of van Duijneveldt^a contracted 6111 to form 4s contracted functions.

Exponent	Coefficient
2732.328145	0.000745
410.319811	0.005724
93.672648	0.028888
26.587957	0.107092
8.629560	0.280109
<u>3.056254</u>	<u>0.445089</u>
<u>1.132424</u>	<u>1.000000</u>
<u>0.181732</u>	<u>1.000000</u>
<u>0.059170</u>	<u>1.000000</u>

The two uncontracted 2p functions^b.

Exponent	Coefficient
0.509	1.000000
0.118	1.000000

^aReference 38.

^bReference 40.

Double Zeta II

The same s functions were used as Double Zeta I, however four 2p functions contracted 31 replaced the two uncontracted 2p functions^a.

Exponent	Coefficient
2732.323145	0.000745
410.319811	0.005724
93.672643	0.028888
25.527957	0.107092
8.629560	0.280109
<u>3.056254</u>	<u>0.446089</u>
<u>1.132424</u>	<u>1.000000</u>
<u>0.181732</u>	<u>1.000000</u>
<u>0.059170</u>	<u>1.000000</u>

The 2p functions.

Exponent	Coefficient
3.202	0.052912
0.6923	0.267659
<u>0.2716</u>	<u>0.792085</u>
<u>0.08331</u>	<u>1.000000</u>

^aReference 42.